

Organic Chemistry.

Preparation of Tetranitromethane. CONRAD CLAESSEN (D.R.-P. 184229).—The production of tetranitromethane from nitroform, which is itself obtained with difficulty from explosive substances such as mercury fulminate, is too dangerous to admit of this process being employed on a large scale. It is now found that the aromatic hydrocarbons and their nitro-derivatives when warmed with a mixture of nitric-sulphuric acid (40% H_2SO_4 , 60% HNO_3) and fuming sulphuric acid (50% SO_3) furnish a large amount of tetranitromethane; a yield of 50% on the weight of the organic substance being sometimes obtained. Nitrobenzene when gradually heated with excess of the acid mixture to 120° is decomposed, giving rise to tetranitromethane and a large amount of nitrous fumes.

G. T. M.

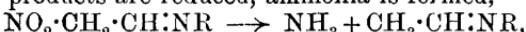
Improved Method for the Preparation of Alkyl Chlorides. WILLIAM M. DEHN and GRANT T. DAVIS (*J. Amer. Chem. Soc.*, 1907, 29, 1328—1334).—A method is described for the preparation of alkyl chlorides by the action of phosphorus trichloride on alcohols in presence of zinc chloride. Propyl chloride has been obtained in a yield amounting to 94% of the theoretical by the use of anhydrous zinc chloride. It has been found that, if a solution of zinc chloride (b. p. 150—160°) is used instead of the anhydrous salt, the yield of propyl chloride is decreased, but that in the case of *isobutyl* and *isoamyl* chlorides larger yields (85% and 88% respectively) are produced.

The reaction takes place in accordance with the equation : $6ROH + 2PCl_3 + ZnCl_2 = Zn(H_2PO_3)_2 + 6RCl + 2HCl$. Evidence has been obtained, however, of the formation of complex intermediate products.

By the action of stannic chloride on propyl alcohol, an additive compound, b. p. 148°, is obtained.

E. G.

Constitution of Methazonic Acid. WILHELM MEISTER (*Ber.*, 1907, 40, 3435—3449. Compare Dunstan and Goulding, *Trans.*, 1900, 77, 1262; Scholl, *Abstr.*, 1901, i, 359).—Methazonic acid behaves as a primary nitro-compound, since it gives the nitrolic acid reaction and Konowaloff's reaction, and hence contains the grouping $\cdot CH_2 \cdot NO_2$. It reacts with primary aromatic amines and hydrazines, yielding products which also contain the primary nitro-group. These products are formed by the replacement of NHO by :NR, and hydroxylamine is also formed. The reactions are most readily explained by the presence of the oximino-group in methazonic acid, and the formula thus arrived at is $NO_2 \cdot CH_2 \cdot CH \cdot N \cdot OH$. When the condensation products are reduced, ammonia is formed,



and the residue, when distilled with acid, yields an amine and acet-

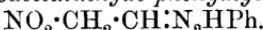
aldehyde, $\text{CH}_3\cdot\text{CH}\cdot\text{NR} + \text{H}_2\text{O} \rightarrow \text{CH}_3\cdot\text{CHO} + \text{NH}_2\text{R}$. They closely resemble Schiff's bases.

An isonitro-formula, β -isonitroacetaldoxime,
 $\text{OH}\cdot\text{NO}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{OH}$,

is also possible. The formation and reactions of methazonic acid are discussed from the point of view of the new formula.

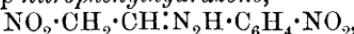
Attempts have been made to synthesise methazonic acid from β -chloro- or β -iodo-acetaldoxime and silver nitrite, but without success.

Methazonic acid and phenylhydrazine in the presence of hydrochloric acid yield β -nitroacetalddehyde-phenylhydrazone,



It may be crystallised in small amounts (0·1—0·2 gram) from light petroleum and forms glistening, white plates, m. p. 74—74·5°. When kept in closed vessels, it rapidly decomposes, but can be kept at 0° in open vessels if protected from sunlight. It dissolves in alkalis, gives the nitrolic acid reaction, and yields precipitates with the salts of the heavy metals.

Nitroacetalddehyde-p-nitrophenylhydrazone,



forms orange-brown flakes which decompose at 141—142°.

β -Nitroethylidene-p-chloroanil, $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$, obtained from the acid and *p*-chloroaniline, crystallises from light petroleum in minute, canary-yellow needles decomposing at about 165°. The corresponding *p*-nitroanil, $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, crystallises from chloroform in shimmering, yellow needles which decompose at about 183°.

β -Nitroethylideneanil, $\text{NO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}$, forms golden-yellow needles, m. p. 94—95° after sintering at 90°.

When hydrolysed with alkali, the *p*-chloroanil yields *p*-chloroaniline, ammonia, hydrogen cyanide, formic acid, methazonic acid, and carbon dioxide. With acids, the same compound yields the same products with the exception of ammonia and methazonic acid, hydroxylamine being formed in place of ammonia.

J. J. S.

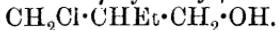
The Series Resulting from the Methylation of Ethyl Alcohol, with Regard to the Aptitude for Isomeric Change of the Halide Ethers. LOUIS HENRY (*Compt. rend.*, 1907, 145, 547—549).—A comparison is given of the facility with which the halide ethers derived from the ethyl halides, $\text{CH}_3\cdot\text{CH}_2\text{X}$, by replacement (1) in the $\cdot\text{CH}_3$ group exclusively; (2) in the $\cdot\text{CH}_2\text{X}$ group exclusively, and (3) in the $\cdot\text{CH}_3$ and $\cdot\text{CH}_2\text{X}$ group simultaneously of hydrogen by methyl, undergo isomeric change. (1) The normal propyl derivatives change into the *isocompounds*, the *isobutyl* more readily into the tertiary butyl, and the trimethylethyl halides still more readily into the tertiary amyl derivatives. (2) The *isopropyl* and *tert.-butyl* halides do not change isomerically. (3) The secondary butyl halides are stable, but the methyl*isopropyl* carbinol and the methyl *tert.-butyl* carbinol halide ethers are easily transformed into tertiary halide derivatives. The tertiary halide compounds are stable. This review reveals the fact that isomeric change occurs the more

readily the less the number of hydrogen atoms combined with the carbon atom attached to the halide-ether chain. Thus the abundant presence of hydrogen confers stability on the polycarbon chains.

E. H.

Beeswax. II. Psyllostearyl Alcohol as a Constituent. ERNST EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1907, **53**, 365—369. Compare Abstr., 1898, i, 617; 1901, i, 358).—By the use of improved methods, the surmise that psyllostearyl alcohol is present in beeswax was confirmed. The wax of *Bombus terrestris* was used in the present instance, acetone being used as the extracting agent. W. D. H.

Propylene Oxide, $\text{CH}_2\text{C}(\text{O})=\text{CHMe}$. LOUIS HENRY (*Compt. rend.*, 1907, **145**, 453—456).—The action of magnesium ethyl bromide on propylene oxide has been studied in order to ascertain whether it gives rise to a product by simple addition as in the case of ethylene oxide (this vol., i, 745), or whether isomeric change initially occurs as with *s*-dimethylethylene oxide (this vol., i, 817) and *as*-dimethyl-ethylene oxide (this vol., i, 744). The product actually obtained was methyl-*n*-propylcarbinol, $\text{CHMePr}^a\cdot\text{OH}$, which was identified by means of the semicarbazone (m. p. 100°) of the ketone, COMePr^a , formed on oxidation. The behaviour of propylene oxide is thus similar to that of ethylene oxide; the substitution of a single methyl group is not sufficient to bring about the possibility of undergoing isomeric change which exists in the dimethylated derivatives. It is to be observed that epichlorohydrin on combining with magnesium ethyl bromide gives α -chloro- γ -hydroxy- β -ethylpropane,



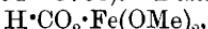
W. A. D.

Bisecondary Butylene Monochlorohydrin,
 $\text{OH}\cdot\text{CHMe}\cdot\text{CHMeCl}$.

LOUIS HENRY (*Compt. rend.*, 1907, **145**, 498—499).—*Bisecondary butylene monochlorohydrin* (γ -chloro-*sec.*-butyl alcohol) is prepared by the addition of hypochlorous acid to *s*-dimethylethylene obtained by the action of alcoholic potash on *sec.*-butyl iodide, CHMeEtI ; it is a colourless, somewhat viscous liquid, soluble in about 15 vols. of water at 20°, D^{20} 1.105, μ 1.44376, mol. refraction 26.05 (calc. 26.98), b. p. 138—139°/753 mm. It is very sensitive to alkalis and alkali carbonates, being converted into *s*-dimethylethylene oxide, $\text{CHMe}=\text{CHMe}$

(b. p. 56°).

Crystalline Iron Methoxides. KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, **40**, 3764—3766).—*Dimethoxyferric formate*,



and *dimethoxyferric acetate*, $\text{Me}\cdot\text{CO}_2\cdot\text{Fe}(\text{OMe})_2$, are obtained by dissolving iron wire in formic or acetic acid, evaporating the solution, and treating the residue with methyl alcohol in an atmosphere of carbon dioxide; both form yellow, double-refracting crystals, yield formaldehyde in contact with a glowing copper spiral, and decompose

gradually in contact with water and immediately with hydrochloric acid, the solution showing the reactions of a ferric salt.

The formation of these compounds depends on the esterification of the basic ferric salts formed intermediately (compare Hofmann and Höchtlen, Abstr., 1905, i, 38).

The *substance*, $(\text{MeCO}_2)_2\text{Fe}^{\cdot}\text{OEt}$, is a red powder, which is obtained by the evaporation in a vacuum of an ethyl-alcoholic solution of ferrous acetate after rapid oxidation in air.

C. S.

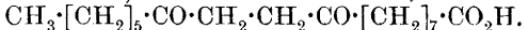
Some Salts of Glucinum and Zirconium. SEBASTIAN TANATAR and E. KURORSKI (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 936—943. Compare this vol., i, 261).—The salts obtained by the action of organic acids on glucinum carbonate mostly correspond with the formula Gl_4OX_6 . They are non-volatile, but most are soluble in benzene, some also in other organic solvents and in water. In the liquid state they are non-conductors of electricity. The following salts are described. *Formate* [the compound $\text{Gl}(\text{CHO}_2)_2$ was also obtained], *crotonate*, *isocrotonate*, *lævulate*, and *propionate*. Glucinum also forms compounds of the type $\text{Gl}_4\text{OX}_2\text{X}'_4$ and $\text{Gl}_4\text{OX}_3\text{X}'_3$; thus, by heating glucinum butyrate with acetyl chloride, the compound $\text{Gl}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_3\text{O}_2)_2$ is obtained as a viscous liquid solidifying at -15° , b. p. 351° . Similarly, the compound $\text{Gl}_4\text{O}(\text{C}_3\text{H}_5\text{O}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_3$ was obtained as a crystalline substance, m. p. 127° , b. p. 330° . The normal salts of glucinum with dibasic acids can be obtained quite readily; the following are described: *succinate*, *citraconate*, *maleate*, and *fumarate*. The salts of glucinum are very similar in constitution and solubility to the corresponding zirconium salts. Zirconium *propionate*, *isobutyrate*, *crotonate*, and *succinate* are described. The quadrivalence of glucinum is again insisted on; thus the compounds formed by the metals of the fourth group with acetylacetone are analogous in properties to the corresponding glucinum compound, whereas the compounds of the metals of the second group are quite different.

Z. K.

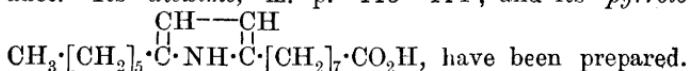
Preparation of Double Lactates containing Antimony. CHEMISCHE FABRIK VON HEYDEN (AKTIEN-GESELLSCHAFT) (D.R.-P. 184202).—Antimonyl sulphate, obtained by the action of sulphuric acid on antimonious sulphide, is introduced into a neutral solution of sodium lactate, the solution is concentrated until the sodium sulphate has separated, and the filtrate then evaporated to dryness. The *sodium antimonyl lactate* thus obtained is a crystalline double salt which dissolves in water without decomposition. *Sodium calcium antimonyl lactate*, a soluble, crystalline, slightly hygroscopic salt, is obtained by partially replacing sodium lactate by the corresponding calcium salt in the foregoing double decomposition.

G. T. M.

Preparation of $\theta\kappa$ -Diketostearic Acid. ANDREAS G. GOLD-SOBEL (D.R.-P. 180926).— $\theta\kappa$ -*Diketostearic acid*,



m. p. 96.5°, obtained by oxidising $\theta\kappa$ -ketohydroxystearic acid with chromic and acetic acids, was crystallised from water and obtained in white, lustrous leaflets soluble in warm alcohol or benzene. With the exception of its sparingly soluble alkali and ammonium compounds, its salts are insoluble in water. This acid behaves as a δ -diketone, and owing to this circumstance yields derivatives of technical importance. Its *dioxime*, m. p. 113—114°, and its *pyrrole* derivative,



G. T. M.

Xanthophanic Acid. II. CARL LIEBERMANN and SIMON LINDEMBAUM (*Ber.*, 1907, 40, 3570—3583. Compare *Abstr.*, 1906, i, 556).—The products obtained from xanthophanic acid methyl and ethyl ethers have been further investigated. The acid, m. p. 256° (255°: *loc. cit.*), obtained from the magnesium methoxide “transformation product” of xanthophanic acid methyl or ethyl ether, is shown to be a resacetophenonecarboxylic acid, having probably the

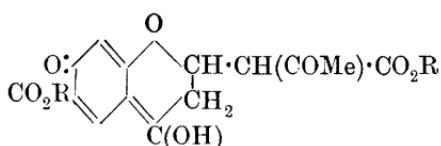
annexed structure; the *bromophenylhydrazone* of this, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CMe:N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$, crystallises in white needles, m. p. 243°. The acid cannot be esterified by means of alcohol and hydrogen chloride. The *methyl ester*, $\text{C}_{10}\text{H}_{10}\text{O}_5$, formed by the action of methyl iodide on the silver salt, crystallises in colourless needles, m. p. 124—125°, is hydrolysed by boiling alkalies, and when treated with hydrazine hydrate in methyl-alcoholic solution yields a white *hydrazone*, m. p. 174°, solidifying to a yellow *substance*, m. p. above 300°.

The *bromophenylhydrazone*, $\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_2\text{Br}$, m. p. 224° (*loc. cit.*), has the constitution $\text{CO}_2\text{Me} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{CMe:N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Br}$, and is a *hydrazone*, not of the “transformation product” from which it is prepared, but of methyl resacetophenonecarboxylate; when heated with hydrogen chloride in glacial acetic acid at 125—130°, it yields a mixture of resacetophenonecarboxylic acid and its *methyl ester*.

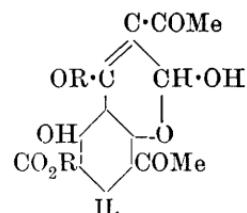
The “transformation products,” m. p. 162°, obtained by the action of magnesium methoxide on xanthophanic acid methyl and ethyl ethers respectively, are not identical, as they yield different bromides on treatment with hydrogen bromide in benzene solution. The *bromide*, $\text{C}_{17}\text{H}_{17}\text{O}_7\text{Br}$, derived from the ethyl ester, crystallises in lemon-yellow needles, m. p. 208° (decomp.), and when shaken with methyl or ethyl alcohol, acetone, or water is hydrolysed, yielding the “transformation product,” $\text{C}_{17}\text{H}_{18}\text{O}_8$. The *bromide*, $\text{C}_{16}\text{H}_{15}\text{O}_7\text{Br}$, derived from the methyl ester, crystallises in similar needles, m. p. 188° (decomp.), and on hydrolysis yields the “transformation product,” $\text{C}_{16}\text{H}_{16}\text{O}_8$.

The constitutions of these substances are discussed; it is concluded that the xanthophanic acid ethers have the structure I, and under the influence of magnesium methoxide are transformed into derivatives of the type II. In the transformation of the ethyl ether, a methyl is substituted for the carboxylic ethyl group. The hydroxyl substi-

tuted by bromine by the action of hydrogen bromide is that in the heterocyclic nucleus:



I.



II.

When boiled with hydrazine sulphate and sodium acetate in alcoholic solution, xanthophanic acid ethyl ether forms a *hydrazone* crystallising in white needles, m. p. 193—195°, which is considered to have the annexed constitution, and is formed also by the action of semicarbazide on the ethyl ether.

The corresponding *hydrazone*, $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$, derived from the methyl ether, crystallises in needles, m. p. 220°. When heated with fuming hydrochloric acid or hydrogen iodide in acetic anhydride or 10% alkali, these hydrazones yield the *acid*, $\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2$, crystallising in yellowish-green needles, m. p. 331—333° (decomp.), and forming solutions with slight blue fluorescence.

G. Y.

Glaucophanic Acid. III. CARL LIEBERMANN and H. TRUCHSÄSS (*Ber.*, 1907, 40, 3584—3588. Compare *Abstr.*, 1906, i, 556; and preceding abstract).—Glaucophanic acid methyl and ethyl ethers, which are formed as by-products in the preparation of xanthophanic acid methyl and ethyl ethers respectively, undergo reactions similar to those of the xanthophanic acid ethers, differing only in that the methyl and ethyl ethers yield identical magnesium methoxide “transformation products.” In the case of glaucophanic acid ethyl ether, therefore, the action of magnesium methoxide must lead to complete substitution of the ethoxy- by methoxy-groups, whereas only the carboxylic ethoxy-group of xanthophanic acid ethyl ether is substituted. The glaucophanic acid and xanthophanic acid ethers must have a C_{12} nucleus in common, as the action of hydrazine sulphate and sodium acetate on glaucophanic acid ethyl ether leads to the formation of the hydrazone, m. p. 193—195°, obtained from xanthophanic acid ethyl ether.

The magnesium methoxide “transformation product,” $\text{C}_{20}\text{H}_{18}\text{O}_9$, is formed from glaucophanic acid methyl ether in a 79% yield; it crystallises in yellow needles, m. p. 217°, and when heated with acetic anhydride and sodium acetate yields a *triacetate*, $\text{C}_{20}\text{H}_{15}\text{O}_9\text{Ac}_3$, which crystallises in needles, m. p. 130°, and is hydrolysed to the “transformation product” by cold concentrated sulphuric acid. In presence of a limited amount of acetic anhydride, a yellow *dacetate*, $\text{C}_{20}\text{H}_{16}\text{O}_9\text{Ac}_2$, m. p. 166°, is formed. The *bromide*, $\text{C}_{20}\text{H}_{17}\text{O}_8\text{Br}$, crystallises in orange-red needles, m. p. 245°, and is stable when dry, but is readily hydrolysed by moist solvents. A *dibromo-compound*, $\text{C}_{20}\text{H}_{16}\text{O}_9\text{Br}_2$ or $\text{C}_{20}\text{H}_{18}\text{O}_9\text{Br}_1$, formed by the action of bromine on the

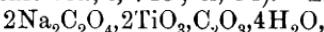
"transformation product" in carbon disulphide solution, separates from ethyl acetate in crystals, m. p. 225° (decomp.).

The "transformation product" forms a *hydrazone*, $C_{20}H_{20}O_8N_2$, crystallising in white needles, m. p. 217° (decomp.), but when heated with bromophenylhydrazine in boiling methyl-alcoholic solution forms the *bromophenylhydrazone* of a decomposition product, $C_{17}H_{17}O_4N_2Br$, which crystallises in needles, m. p. 161—163° (decomp.), and resembles, but is not identical with, the bromophenylhydrazone obtained from the "transformation product" of xanthophanic acid methyl ether.

The mol. formula of glaucophanic acid ethyl ether, which remains undecided, must lie between C_{23} and C_{27} (compare Claisen, *Abstr.*, 1897, i, 594).

G. Y.

Certain Complex Salts of Titanium Peroxide. ARRIGO MAZZUCCELLI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 265—273, 349—352; compare this vol., i, 748; ii, 54).—The compound,



prepared by adding excess of hydrogen peroxide to a solution of sodium titano-oxalate and precipitated from solution by the addition of alcohol, is a dense, dark orange, sandy powder, which dissolves readily in water and is extremely hygroscopic in presence of alcohol. It remains unaltered for some time in a dry atmosphere, but in ordinary air it deliquesces, swells, and begins to decompose. The corresponding *potassium* compound, $2K_2C_2O_4 \cdot 2TiO_3 \cdot C_2O_3 \cdot 2H_2O$, prepared by adding alcoholic potassium acetate solution to alcoholic titanium hydrogen oxalate solution containing hydrogen peroxide, resembles the sodium derivative.

By adding an insufficient amount of barium chloride, together with ammonium acetate, to a solution of sodium titano-oxalate containing the three constituents in the proportions $TiO_2 : 2H_2C_2O_4 : 2Na$ and mixed with hydrogen peroxide, various fractions are precipitated which consist apparently of mixtures of $2BaC_2O_4$, $2TiO_3$, C_2O_3 , and BaC_2O_4 .

The complexity of the titano-oxalates is shown by the ease with which they can be recrystallised, almost unchanged, from their solutions and by their resistance to hydrolysis by the action of heat. That the degree of complexity is not high is seen from the fact that these salts are decomposed, not only by alkalis, but even by an excess of a barium or calcium salt (compare Rosenheim and Schütte, *Abstr.*, 1901, ii, 244). The alkali pertitano-oxalates, however, are more highly complex, since they are not completely precipitated by ammonia. The introduction of active oxygen into the molecule of titanium oxide is hence, in general, favourable to the formation of complex anions. The statement of Melikoff and Pissarjewsky (*Abstr.*, 1898, ii, 374) that, in the preparation of titanium peroxide, by Classen's method, the clear liquid at first contains an ammonium pertitanate, which decomposes with precipitation of $TiO_3 \cdot Aq$, is probably inaccurate; it is more likely that the TiO_3 is present initially as a complex anion, which is gradually decomposed by the alkali.

The so-called acetate of titanium peroxide (Faber, this vol., ii, 557) is most probably a mixture of peroxide and basic acetate of titanium

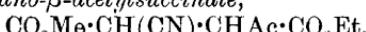
dioxide. The existence of the phosphate is in accord with the views of the author (*loc. cit.*). T. H. P.

Velocity of the Decomposition of Malonic Acid into Carbon Dioxide and Acetic Acid. JOSEF LINDNER (*Monatsh.*, 1907, 28, 1041—1047).—The decomposition of malonic acid into carbon dioxide and acetic acid takes place with measurable velocity in glacial acetic acid at 100°. The velocity constant when calculated with the aid of the equation for unimolecular reactions remains satisfactorily uniform throughout the course of the decomposition. The graph formed by plotting the velocity constants determined at 98.5° to 104° against the temperatures is approximately a straight line. G. Y.

Action of α -Chloroacetoacetic Esters on Sodiocyanooacetic Esters. J. CHASSAGNE (*Bull. Soc. chim.*, 1907, [iv], 1, 914—916. Compare Haller and Barthe, *Abstr.*, 1888, 937).—*Ethyl α -cyano- β -acetylsuccinate*, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, prepared by the action of ethyl α -chloroacetoacetate on ethyl sodiocyanooacetate, separates from alcohol in crystals, m. p. 83.5—84.5° (corr.), and has the normal molecular weight in freezing acetic acid.

Methyl α -cyano- β -acetylsuccinate, $\text{CO}_2\text{Me}\cdot\text{CH}(\text{CN})\cdot\text{CHAc}\cdot\text{CO}_2\text{Me}$, similarly prepared, separates in crystals, m. p. 89.5—90.5°.

Methyl ethyl α -cyano- β -acetylsuccinate,



obtained by the interaction of ethyl α -chloroacetylacetate and methyl sodiocyanooacetate, forms crystals, m. p. 93.5—94.5°. The *isomeric ester*, $\text{CO}_2\text{Me}\cdot\text{CHAc}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$, prepared from methyl α -chloroacetylacetate and ethyl sodiocyanooacetate, has m. p. 88.5—89.5°.

Since these compounds in alcoholic solution give no red coloration with ferric chloride, it is possible that they have an enolic structure.

T. H. P.

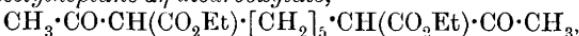
Conversion of Methyl Alcohol into Formaldehyde. Preparation of Formalin. E. J. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 855—868).—Experiment shows that the ordinarily accepted view of the conversion of methyl alcohol into formaldehyde as well as the ordinary method of preparation are essentially wrong. An elaborate apparatus has been devised which yields satisfactory results for technical purposes. The first stage in the reaction is the catalytic decomposition of methyl alcohol, thus: $\text{MeOH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$. The catalysts employed were freshly reduced copper and asbestos containing precipitated lower oxides of vanadium. The former is the most efficient catalyst, but not more than 60% of the alcohol is ever thus changed. In addition, the formaldehyde decomposes, forming carbon monoxide and hydrogen, which together with carbon dioxide are generally found in the gaseous products. The presence of impurities such as acetone makes no difference in the decomposition of the alcohol.

Z. K.

The Effect of Light and Temperature on the Preservation of Formaldehyde Solutions. J. W. de WAAL (*Pharm. Weekblad*, 1907, 44, 1207—1213).—At the ordinary temperature when exposed to light, formaldehyde solutions are not oxidised to formic acid, even in presence of traces of ferric chloride. Rise of temperature promotes the oxidation somewhat, although the effect produced by a temperature of 50° during 400 hours is only slight.

A. J. W.

Synthesis of Ketones by aid of Dibromopentane. JULIUS VON BRAUN (*Ber.*, 1907, 40, 3943—3948. Compare Perkin and Freer, *Trans.*, 1888, 53, 202; Perkin and Kipping, *ibid.*, 1890, 57, 320).— α -Dibromopentane, ethyl acetoacetate, and sodium react in warm alcoholic solution to form two compounds. *Ethyl 1-acetyl-cyclohexane carboxylate*, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_{10}\cdot\text{COMe}$, b. p. 241—245° (decomp.), or 120—124°/11 mm., is a colourless liquid with a piercing aromatic odour, which forms a *semicarbazone*, m. p. 144°, and a *p-nitrophenylhydrazone*, m. p. 145°, and is hydrolysed by aqueous-alcoholic alkali, yielding *cyclohexanecarboxylic acid* and Darzens' and Bouveault's methyl *cyclohexanyl ketone*, which has D^{22} 0.893 and forms a reddish-violet *p-nitrophenylhydrazone*, m. p. 154°. The second compound is *ethyl α -diacetylheptane- α -dicarboxylate*,



which is very difficultly volatile with steam, and cannot be distilled without decomposing into the *diketone*, $\text{COMe}\cdot[\text{CH}_2]_7\cdot\text{COMe}$, the formation of which is completed by boiling with alkali. The diketone, m. p. 65°, crystallises in glistening leaflets, and forms a *semicarbazone*, $\text{C}_{13}\text{H}_{26}\text{O}_2\text{N}_4$, m. p. 184°, *p-nitrophenylhydrazone*, $\text{C}_{23}\text{H}_{30}\text{O}_4\text{N}_6$, m. p. 88°, softening at 85°, and an oxime which yields apparently a mixture of two benzoyl derivatives, of which one has been isolated and has m. p. 90°.

C. S.

Isolation of Carbohydrates and Glucosides by Precipitation with Metallic Salts. G. MEILLÈRE (*J. Pharm. Chim.*, 1907, 26, 300—304).—The method of precipitating carbohydrates and glucosides by means of the lead acetates under different conditions is discussed, and attention is drawn to various causes which tend to complicate the fractional precipitation. It is shown that copper acetate may be employed in place of lead acetate for precipitating glucosides, the only difference being that the precipitates are most readily formed in hot solutions. Fractional precipitation may be accomplished by working in acetic acid, neutral, and finally in ammoniacal solutions.

The copper method does not yield good results with many carbohydrates, especially lactose and maltose, as they reduce the copper salt, but may be employed for isolating inositol provided the liquid is neutralised with ammonia.

J. J. S.

Action of Cold Aqueous Sodium Hydroxide on Cellulose. WALther VIEWEG (*Ber.*, 1907, 40, 3876—3883).—Wichelhaus and the author (this vol., i, 186) have shown that natural and mercerised cellulose differ from one another in chemical properties. The author now shows the effect of the variation in strength of the sodium

hydroxide on cellulose. Experiments are quoted to show the amount of sodium hydroxide taken up by cellulose from alkaline solutions of varying concentration; the conclusion is drawn that a chemical action takes place. The compounds of sodium hydroxide and cellulose are completely decomposed by water, and a product remains which takes up more sodium hydroxide than the original cellulose. Specimens of cellulose were found to differ with respect to the amount of sodium hydroxide which they take up; the "degree of mercerisation" varies from 1 to 3%, and may be estimated by the Schotten-Baumann method.

A. McK.

Chemistry and Physiological Action of the Humic Acids.

R. A. ROBERTSON, JAMES C. IRVINE, and MILDRED E. DOBSON (*Bio-Chem. J.*, 1907, 2, 458—480).—The natural humic acids prepared from peat differ greatly in composition, and also from the artificial form prepared from sucrose. The acids themselves and their potassium salts serve as organic food for *Penicillium*, both as regards carbon and nitrogen.

W. D. H.

Further Observations on the Behaviour of Alkyl Attached to Nitrogen towards Boiling Hydriodic Acid. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1907, 28, 1063—1068. Compare this vol., i, 30; Goldschmidt and Hönigschmid, *Abstr.*, 1904, ii, 94).—Whilst many substances containing an alkyl group attached to nitrogen have been found when boiled with hydriodic acid to yield the alkyl iodide, with greater or less ease depending on the structure of the nucleus, only negative results have been obtained previously with aliphatic compounds, including tetramethylammonium iodide, benzylidimethylamine, and compounds such as betaine, sarcosine, and methylaminoacetophenone, containing the grouping $\text{CO}\cdot\text{C}\cdot\text{C}\cdot\text{NMe}$, which in the piperidine series yields methyl iodide with special ease. The behaviour towards boiling hydriodic acid of a number of compounds having the group $\text{N}\cdot\text{Alkyl}$ attached to a tertiary aliphatic carbon has now been investigated, as such substances resemble aromatic compounds in certain respects.

When boiled with hydriodic acid, b. p. 127°, for six hours, and then for a further six hours with hydriodic acid, D 1·9, the following substances yield the percentages quoted of the *N*-alkyl group as the alkyl iodide: 1:2:4:4-tetramethyltrimethyleneimine, 5·4%; 2:4:4-trimethyl-1-ethyl-trimethyleneimine, 2·5%; methyldiacetonealkamine, 7·0%; methylpropylacetonealkamine, 20·5%; β -dimethylamino- β -methyl- Δ^{δ} -pentene, 4·4%. On the other hand, α -methylamino- α -phenylbutan- γ -ol, in which the methylamino-group is attached to a secondary carbon atom, does not yield methyl iodide. Since the propyl group must be less reactive than the ethyl group, the high result obtained with methylpropylacetonealkamine cannot be ascribed to the formation of propyl iodide.

Whilst the average stability of the methyl groups of a dimethylarylamine is greater than the stability of the methyl of a methylarylamine, the average stability of the methyls of a trimethylarylarnonium iodide is much smaller, and the velocity of the formation

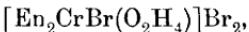
of methyl iodide correspondingly greater. Thus methylaniline in sixteen and a half hours yields 3·4%, dimethylaniline in eleven and a half hours, 3·9%, and phenyltrimethylammonium iodide in two hours, 6·5% of the total methyl as methyl iodide. Of interest as compared with the behaviour of dimethylaniline is that of tetramethylbenzidine, which in eleven and a half hours yields 7·02% of its methyl as methyl iodide.

When boiled with hydriodic acid, *as*-phenylmethylhydrazine yields 2·93% of the methyl as methyl iodide; at the same time, free iodine is formed in consequence of the reduction of the hydrazine. Which of these is the primary reaction cannot be decided.

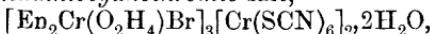
G. Y.

Bisaquochromium Salts. PAUL PFEIFFER [and, in part, ARMIN TRIESCHMANN, STERN, and PRADE] (*Ber.*, 1907, 40, 3828—3839).—A number of salts of the diethylenediaminechromium series have been prepared corresponding with the recently described diaquotetraamminechromium salts (Pfeiffer, this vol., ii, 694). In each case, however, it is found that the diethylenediamine salt contains twice the quantity of water not removed in a desiccator which is present in the corresponding diethylenediamine compound; consequently it is necessary to assume that the single water molecules in the metal complex of the diammine salt are replaced by O_2H_4 molecules in the diethylenediamine compound. The author proposes to name such salts containing the O_2H_4 complex, *bisaquo-salts* (compare Werner and Gubser, *Abstr.*, 1906, ii, 452).

cis-Bromobisaquodiethylenediaminechromium bromide,

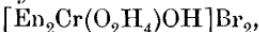


was originally wrongly described as a mono aquo-salt (*Abstr.*, 1905, i, 34). A concentrated solution of the salt yields with potassium iodide the *iodide*, a brilliant, crystalline, red powder; with potassium thiocyanate, the orange *cis-dithiocyanodiethylenediaminechromium thiocyanate*, $[En_2Cr(SCN)_2]SCN$; with ammonium oxalate, the bordeaux-red *double salt*, $[En_2CrC_2O_4][EnCr(C_2O_4)_2]$; with potassium chromothiocyanate, the *hexathiocyanochromic salt*,



crystallising in brilliant, violet-red, transparent needles, which are decomposed by light. Concentrated nitric acid probably converts the bromide into the *nitrate*: obtained as an orange-red precipitate.

cis-Hydroxybisaquodiethylenediaminechromium bromide,



prepared by the action of pyridine on the bromobisaquo-bromide, forms compact, bordeaux-red crystals. A concentrated solution of the salt gives with silver nitrate a precipitate of silver bromide free from silver hydroxide; with potassium iodide, a red, crystalline precipitate of the *iodide*. Concentrated hydrobromic acid converts the salt into *cis-dibisaquodiethylenediaminechromium bromide*,



crystallising in small, orange-red, transparent plates. This salt is converted by pyridine into the hydroxybisaquo-bromide and slowly by hydrobromic acid at the ordinary temperature into the bromobisaquo-bromide. A concentrated aqueous solution of the salt yields with

solid potassium oxalate, small, brilliant, orange leaflets of the *oxalate*. The salt is converted when heated alone at 100–120°, also when evaporated with hydrobromic acid on a water-bath, into the *anhydrous* form of *cis-dibromodiethylenediaminechromium bromide*, $[\text{En}_2\text{CrBr}_2]\text{Br}$. This substance is also obtained, by evaporating a solution of the bromobisquo-bromide with a drop of hydrobromic acid on a water-bath, in the form of a violet powder. The anhydrous salt is converted by small quantities of water into a *monohydrate*: obtained as a fine crystalline, violet powder. The *iodide* forms glittering, violet leaflets; the *dithionate* forms brilliant bluish-violet needles; the *nitrate* is obtained as a violet powder.

W. H. G.

Complex Derivatives of Optically-Active *l*-Propylenediamine. LEO TSCHUGAEFF and W. SOKOLOFF (*Ber.*, 1907, 40, 3461–3465).—The great increase in optical activity caused by the addition of certain salts to various optically-active compounds, containing hydroxy-groups, has been ascribed by Walden and others to the formation of cyclic complexes. The influence of ring formation on rotation has been investigated by the authors with certain metal derivatives of *l*-propylenediamine, the cyclic nature of metallic derivatives of *dl*-propylenediamine having already been demonstrated by Werner.

l-Propylenediamine, obtained by the resolution of the *dl*-base by *d*-tartaric acid, has b. p. 121°, $D_4^{23} 0.8633$, $[\alpha]_D - 28.04^\circ$, whereas Baumann gives $D_4^{23} 0.91186$ and $[\alpha]_D - 20.96^\circ$.

l-*Propylenediamine hydrochloride*, $\text{C}_3\text{H}_6(\text{NH}_2)_2 \cdot 2\text{HCl}$, has m. p. 240°, $D_4^{25} 1.0575$, and $[\alpha]_D^{25} - 4.04^\circ$ (in aqueous solution, $\nu = 19.92$).

The platinum compounds studied were prepared by the interaction of platinum *cis*-dichloro-*l*-propylenediamine, $[\text{PtPnCl}_2]$, in aqueous solution at 100° and the calculated amount of the corresponding bases (*l*-propylenediamine, ammonia, ethylenediamine, or trimethylene-diamine); the resulting solutions were concentrated and the compounds precipitated by the addition of alcohol or a mixture of ether and alcohol.

The compound, $l\text{-}[\text{PtPn}_2]\text{Cl}_2$ (where $\text{Pn} = \text{NH}_2\text{-CHMe-CH}_2\text{-NH}_2$), has $[\alpha]_D^{25} + 46.37^\circ$ for p 16.61 and $D_4^{25} 1.0958$. [Solvent not stated in this and other cases.—ABSTRACTOR.]

The compound, $l\text{-}\left[\text{Pt}_{2\text{NH}_3}^{\text{Pn}}\right]\text{Cl}_2$, has $[\alpha]_D^{25} + 25.17^\circ$ for p 17.47 and $D_4^{25} 1.1141$.

The compound, $l\text{-}\left[\text{Pt}_{\text{En}}^{\text{Pn}}\right]\text{Cl}_2$, has $[\alpha]_D^{25} + 24.07^\circ$ for p 19.08 and $D_4^{25} 1.1195$.

The compound, $l\text{-}\left[\text{Pt}_{\text{Tr}}^{\text{Pn}}\right]\text{Cl}_2$, has $[\alpha]_{\text{Auer}}^{25} + 23.60$ for p 13.09 and $D_4^{23} 1.0747$.

The compound, $l\text{-}[\text{PdPn}_2]\text{Cl}_2$, obtained from K_2PdCl_4 and *l*-propylenediamine, has $[\alpha]_D^{25} + 79.25^\circ$ for p 17.68 and $D_4^{25} 1.0772$.

The compound, $[\text{NiPn}_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, has $[\alpha]_D^{25} + 14.13^\circ$ for p 11.04 and $D_4^{25} 1.0253$.

It will be observed that, although *l*-propylenediamine and its hydro-

chloride are laevorotatory, the metallic derivatives examined are dextrorotatory.

The influence of the number of propylenediamine molecules in the complex molecule of the platinum derivatives is clearly seen by a comparison of the molecular rotations of these compounds. A. McK.

Isomeric $\alpha\beta$ -Dialkylhydroxylamines. I. α -Methyl- β -ethylhydroxylamine. II. β -Methyl- α -ethylhydroxylamine. LAUDER W. JONES (*Amer. Chem. J.*, 1907, 38, 253—257).—It has been shown previously (Abstr., 1898, i, 174) that when the sodium salt of hydroxyurethane (carbethoxyhydroxamic acid) is treated with methyl iodide, the methyl ether, $\text{OEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{OMe}$, is produced together with $\alpha\beta$ -dimethylcarbethoxyhydroxylamine (hydroxymethylurethane methyl ether), $\text{CO}_2\text{Et}\cdot\text{NMe}\cdot\text{OMe}$, which on hydrolysis yields $\alpha\beta$ -dimethylhydroxylamine. The corresponding ethyl derivatives were obtained in a similar manner.

When hydroxyurethane methyl ether is treated with ethyl iodide in presence of sodium ethoxide, carbethoxy- α -methyl- β -ethylhydroxylamine (*hydroxyethylurethane methyl ether*), $\text{CO}_2\text{Et}\cdot\text{NMe}\cdot\text{OMe}$, b. p. 165—166°, is produced as a colourless oil which has a peculiar, rather unpleasant odour. If this compound is heated with strong hydrochloric acid, it is converted into α -methyl- β -ethylhydroxylamine, $\text{NHEt}\cdot\text{OMe}$, b. p. 60—61°, which is a colourless, alkaline liquid, readily soluble in water, and does not reduce silver nitrate; the *hydrochloride*, m. p. 46—47° (approx.), and the *platinichloride*, m. p. 174—175° (decomp.), are described.

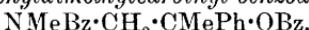
Similarly, methyl iodide reacts with hydroxyurethane ethyl ether to form carbethoxy- β -methyl- α -ethylhydroxylamine (*hydroxymethylurethane ethyl ether*), $\text{CO}_2\text{Et}\cdot\text{NMe}\cdot\text{OEt}$, b. p. 166—167°, which on hydrolysis yields β -methyl- α -ethylhydroxylamine, $\text{NHMe}\cdot\text{OEt}$, b. p. 65—65.5°, which furnishes a *hydrochloride*, m. p. 74—75°, and a *platinichloride*, m. p. 170—171° (decomp.). E. G.

Preparation of Acylated Aminoalkyl Esters. J. D. RIEDEL (D.R.-P. 181175. Compare Abstr., 1906, i, 631).—This patent deals with the preparation of substances having the general formula $\text{NR}^{\text{III}}\text{R}^{\text{IV}}\cdot\text{CH}_2\cdot\text{CR}^{\text{I}}\text{R}^{\text{II}}\cdot\text{OR}$, where R and R^{IV} are acyl groups and R^{I} , R^{II} , and R^{III} are alkyl, aryl, or mixed arylalkyl groups. These compounds have useful antipyretic and hypnotic properties.

Methylaminodimethylmethylethylcarbinol, $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$, an oil, b. p. 80°/52 mm., was obtained by heating chlorodimethylmethylethylcarbinol with methylamine in 25% alcoholic solution.

Valeryl methylaminodimethylmethylethylcarbinyl valerate, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}_2$, b. p. 162°/26 mm., was prepared by the action of valeryl chloride and aqueous sodium hydroxide on the preceding compound.

Methylaminophenyldimethylcarbinol, $\text{NHMe}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{OH}$, b. p. 136—138°/31 mm., obtained from chlorophenyldimethylcarbinol and methylamine on treatment with benzoyl chloride at 150°, yielded *benzoylmethylaminophenyldimethylcarbinyl benzoate*,



m. p. 122°.

G. T. M.

Hydroxy- and Ethoxy-Derivatives of Normal Primary Butylamine. LOUIS HENRY (*Bull. Acad. roy. Belg.*, 1907, 384—397).— δ -Ethoxybutylamine, $OEt \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$, b. p. 153—154°/746 mm., D^{20} 0·8640, n_D^{20} 1·42751, obtained by reducing γ -ethoxybutyronitrile by Ladenburg's method, is a colourless, mobile liquid of disagreeable odour and piquant taste, and dissolves in water with development of heat, probably forming a hydrate.

Aminoethyl ether, $NH_2 \cdot C_2H_4 \cdot OEt$, boils at 73° higher than ethyl ether and 89° higher than ethylamine, whilst δ -ethoxybutylamine boils only 62° higher than ethyl butyl ether and 78° higher than normal primary butylamine, so that the influence on volatility of the two components, $-CH_2 \cdot NH_2$ and $-CH_2 \cdot OEt$, is less marked when they are separated by the system $-CH_2 - CH_2 -$ than when they are close together.

The fall in boiling point due to the conversion of normal primary butyl alcohol into the corresponding ethyl ether is 25°, and that resulting from the change of δ -hydroxybutylamine into its ethyl ether is 53°. Similarly, the increase in boiling point due to the introduction of the NH_2 group into normal butane is 74°, whilst that due to the introduction of the same group in the δ -position in normal butyl alcohol is 90°. These differences are probably due to mutual action between the $-CH_2 \cdot OH$ and $-CH_2 \cdot NH_2$ groups being greater than that between the groups $-CH_2 \cdot OEt$ and $-CH_2 \cdot NH_2$.

The increase of boiling point resulting from the conversion of the normal paraffins into the corresponding primary alcohols is greater than that due to their conversion into the corresponding primary amines, probably because the alcohols are associated. Similarly, the increase in boiling point on passing from alcohols to the corresponding glycols is greater than that observed in changing from monoamines to the corresponding diamines.

The transformation of an amine into the corresponding amino-alcohol is accompanied by a rise of boiling point almost as great as that observed on passing from the hydrocarbon to the corresponding alcohol, and greater than that due to the conversion of the alcohol into the corresponding amino-alcohol, as the following example shows: $CH_3 \cdot CH_2 \cdot NH_2 \rightarrow OH \cdot CH_2 \cdot CH_2 \cdot NH_2 = +152^\circ$. $CH_3 \cdot CH_2 \cdot OH \rightarrow NH_2 \cdot CH_2 \cdot CH_2 \cdot OH = +93^\circ$. This difference is probably due, in part, to association in the case of the hydroxy-compounds, and, in part, to mutual action between the $-CH_2 \cdot NH_2$ and $-CH_2 \cdot OH$ groups.

The increase in boiling point resulting from the change from the simple alcohol to the glycol or from the monoamine to the diamine is less than that due to the conversion of the hydrocarbon into the simple alcohol or monoamine respectively, and as the difference between the increases due to the two changes, hydrocarbon \rightarrow alcohol \rightarrow glycol, is greater than that exhibited in the case of the two changes, hydrocarbon \rightarrow monoamine \rightarrow diamine, it may be assumed that the mutual action between two $-CH_2 \cdot OH$ groups is greater than that between two $-CH_2 \cdot NH_2$ groups. This also explains the fact that a greater difference in volatility is shown between successive members in a homologous series of diamines than between successive members of a homologous series of glycols. The differences observed in the

latter series are of the same order as those which obtain in a homologous series of amino-alcohols. The replacement of a $-OH$ group in a glycol by a $-NH_2$ group gives rise at the stages C_2 , C_3 , and C_4 to the same lowering ($24-26^\circ$) of the boiling point, and this value is less than that ($41-59^\circ$) due to the replacement of $-OH$ in a simple alcohol by $-NH_2$. The former case affords a further example of the mutual influence exerted by the groupings $-CH_2\cdot NH_2$ and $-CH_2\cdot OH$.

T. A. H.

Diacetoneamine. MORITZ KOHN (*Monatsh.*, 1907, 28, 1049—1053).—It has been shown previously that the action of magnesium methyl iodide on diacetone alcohol leads to the formation of $\beta\delta$ -dimethylpentane- $\beta\delta$ -diol (Franke and Kohn, *Abstr.*, 1905, i, 111; this vol., i, 171). The action of magnesium methyl iodide on diacetone-amine is found now to lead in the same manner to the formation of β -amino- $\beta\delta$ -dimethylpentane- δ -ol, only a small amount of the diacetone-amine undergoing decomposition into ammonia and mesityl oxide.

β -Amino- $\beta\delta$ -dimethylpentane- δ -ol, $NH_2\cdot CMe_2\cdot CH_2\cdot CMe_2\cdot OH$, is obtained as a mobile oil, b. p. $82^\circ/19-20$ mm., has a slight ammoniacal odour, and absorbs carbon dioxide rapidly on exposure to air. The *platinichloride*, $(C_7H_{17}ON)_2H_2PtCl_6$, crystallises in scarlet, rhombohedral plates; the *picrate*, $C_{13}H_{20}O_8N_4$, forms monoclinic crystals, m. p. $153-155.5^\circ$; the *oxalate*, m. p. 212° (decomp.). The action of methyl iodide on β -amino- $\beta\delta$ -dimethylpentane- δ -ol leads to the formation of a base which yields an *aurichloride*, $C_{10}H_{23}ON\cdot HAuCl_4$, crystallising in golden leaflets, m. p. $142-143^\circ$. β -Phenylthiocarbamino- $\beta\delta$ -dimethylpentane- δ -ol, $C_{14}H_{22}ON_2S$, formed by the action of phenylthiocarbimide on β -amino- $\beta\delta$ -dimethylpentane- δ -ol, crystallises in white leaflets, m. p. $115-117^\circ$.

G. Y.

Cyanogen Bromide as a Means of Testing the Stability of Groups attached to Nitrogen. JULIUS VON BRAUN (*Ber.*, 1907, 40, 3933—3943).—Previous investigations (*Abstr.*, 1900, i, 430, 641, 687; 1902, i, 365; 1903, i, 464) have shown that the reaction between tertiary bases and cyanogen bromide is represented by $NR^I R^{II} R^{III} + Br\cdot CN = NR^I R^{II} \cdot CN + R^{III} Br$, and that the series allyl, benzyl, methyl, ethyl, propyl, *isopropyl*, and phenyl denotes the increasing order of difficulty with which the group R^{III} is eliminated. Tertiary bases containing the group $\cdot CH_2\cdot CN$ or $\cdot CH_2\cdot CO_2Et$ (=X) react thus: $NR_2X + BrCN \rightarrow$ (I) $NR_2\cdot CN + BrX$ or (II) $NRX\cdot CN + RBr$. Reaction (I) increases and (II) diminishes as R increases from methyl to butyl.

Biscyanomethylpiperidinium bromide, $C_5NH_{10}(CH_2\cdot CN)_2Br$, obtained from piperidinoacetonitrile and bromoacetonitrile, has m. p. 173° (decomp.); the *platinichloride*, m. p. 192° (decomp.), forms reddish-yellow needles.

Dimethylaminoacetonitrile and cyanogen bromide react energetically to form *cyanomethylaminoacetonitrile*, $CN\cdot NMe\cdot CH_2\cdot CN$, b. p. $150-151^\circ/12$ mm., and methyl bromide; the latter reacts with the unchanged dimethylaminoacetonitrile to form *trimethylcyanomethylammonium bromide*, $CN\cdot CH_2\cdot NMe_3Br$, which is readily converted into

betaine. The odour of bromoacetonitrile is perceptible only when large quantities of dimethylaminoacetonitrile and cyanogen bromide are reacting.

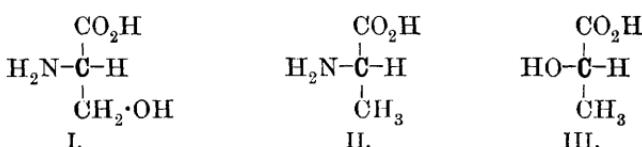
Diethylaminoacetonitrile and cyanogen bromide react to form diethylcyanamide, bromoacetonitrile, *cyanethylaminoacetonitrile*, $\text{CN}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CN}$, b. p. $150^\circ/9$ mm., and *ethylaminoacetonitrile hydrobromide*, $\text{NHEt}\cdot\text{CH}_2\cdot\text{CN}, \text{HBr}$. Ethyl diethylglycine and cyanogen bromide yield diethylcyanamide, ethyl bromoacetate, and *ethyl ethylcyanoglycine*, $\text{CN}\cdot\text{NEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, b. p. 139° .

Dipropylaminoacetonitrile, $\text{NPr}^a_2\cdot\text{CH}_2\cdot\text{CN}$, b. p. $89-90^\circ/12$ mm., is obtained from dipropylamine by Knoevenagel's method (Abstr., 1904, i, 981); the *methiodide* sinters at 130° and has m. p. 150° (decomp.). It reacts with cyanogen bromide at 100° , and yields dipropylcyanamide, bromoacetonitrile, and 20–25% of *cyanopropylaminoacetonitrile*, $\text{CN}\cdot\text{NPr}^a\cdot\text{CH}_2\cdot\text{CN}$, b. p. $155-156^\circ/12$ mm.

Ethyl dipropylglycine, $\text{NPr}^a_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained from dipropylamine and ethyl bromoacetate, has b. p. 204° (decomp.) or $104^\circ/15$ mm., and reacts with cyanogen bromide to form probably ethyl bromoacetate, dipropylcyanamide, and ethyl propylecyanoglycine. *Düisobutylaminoacetonitrile*, $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CH}_2\cdot\text{CN}$, b. p. $95-96^\circ/11$ mm., requires heating for thirty hours with cyanogen bromide; the products have not been definitely isolated. *α-Düisobutylaminopropionitrile*, $\text{N}(\text{C}_4\text{H}_9)_2\cdot\text{CHMe}\cdot\text{CN}$, b. p. $101-102^\circ/10$ mm., and *α-düisobutylpropionitrile*, $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{CHMe}\cdot\text{CN}$, b. p. $129^\circ/12$ mm., react even less favourably with cyanogen bromide.

C. S.

Conversion of *l*-Serine into *d*-Alanine. EMIL FISCHER and KARL RASKE (Ber., 1907, 40, 3717—3724).—The conversion of *l*-serine into *d*-alanine is effected by treating the hydrochloride of *l*-serine methyl ester with acetyl chloride and phosphorus pentachloride at 0° , whereby the *hydrochloride of methyl l-β-chloro-α-aminopropionate*, m. p. 157° (decomp.), is obtained (Fisher and Jacobs, this vol., i, 393), which by hydrolysis with 20% hydrochloric acid at 100° yields the hydrochloride of *l*-β-chloro-α-aminopropionic acid; the free acid, liberated by lithium or ammonium hydroxide, is reduced to *d*-alanine by sodium amalgam in faintly acid solution. It is highly probable that these reactions are optically normal, and therefore the known configuration of *l*-serine (I) determines that of *d*-alanine (II) and also of *d*-lactic acid (III) obtained from the latter by the action of nitrous acid:



The following constants are given. In aqueous solution, the *hydrochloride of l-β-chloro-α-aminopropionic acid*,



has $[\alpha]_D^{20} + 0.7^\circ$, and the acid itself, $[\alpha]_D^{20} - 15.46^\circ$. *r-β-Chloro-α-aminopropionic acid*, m. p. 160° (decomp.), is reduced to *r*-alanine by sodium

amalgam in acid solution; the *hydrochloride*, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{NH}_2\cdot\text{HCl})\cdot\text{CO}_2\text{H}$, m. p. 172° (decomp.), crystallises in slender needles, and is converted by ammonium hydroxide at 100° into Kleb's hydrochloride of *r*-aminopropionic acid. The *hydrochloride* of *methyl r*- β -chloro-*a*-aminopropionate has m. p. 134° (decomp.). C. S.

Aminotrimethylacetic [β-Amino-*aa*-dimethylpropionic] Acid. MORITZ KOHN and AUGUST SCHMIDT (*Monatsh.*, 1907, 28, 1055—1062).—Four of the twelve possible aminovaleric acids have been prepared by Slimmer (*Abstr.*, 1902, i, 206). A fifth isomeride is described in the present paper.

β-Bromo-*aa*-dimethylpropionic acid, m. p. 47° (40.5 — 41° : Blaise and Marcilly, *Abstr.*, 1904, i, 283), is obtained in a 65—70% yield by treating hydroxypivalic acid at 80° and then at 100° with aqueous hydrogen bromide saturated at 0° . *β*-*Iodo-aa-dimethylpropionic acid*, $\text{CH}_2\text{I}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, prepared by boiling hydroxypivalic acid with hydriodic acid, D 1.7, and amorphous phosphorus in a reflux apparatus, crystallises in glistening prisms, m. p. 54° .

β-*Amino-aa-dimethylpropionic acid*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$, obtained in a 60% yield by the action of alcoholic ammonia, saturated at 0° , on *β*-bromo-*aa*-dimethylpropionic acid at the ordinary temperature, crystallises in leaflets, decomp. about 220° , and forms a copper salt crystallising in microscopic, hexagonal plates. The *benzoyl* derivative, $\text{C}_5\text{H}_{10}\text{O}_2\text{N}\text{Bz}$, crystallises in thin needles, m. p. 149 — 151° . The *phenylcarbamyl* derivative, $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$, crystallises in needles, m. p. 173 — 175° . The *methylated base* forms a *hydrochloride* as a white, crystalline mass; the *aurichloride*, $\text{C}_8\text{H}_{16}\text{O}_2\text{N}\cdot\text{HAuCl}_4$, crystallises in needles, m. p. 195 — 201° (decomp.); the *picrate* crystallises in plates, m. p. 223 — 225° (decomp.). G. Y.

Polypeptides. XXI. Derivatives of Tyrosine and of Glutamic Acid. EMIL FISCHER (*Ber.*, 1907, 40, 3704—3717). Compare this vol., i, 652, 684, 737).—*d*-Alanylglycyl-*l*-tyrosine and *l*-leucyltriglycyl-*l*-tyrosine have been examined in anticipation of the study of the complex derivatives of tyrosine obtained, among other products, by the partial hydrolysis of silk-fibroin. *d-a-Bromopropionylglycyl-l-tyrosine*,

$\text{CHMeBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$, m. p. 157° (corr.), obtained by the interaction of glycyl-*l*-tyrosine and *d-a*-bromopropionyl chloride in cold alkaline solution, separates from water in elongated leaflets, and has in aqueous solution $[\alpha]_D^{20} + 50.6^\circ$. By treatment with 25% ammonium hydroxide for three and a half days at 25° , it is converted into *d-alanylglycyl-l-tyrosine*,

$\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$, which froths at 140° and darkens at 180° , responds to Millon's and the biuret reactions, and has $[\alpha]_D^{20} + 41.9^\circ$ in aqueous solution. *d-a-Bromoisohexyloyltriglycyl-l-tyrosine*,

$\text{C}_4\text{H}_9\cdot\text{CHBr}\cdot\text{CO}\cdot[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_3\cdot\text{NH}\cdot\text{CH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{CO}_2\text{H}$, is prepared from *l*-tyrosine and *d-a*-bromoisohexyldiglycylglycyl chloride in cold alkaline solution; it crystallises in needles, and has $[\alpha]_D^{20} + 28.7^\circ$ in aqueous solution. The air-dried substance softens at

100°, and has m. p. 115° (decomp.), whilst the anhydrous compound softens at 100°, gradually darkens, and has m. p. 220°. *l-Leucyl-triglycyl-l-tyrosine*, C₂₁H₃₁O₇N₅, obtained from the preceding compound and 25% ammonium hydroxide at 25°, is a colourless, amorphous substance, which begins to decompose at 160°, and has [α]_D²⁰ + 36.5° in aqueous solution. It has a bitter taste and an acid reaction, responds to Millon's and the biuret tests, and forms an amorphous *nitrate*, oily *picrate*, and *picrolonate*, and a dark blue *copper* salt. Characteristic of this pentapeptide and of the preceding tripeptide is the property of being precipitated from aqueous solution by ammonium sulphate, a behaviour which recalls that of the albumoses and also of the tetrapeptide obtained by Fischer and Abderhalden (this vol., i, 737) by the partial hydrolysis of silk fibroin.

Glutamic acid is contained in many proteins, but the study of its polypeptides has hitherto been retarded by the difficulty of obtaining crystalline derivatives of the acid. *l-Leucyl-d-glutamic acid*,

CHMe₂·CH₂·CH(NH₂)·CO·NH·CH(CO₂H)·CH₂·CH₂·CO₂H, m. p. 232° (decomp. corr.), obtained by the action of 25% ammonium hydroxide on *d-a*-bromoisohexyoyl-*d*-glutamic acid, separates from water in long needles, has [α]_D²⁰ + 10.5° in *N*-hydrochloric acid, is not precipitated from a solution in dilute sulphuric acid by phosphotungstic acid, and forms easily soluble *sodium* and *barium* salts. On the other hand, the *silver* salt is sparingly soluble in water; in virtue of this property, many derivatives of glutamic and also of aspartic acid may be separated from other polypeptides.

The *d-a*-bromoisohexyoyl-*d*-glutamic acid, m. p. 108—109° (corr.), required in the preceding preparation, is prepared from *d*-glutamic acid and *d-a*-bromoisohexyoyl chloride in cold alkaline solution.

Triglycylglycinamide,

NH₂·CH₂·CO·[NH·CH₂·CO]₂·NH·CH₂·CO·NH₂, is prepared by heating methyl triglycylglycine for two hours at 80—100° with methyl alcoholic ammonia saturated at 0°. It crystallises in slender needles, sinters and darkens at 225°, and by solution in the dilute acid yields the *nitrate* and the *hydrochloride*; the *picrate* forms orange-red leaflets, and has m. p. 240° (decomp.). Methyl pentaglycylglycine is converted only partially into the amide by liquid ammonia at the ordinary temperature, or by methyl or ethyl alcoholic ammonia at 100°.

The molecular weights of glycyl-*l*-tyrosine, diglycylglycine, tri-glycylglycine, leucyldiglycylglycine, *l*-alanyldiglycyl-*l*-alanylglycylglycine, and glycyl-*d*-valine anhydride, determined in aqueous solution by the cryoscopic method, are approximately normal.

The acylation of tyrosine leads, as a rule, to the formation of diacyl derivatives; formic acid, however, yields *formyl-l-tyrosine*,

OH·C₆H₄·CH₂·CH(CO₂H)·NH·CHO, H₂O, which has m. p. 171—174° (decomp. corr.) in the anhydrous state and [α]_D²⁰ + 84.9° in alcoholic solution. C. S.

Preparation of Alkyl Dialkylmalonamates. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 182045).—The alkyl dialkylmalonamates are employed in the production of the dialkyl-

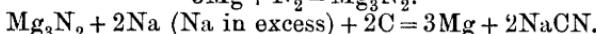
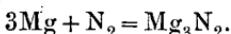
barbituric acids. *Ethyl diethylmalonamate*, $\text{NH}_2\cdot\text{CO}\cdot\text{CET}_2\cdot\text{CO}_2\text{Et}$, needles, m. p. 79° , is preferably produced by alkylating ethyl malonamate in two stages by the repeated action of ethyl iodide in alcoholic sodium ethoxide.

Ethyl dipropylmalonamate, $\text{NH}_2\cdot\text{CO}\cdot\text{CPr}_2\cdot\text{CO}_2\text{Et}$, white needles, m. p. 92° , is prepared by the action of sodium (2 atoms) and propyl iodide (2 mols.) on ethyl malonamate in alcoholic solution.

The alkyl sulphates may also be employed in producing the alkyl dialkylmalonamates.

G. T. M.

Production of Alkali Cyanides. OTTO SCHMIDT (D.R.-P. 180118. Compare this vol., i, 299).—By passing nitrogen over a mixture of magnesium, carbon, and an alkali carbonate, an amount of alkali cyanide is obtained equivalent to the quantity of the magnesium present. If, however, the carbonate is replaced by the alkali metal itself, it becomes possible to convert a much larger proportion of alkali metal into cyanide.



One molecule of magnesium will bring about the transformation of 4 molecules of sodium into sodium cyanide. The magnesium has undoubtedly a specific action on the absorption of nitrogen, and the formation of sodium cyanide occurs far more rapidly and completely than in the absence of this metal.

G. T. M.

Glutamine. ERNST SCHULZE and CH. GODET (*Landw. Versuchs-Stat.*, 1907, 67, 313—319. Compare this vol., i, 114).—Fresh preparations of glutamine from (1) sugar-beet and (2 and 3) mangolds gave $[\alpha]_D + 6.45^\circ$, $+ 8.2^\circ$, and $+ 9.5^\circ$ respectively. At 16° , it dissolves in 25.7 parts of water; the copper derivative, $\text{Cu}(\text{C}_5\text{H}_9\text{O}_3\text{N}_2)_2$, can be obtained in small, bluish-violet crystals by heating a solution of glutamine with copper acetate. The cadmium derivative, $\text{Cd}(\text{C}_5\text{H}_4\text{O}_3\text{N}_2)_2$, obtained by adding freshly precipitated cadmium hydroxide to a heated solution of glutamine until no longer dissolved, separates in fine prisms; when boiled with water, the compound is slowly hydrolysed.

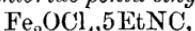
Glutamine (1 mol.) forms a compound with tartaric acid (1 mol.) which separates in rather large, transparent crystals. N. H. J. M.

Calcium Cyanamide. II. GEORG BREDIG, W. FRAENKEL, and E. WILKE (*Zeitsch. Elektrochem.*, 1907, 13, 605—612. Compare this vol., i, 369).—The influence exerted by various substances on the absorption of nitrogen by calcium carbide has been further studied. Experiments with glucinum, magnesium, and strontium chlorides confirm the view that for metals in the same periodic group the acceleration of the reaction is greater the lower the atomic weight of the metal. This relationship holds for 10% admixture. The formation of cyanide increases, on the other hand, with the atomic weight of the metal, but the quantity is always small. Metallic calcium, magnesium and sodium do not appreciably accelerate the absorption of nitrogen when mixed with the carbide. The view that the nitrogen absorption is directly due to calcium produced from the carbide is not supported

by these experiments. Water vapour and calcium oxide, either alone or mixed with other substances, have no influence on the rate of the reaction. The authors suppose that the acceleration phenomena are connected with the fusibility of the added substance and the solubility of the carbide in the flux. For each flux, however, there may be a specific reaction constant. Determination of the velocity of the nitrogen absorption in nitrogen at different pressures shows that this is proportional to the pressure of the gas. Whether diffusion, absorption, or chemical reaction is the determining factor in the velocity of the reaction has not yet been ascertained. H. M. D.

Compounds of Ethylcarbylamine with Cobaltous, Ferrous, and Ferric Chlorides. KARL A. HOFMANN and GÜNTHER BUGGE (*Ber.*, 1907, 40, 3759—3764. Compare this vol., i, 419; Ramberg, *ibid.*, 604).—Guillemard, in another way (this vol., i, 300), has arrived at the authors' conclusion that metallic cyanides are of the carbylamine type.

Cobaltous chloride bisethylcarbylamine, $\text{CoCl}_2 \cdot 2\text{EtNC}$, obtained from its constituents in methyl-alcoholic solution, forms green crystals; the chlorine is precipitated completely by silver nitrate. *Ferric chloride bisethylcarbylamine*, $\text{FeCl}_3 \cdot 2\text{EtNC}$, similarly obtained in ethereal solution, forms stout, yellow prisms. *Ferric chloride trisphenylcarbylamine*, $\text{FeCl}_3 \cdot 3\text{PhNC}$, crystallises in greenish-yellow plates. *Ferric oxychloride tetra-ethylcarbylamine*, $\text{Fe}_2\text{OCl}_4 \cdot 4\text{EtNC}$, obtained from ferrous chloride and ethylcarbylamine in ether, forms yellow plates. *Ferric oxychloride penta-ethylcarbylamine*,



is obtained in golden-yellow crystals from a 6% methyl-alcoholic solution of ferrous chloride and ethylcarbylamine (3 mols.).

All these compounds are decomposed by alkalis, but the last-mentioned exhibits its greater stability in giving a precipitate with silver nitrate only in the presence of dilute nitric acid, and in forming Prussian-blue only in the presence of hydrochloric acid. C. S.

Cobalt Dioximines. II. LEO TSCHUGAEFF (*Ber.*, 1907, 40, 3498—3504. Compare *Abstr.*, 1906, i, 814).—Since metal-ammonia derivatives, which contain all the components of the complex molecules in the non-ionisable form, are of especial interest, the author describes two general reactions for preparing compounds of this type.

The compounds $[\text{CoNH}_3\text{ClD}_2\text{H}_2]$ and $[\text{CoD}_2\text{H}_3\text{NH}_3\text{NO}_2]$ (where $\text{DH}_2 = \text{R}^1 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{R}^2$), obtained by the interaction of dimethylglyoxime with derivatives of the pentammine series, $[\text{Co}_5\text{NH}_5\text{Cl}]X_2$ and $[\text{Co}_5\text{NH}_5\text{NO}_2]X_2$, in the presence of an excess of ammonium acetate have already been described.

It is found that the presence of an excess of acid is important for the success of this reaction in order to prevent the formation of a derivative of the diammine series, thus: $[\text{CoNH}_3\text{XD}_2\text{H}_2] + \text{NH}_3 = [\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]\text{X}$.

Bromopentammine bromide reacts with dimethylglyoxime, thus: $[\text{Co}_5\text{NH}_5\text{Br}] \text{Br}_2 + 2\text{DH}_2 = [\text{CONH}_3\text{BrD}_2\text{H}_2] + 2\text{NH}_4\text{Br} + 2\text{NH}_3$. The

resulting compound is a typical non-electrolyte and reacts very slowly with silver nitrate in the cold ; it separates from dilute acetic acid in glistening, reddish-brown needles ; its solution in concentrated sulphuric acid is red.

The compound $[\text{CoNH}_3(\text{NO}_2)\text{D}_2\text{H}_2]$, obtained by the interaction of the xantho- or isoxantho-salts, $[\text{Co}_5\text{NH}_3\text{NO}_2]\text{X}_2$, and methylglyoxime, separates from alcohol in yellowish-brown crystals and is also a non-conductor. The compound $[\text{CoNH}_3\text{D}_2\text{H}_2\text{Cl}]$ was also obtained from methylglyoxime and purpureo-cobalt chloride, $[\text{Co}_5\text{NH}_3\text{Cl}]\text{Cl}_2$. The reaction failed when an attempt was made to prepare the compound $[\text{CoD}_2\text{H}_2\text{NH}_3\text{NO}_3]$. The compound $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]\text{NO}_3$ was the only product of the action of dimethylglyoxime on the pentammine nitrate, $[\text{Co}_5\text{NH}_3\text{NO}_3](\text{NO}_3)_2$.

The compound $[\text{CoNH}_3\text{ID}_2\text{H}_2]$, obtained from dimethylglyoxime and roseopentammine iodide, $[\text{Co}_5\text{NH}_3\text{H}_2\text{O}]\text{I}_3$, crystallises in dark brown needles. The iodine atom in this compound is not so firmly bound as in the corresponding chloro- and bromo-compounds. When heated with dilute ammonia at 100° , it forms the compound $[\text{Co}_2\text{NH}_3\text{D}_2\text{H}_2]\text{I}$, an iodide of the diammine series, which contains an ionisable iodine atom.

The behaviour of the roseo-iodide in comparison with the corresponding chloro- and bromo-salts is remarkable, since the bromide gives with dimethylglyoxime only traces of the compound $[\text{CoNH}_3\text{BrD}_2\text{H}_2]$, whilst the roseo-chloride does not give the compound $[\text{CoClNH}_3\text{D}_2\text{H}_2]$.

The praseo-halogen salts of the tetrammine series, $[\text{Co}_4\text{NH}_3\text{Cl}_2]\text{Cl}$ and $[\text{Co}_4\text{NH}_3\text{Br}_2]\text{Br}$, behave towards dimethylglyoxime like the corresponding pentammine compounds, giving the compounds $[\text{CoClNH}_3\text{D}_2\text{H}_2]$ and $[\text{CoBrNH}_3\text{D}_2\text{H}_2]$. The isomeric croceo- and flaveo-salts appear to behave similarly, and are at present under investigation.

Another method for preparing the compounds in question is described. A process of autoxidation takes place between 1 mol. of cobalt salt and 1 mol. of dimethylglyoxime in alcoholic solution and in the presence of pyridine, or a similar base in the presence of air. The formation of the compound $[\text{CoClPyD}_2\text{H}_2]$ is expressed by the equation : $2\text{CoCl}_2 + 4\text{DH}_2 + 4\text{Py} + \text{O} = 2[\text{CoClPyD}_2\text{H}_2] + 2\text{PyHCl} + \text{H}_2\text{O}$. The reaction was also conducted with α -picoline, isoquinoline, and acridine. In addition to the chlorine atom, there may be substituted bromine or iodine atoms or the electronegative groups, NO_2 , SCN , NCO , and N_3 . For dimethylglyoxime, other 1:2-dioximes, for example, methylglyoxime, may be substituted. The compounds obtained are crystalline and brown to reddish-brown in colour ; they are soluble in water with difficulty and exhibit properties typical of non-electrolytes. The compound $[\text{CoPyClD}_2\text{H}_2]$ forms yellowish-brown crystals. The compounds $[\text{CoPyNCOD}_2\text{H}_2]$ and $[\text{CoPyN}_3\text{D}_2\text{H}_2]$ are the first metal ammine derivatives of cyanic acid and hydrazoic acid respectively known which are non-conductors. The compound $[\text{CoPyN}_3\text{D}_2\text{H}_2]$ forms reddish-brown crystals and is very stable. The following derivatives of dimethylglyoxime have been prepared : $[\text{CoNH}_3\text{ClD}_2\text{H}_2]$, $[\text{CoNH}_3\text{BrD}_2\text{H}_2]$, $[\text{CoNH}_3\text{ID}_2\text{H}_2]$, $[\text{CoNH}_3\text{NO}_2\text{D}_2\text{H}_2]$, $[\text{C}\cdot\text{PyClD}_2\text{H}_2]$,

[CoPyID₂H₂], [CoPyNO₂D₂H₂], [CoPySCND₂H₂], [CoPyNCOD₂H₂], [CoPyN₃D₂H₂], [Co isoquinoline ClD₂H₂], [Co acridine ClD₂H₂].

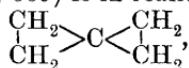
The following derivatives of methylmethylethyglyoxime have been prepared : [CoNH₃NO₂D₂H₂] and [CoPySCND₂H₂]. The following derivative of methylglyoxime has been prepared : [CoClNH₃D₂H₂].

A. McK.

Action of Nitrous Oxygen Compounds with Organo-zinc and -magnesium Compounds. IWAN J. BEWAD (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 947—973. Compare Abstr., 1900, i, 629; this vol., i, 671).—The group —N:O in organic nitrites behaves towards zinc alkyls similarly to the >C:O group in aldehydes, consequently nitrosyl chloride and zinc ethyl react thus : O:NCl + Zn(C₂H₅)₂ → ZnEt₂·O·NEt₂ → OH·NEt₂ from analogy to O:CCl₂, which also forms OH·CEt₃. The β-diethylhydroxylamine thus produced is identical with the product obtained by the action of zinc ethyl on organic nitrites. An abstract of the rest of this paper has already appeared (this vol., i, 671).

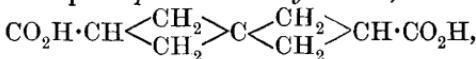
Z. K.

Spirocyclanes. HERMANN FECHT (*Ber.*, 1907, 40, 3883—3891. Compare Baeyer, Abstr., 1901, i, 135, for nomenclature).—Vinyltrimethylene (Abstr., 1896, i, 669) is in reality spiropentane,



for the nitrile, obtained from its dibromide, yields on hydrolysis *aa-ethyleneglutaric acid*, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{C}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \\ | \\ \text{CH}_2 \end{array}$, m. p. 162°, identical with the acid prepared from ethyl glutaconate, ethylene dibromide, and sodium ethoxide in alcoholic solution.

The reaction between pentaerythritol tetrabromohydrin, sodium, and methyl malonate in boiling amyl-alcoholic solution leads ultimately to the formation of spiroheptanedicarboxylic acid,

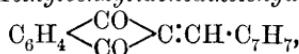


m. p. 210°, which is stable to potassium permanganate, bromine, hydrobromic acid at 150°, and fused potassium hydroxide.

Pentaerythritol tetrabromohydrin, benzene, and aluminium chloride react on the water-bath to give, in very bad yield, a deep yellow hydrocarbon, m. p. 148°, and a pale yellow, fluorescent hydrocarbon, m. p. 161°. The formula C₆H₄ $\begin{array}{c} \text{CH}_2 \\ | \\ \text{C} > \end{array}$ C $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ C₆H₄ is not ascribed to either of these substances, because their properties are not analogous to those of *xylylenefluorene*, C₆H₄ $\begin{array}{c} \text{CH}_2 \\ | \\ \text{C} > \end{array}$ C $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ C₆H₄, m. p. 220°, which is prepared from fluorene, *o*-xylylene dibromide, and potassium hydroxide at 230°, crystallises in colourless, refractive needles, and is stable to acids or alkalis.

Xylylenediketohydrindene, C₆H₄ $\begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array}$ C $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ C₆H₄, m. p. 150°, is obtained by the addition of an alcoholic solution of sodium ethoxide

to *o*-xylylene dibromide and diketohydrindene dissolved in ethyl acetate; it crystallises in yellow needles, decomposes by warming with alkalis, develops a violet colour with concentrated sulphuric acid, and in hot alcoholic solution changes to a yellow polymeride, m. p. 245° (decomp.). The *dioxime* has m. p. 215°; the yellow *phenylhydrazone* has m. p. 177°, and the brown *diphenylhydrazone*, C₂₉H₂₄N₄, has m. p. 225°. 2-*o*-*Methylbenzylidenediketohydrindene*,



m. p. 156°, forms pale yellow needles, gives a yellow colour with concentrated sulphuric acid, and does not show any tendency to polymerise.

C. S.

Preparation of *tert*.-Butyltoluene and *tert*.-Butylxylene.

AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 184230).—*tert*.-Butyl-*m*-xylene, employed in the production of artificial musk, is obtained in almost theoretical amount by passing *isobutylene* gas through a mixture of *m*-xylene and aluminium chloride to which some *isobutyl* chloride has been added, or into which hydrogen chloride has been introduced. *isoButyl* bromide or hydrogen bromide may also be employed to start the reaction, and *tert*.-butyltoluene may be produced in a similar manner. The aluminium chloride may be replaced by other condensing agents, such as the chlorides of magnesium, zinc, or iron; the corresponding bromides may also be employed.

G. T. M.

Reductions with Amorphous Phosphorus. III. Action of Amorphous Phosphorus and Hydrochloric Acid, D 1·19, on Nitrobenzene. THEODOR WEYL (*Ber.*, 1907, 40, 3608—3612. Compare this vol., i, 118, 305).—Nitrobenzene is reduced to only a very small extent when heated with red phosphorus and hydrochloric acid, D 1·19, at temperatures not above 140°, but at 140—160° considerable amounts of aniline and *p*-chloroaniline are formed. In one experiment, 75% of the nitrobenzene entering into the reaction formed *p*-chloroaniline.

As aniline and *p*-chloronitrobenzene do not form chloroaniline when heated with phosphorus and hydrochloric acid, D 1·19, at temperatures up to 220°, but according to Bamberger, Büsdorf, and Szolayski (*Abstr.*, 1899, i, 341) *p*-chloroaniline is formed by the action of hydrochloric acid on phenylhydroxylamine or on nitrosobenzene, one or both of these substances must be formed intermediately in the reduction of nitrobenzene by phosphorus and hydrochloric acid.

Whilst aniline gives the well-known violet-purple coloration with calcium hypochlorite in aqueous, but a yellow coloration in acetone, solution, *o*- and *m*-chloroaniline give no coloration in aqueous, but a yellow becoming brown in acetone, solution, and *p*-chloroaniline gives a reddish-brown in both solvents.

p-Chloroacetanilide has m. p. 182° (172·5°; Beilstein and Kurbatoff, this Journ., 1877, i, 473).

G. Y.

Mercury Derivatives of *o*-Nitrotoluene. ARNOLD REISSERT (D.R.-P. 182217, 182218).—An aqueous suspension of *o*-nitrotoluene when heated for eight hours with freshly precipitated mercuric oxide and 30% sodium hydroxide solution, or an equivalent amount of some other alkali hydroxide or carbonate, furnishes a *mercury* derivative soluble in aqueous alkali hydroxides and precipitated as a very voluminous, yellow mass on addition of dilute acids, including carbonic acid. The *hydrochloride* of this product is obtained in a crystalline form in colourless needles, m. p. 145—158°, by precipitating an ammoniacal solution with hydrochloric acid. The compound contains mercury and *o*-nitrotoluene in the proportion of one atom of the former to two molecules of the latter.

A sparingly soluble *dimercury* derivative is obtained by prolonging the boiling with mercuric oxide until a product insoluble in hydrochloric acid is obtained. The new compound contains one *o*-nitrotoluene residue combined with two atomic proportions of mercury. The sparingly soluble pale yellow chloride is decomposed by dilute aqueous sodium hydroxide, the free dimercury derivative is dissolved in dilute acetic acid, and reprecipitated by alkali as a heavy, micro-crystalline, yellow mass, which explodes on heating, and when gradually warmed decomposes above 220° without melting. It also dissolves in dilute nitric or sulphuric acid, but is insoluble in ammonia.

G. T. M.

Salts and Esters of Benzenesulphonitroanilide. ST. OPOLSKI (*Ber.*, 1907, 40, 3528—3536).—Benzenesulpho-*o*-nitroanilide, m. p. 102—103.5°, forms pale yellow or almost colourless, microscopic crystals, and dissolves in alcohol or benzene with a yellow coloration. The ammonium salt is yellow; the sodium salt orange, m. p. 230°, to a red liquid: when freshly made and cooled to —70° it becomes yellow. The same yellow salt is formed on the addition of sodium ethoxide to a cooled ethereal solution of the *o*-nitroanilide; it becomes orange when rubbed with a glass-rod, but is obtained in silky, glistening, yellow needles when slowly crystallised, or in the orange modification when crystallised quickly.

The *thallium* salt is likewise orange when prepared warm, and yellow when made at lower temperatures; it melts to a red liquid at 150°, which becomes orange again when it solidifies.

The *lithium*, *potassium*, *rubidium*, and *mercury* salts were obtained in one, the yellow, form only; the *silver sodium* double salt is also yellow.

*Benzenesulphomethyl-*o*-nitroanilide*, $C_6H_5\cdot SO_2\cdot NMe\cdot C_6H_4\cdot NO_2$, forms colourless crystals, m. p. 116—117°, and gives colourless solutions.

*Benzenesulpho-*m*-nitroanilide* forms colourless crystals, m. p. 136—137° (Lellmann, *Abstr.*, 1883, 807, describes it as yellow crystals, m. p. 131—132°). The ammonium salt is yellow, likewise the *sodium* and *potassium* salts, which retain this colour on heating and show no tendency to form the red modification. *Benzenesulphomethyl-*m*-nitroanilide* is colourless, m. p. 82—83°. *Benzenesulpho-*

p-nitroanilide, m. p. 139—140°, is colourless and forms yellow salts only ; the *methyl ester*, m. p. 120—121°, is also colourless.

Both the *o*- and *p*-benzenesulphonitroanilides are converted by nitric acid into the same *trinitro*-derivative, $C_6H_5\cdot SO_2\cdot NH\cdot C_6H_2(NO_3)_3$, m. p. 210—211°, crystallising in almost colourless needles which give yellow solutions in acetone.

E. F. A.

Action of Phosphorus Oxychloride on 1-Naphthylamine-8-sulphonic Acid. FREDERIC DANNERTH (J. Amer. Chem. Soc., 1907, 29, 1319—1328).—On heating 1-naphthylamine-8-sulphonic acid with concentrated sulphuric acid, Dressel and Kothe (Abstr., 1894, i, 608) obtained the sulphonic acid of an inner anhydride which they termed naphthasultam. They were unable to obtain the naphthasultam itself, since the anhydride formation was always accompanied by sulphonation in the nucleus. This has now been effected, however, by the action of phosphorus oxychloride on potassium 1-naphthylamine-8-sulphonate, a yield of 60% of the theoretical being obtained.

1 : 8-Naphthasultam, $C_{10}H_6^{SO_2}NH$, m. p. 177—178°, crystallises from hot water in needles and dissolves in many organic liquids to form solutions with an apple-green fluorescence. The *methyl* derivative, m. p. 125°, and the *ethyl* derivative, m. p. 85°, are crystalline, and yield fluorescent solutions ; the former, when heated with potassium hydroxide, is converted into 1-methylnaphthylamine-8-sulphonic acid, thus proving that the methyl group is attached to the nitrogen atom. Naphthasultam forms yellow salts of the alkali earth metals, gives dark blue precipitates with potassium dichromate and ferric chloride, and when treated with nitrous acid is converted into a red, crystalline substance. The *sodium* salt condenses with diazo-compounds to form dyes. *Dibromonaphthasultam*, m. p. 239°, is a white compound which turns blue when boiled with alcohol. *Nitronaphthasultam*, m. p. 253°, forms white crystals which gradually become yellow. The 2 : 4-dinitro-derivative, m. p. 259°, forms six-sided prisms ; this compound can also be prepared by the nitration of 1 : 8-naphthasultam-2 : 4-disulphonic acid (Dressel and Kothe, loc. cit.). 2 : 4-Diamino-1 : 8-naphthasultam is unstable ; its *dihydrochloride* forms slender, pale yellow needles, and its *diacetyl* derivative, m. p. 290°, greenish-yellow needles.

When 1 : 8-naphthasultam is boiled with acetic anhydride, 1 : 8-isomaphthasultam, $C_{10}H_6^{SO_2H}N$, is produced, which forms rhombic crystals and yields a yellow *sodium* salt. When a solution of this compound in methyl alcohol is treated with hydrogen chloride, a *chloro*-derivative, m. p. 200—201°, is produced ; the same substance can be obtained by the action of chlorine on *isomaphthasultam*. The *bromo*-derivative, m. p. 162°, is a white, crystalline substance. The *nitro*-derivative, m. p. 212°, forms pale yellow crystals. 2 : 4-Dinitro-1 : 8-isomaphthasultam, m. p. 256°, forms yellow crystals ; if this compound is heated with sodium hydroxide and the product acidified, the “normal” dinitrosultam is produced.

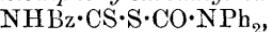
By the action of fuming nitric acid on either naphthasultam or *iso-*

naphthalene, 1:3-dinitronaphthalene-5-sulphonic acid is produced, which does not melt but explodes at about 300°. 1:3-Naphthylene-diamine-5-sulphonic acid forms black needles, and does not melt when heated.

E. G.

Thiocyanates and isoThiocyanates [Thiocarbimides]. VII. *Diphenylcarbamyl Thiocyanate.* TREAT B. JOHNSON and L. H. LEVY (*Amer. Chem. J.*, 1907, 38, 456—461).—When an alkyl halide is treated with ammonium or potassium thiocyanate, an alkyl thiocyanate is first produced, although it sometimes undergoes rearrangement into the corresponding thiocarbimide. In the case of the acyl halides, however, the products of the reaction have always been regarded as thiocarbimides. It has now been found that diphenylcarbamyl chloride reacts smoothly with potassium thiocyanate with formation of diphenylcarbamyl thiocyanate, and it is considered probable that the carbamyl chlorides examined by Dixon (*Trans.*, 1895, 67, 1040; 1896, 69, 855, 1593; 1904, 85, 807) would also yield thiocyanates if treated with potassium thiocyanate under suitable conditions.

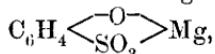
Diphenylcarbamyl thiocyanate, $\text{NPh}_2\cdot\text{CO}\cdot\text{SCN}$, m. p. 138°, forms prismatic crystals, is not affected by hot concentrated hydrochloric acid, and does not react with ammonia or aniline at the ordinary temperature. When heated with thiobenzoic acid, carbon oxysulphide is evolved and *benzoyldithiodiphenylcarbamyl carbamate*,



m. p. 128—129°, is produced, which crystallises in prisms. *Benzoyl-diphenylamine*, m. p. 177°, is also formed in this reaction and separates from alcohol in prismatic crystals. The thiocyanate does not show any tendency to undergo rearrangement at the ordinary temperature, but when heated at 150—160°, a thiocarbimide is produced which reacts with ammonia to form diphenylthiobiuret.

E. G.

Action of Sulphuric Acid on Phenol. JULIUS OBERMILLER (*Ber.*, 1907, 40, 3623—3647).—Kekulé (*Ber.*, 1869, 2, 330) found that the action of concentrated sulphuric acid on phenol at the ordinary temperature leads to the formation of the ortho-, together with traces of the para-, sulphonic acid, whilst at 100—110° the para-acid only is formed. Later authors (Engelhard and Latschinow, *Zeitsch. Chem.*, 1868, 4, 77; Post, this *Journ.*, 1876, i, 388) have been unable to separate the two sulphonic acids completely by Kekulé's method. The present author has found that the two isomerides may be separated readily by means of the barium or magnesium salts. On evaporation of the aqueous solution of the monobarium salts, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Ba}$, the *o*-sulphonate crystallises out, and the para-acid may be obtained from the mother-liquor by conversion by means of magnesium sulphate into the monomagnesium salt, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Mg}$, which crystallises on further evaporation. The monomagnesium *o*-sulphonate crystallises only with great difficulty, whilst the dimagnesium salt,



is only sparingly soluble; the magnesium salts of the para-acid have the converse solubilities.

Contrary to Kekulé's statements, the *o*-sulphonic acid is not converted into the para-isomeride on prolonged boiling with water, and is only partially transformed on prolonged treatment with concentrated sulphuric acid at the ordinary temperature. The two isomerides form an equilibrium dependent on the temperature and concentration, the formation of the ortho-acid being favoured by low temperatures and dilution of the sulphuric acid. It is probable that even at 100—110° the ortho-acid is not transformed completely. The alkali, alkaline earth, lead, and zinc salts of the pure *o*- and *p*-sulphonic acids, and of phenol-2 : 4-disulphonic acid, are described.

The reaction solution after removal of the *o*- and *p*-sulphonic acids and of the 2 : 4-disulphonic acid, which is formed readily in presence of an excess of sulphuric acid, contains small amounts of an acid, probably phenol-*m*-sulphonic acid (Solomanoff, *Zeitsch. Chem.*, 1869, 5, 299). This has been isolated in the form of its *monoaluminium*, *monobarium*, and *monomagnesium*, $(\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3)_2\text{Mg}_8\text{H}_2\text{O}$, salts, which are described. These three salts give a violet coloration with ferric chloride.

Merck's "aseptol," which is stated to be a 33½% aqueous solution of phenol-*o*-sulphonic acid, is found to be a solution of the *p*-sulphonic acid and an amount of the ortho-acid equal to about 6% of the para-acid.

G. Y.

Action of *p*-Nitrobenzyl Chloride on *p*-Aminophenol.
MARUSSIA BAKUNIN and C. PROFILO (*Gazzetta*, 1907, 37, ii, 240—250. Compare *Abstr.*, 1906, i, 496).—As already stated (*loc. cit.*), the condensation of *o*- or *p*-aminophenol with benzyl chloride yields mono- or di-substituted derivatives in which the benzyl groups must be regarded as united directly with the amino-nitrogen. By the interaction of *m*-aminophenol (1 mol.) and *o*-nitrobenzyl chloride (2 mols.) in alcoholic solution and in presence of sodium acetate, Lellmann and Mayer (*Abstr.*, 1893, i, 198) obtained a compound to which they ascribed the structure $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$; from the authors' results, it must be held that substitution occurs in the amino- and not in the hydroxyl-group of the *m*-aminophenol.

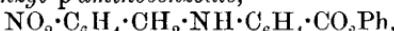
p-Nitrobenzyl-*p*-aminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, obtained by the interaction of *p*-nitrobenzyl chloride and *p*-aminophenol in alcoholic solution, crystallises from water in silky, yellow, hydrated (+ H₂O) needles; from alcohol in yellow, micaceous, hydrated (+ H₂O) scales, m. p. 86—87°, and from anhydrous benzene or chloroform in brownish-red crystals, m. p. 114—115°. The *hydrochloride*,



has m. p. 191°.

Di-p-nitrobenzyl-p-aminophenol, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, also obtained in the reaction between *p*-nitrobenzyl chloride and *p*-aminophenol in alcohol, separates from alcohol in red, acicular crystals, m. p. 179—180°. The *hydrochloride*, $\text{C}_{20}\text{H}_{17}\text{O}_5\text{N}_3\text{HCl}$, m. p. 204°, is readily hydrolysed by water.

Phenyl p-nitrobenzyl-p-aminobenzoate,



prepared by the interaction of *p*-nitrobenzyl chloride and *p*-aminoc-

phenyl benzoate, separates from benzene in crystals, m. p. 218—220°. The *hydrochloride*, $C_{20}H_{16}O_4N_2 \cdot HCl$, m. p. 110—112°, readily undergoes change.

Benzoyl-p-nitrobenzyl-p-aminophenol, $OH \cdot C_6H_4 \cdot NBz \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, prepared by the action of benzoyl chloride on *p*-nitrobenzyl-*p*-aminophenol in benzene solution, crystallises from alcohol in yellow needles, m. p. 208—210°.

p-Nitrobenzyl-*p*-aminophenol gives a violet coloration with ferric chloride and water and a red coloration with Liebermann's reagent and acetic acid. Di-*p*-nitrobenzyl-*p*-aminophenol, being insoluble in water, gives no colour with ferric chloride and water, but its hydrochloride gives a violet coloration; both the base and its hydrochloride give a red colour with Liebermann's reagent and acetic acid. Neither phenyl *p*-nitrobenzyl-*p*-aminobenzoate nor its hydrochloride gives a coloration with ferric chloride, but both yield red colorations with Liebermann's reagent. Benzoyl-*p*-nitrobenzyl-*p*-aminophenol gives no coloration with ferric chloride, possibly owing to its insolubility, but it yields the characteristic red coloration with Liebermann's reagent.

T. H. P.

Binary Solution Equilibrium between Carbamide and the Three Isomeric Cresols. ROBERT KREMMANN (*Monatsh.*, 1907, **28**, 1125—1136. Compare *Abstr.*, 1906, ii, 268).—The melting-point curve for mixtures of carbamide and *p*-cresol falls from the m. p. of carbamide to a break at 25·5°, and then to a eutectic point at 20°, representing mixtures containing 21·5 mol. % and 15 mol. % of carbamide respectively; within these limits of temperature and concentration, carbamide and *p*-cresol form a molecular compound. Mixtures of *p*-cresol-carbamide and carbamide and of *p*-cresol-carbamide and *p*-cresol exist in the solid phase below 25·5° and 20° respectively; above these temperatures, but below the m. p.'s of carbamide and *p*-cresol, the liquid phase is in contact with the one solid component.

Carbamide forms molecular compounds in the same manner, but within wider limits of temperature and concentration, with *o*- and *m*-cresols. The melting-point curve for mixtures of carbamide and *o*-cresol falls from the m. p. of carbamide to a break at about 60°, and then to a eutectic point at about 26°, representing mixtures containing approximately 27·8 mol. % and 10 mol. % of carbamide respectively. The melting-point curve for mixtures of carbamide with *m*-cresol falls to a break at about 65°, and then to a eutectic point at about 2·5°, representing mixtures containing approximately 30 mol. % and 2 mol. % of carbamide.

G. Y.

Derivatives of 6-Nitro-1:3:4-xylenol. RAFFAELE MALTESE (*Gazzetta*, 1907, **37**, ii, 284—288).—6-*Nitro-4-methoxyisophthalic acid*, $C_9H_7O_7N$, prepared by oxidising the methyl ether of 6-nitro-1:3:4-xylenol with potassium permanganate, crystallises from water in slender, silky needles, m. p. 230°. The *dimethyl ester*, $C_{11}H_{11}O_7N$, separates from methyl or ethyl alcohol in minute, hard crystals, m. p. 118°. The *monomethyl ester*, $C_{10}H_9O_7N$, crystallises from methyl or ethyl alcohol in minute, white needles, m. p. 190°; the other mono-

methyl ester (?) has m. p. 222°. The *monoethyl* ester, C₁₁H₁₁O₇N, is deposited from alcohol as a white, crystalline powder, m. p. 108°. The *sodium salt*, C₉H₅O₇Na₂, is obtained as a yellow, anhydrous, crystalline powder.

The two *nitromethoxy-m-toluic acids* (NO₂:OMe = 6:4 and 4:6) have been prepared, but not distinguished. One of them, C₉H₉O₅N, separates from water or aqueous alcohol as a yellowish-white powder, m. p. 174°, which is gradually turned red by the action of light; the other isomeride, m. p. 170° (decomp.), is white, and does not redden under the action of light.

T. H. P.

Isomerism with Schiff's Bases. OTTO ANSELMINO (*Ber.*, 1907, 40, 3465—3474).—The author has shown previously (*Abstr.*, 1906, i, 13) that *p-homosalicylaldehydeanil* occurs in two forms, a yellow and a red, which by crystallisation at definite temperatures can be converted one into the other; when dry, the yellow form can be converted by heat into the red, but the reverse change cannot be effected with the dry substance. The effect of pressure is the same as that of heat.

Evidence is submitted to show that these forms are isomeric and not polymorphous. Density determinations gave different values for the two forms; thus, for the yellow form, D^{17.1} was 1.243, and for the red form 1.262. Solubility determinations in 95% alcohol were carried out at temperatures from 11.8° to 50°. Measurements of the heat of solution in benzene were also made, and the absorption spectra studied. The conclusion is drawn that solutions below 33° contain the yellow form, and above 34° the red.

The behaviour of the anil towards acetyl chloride, acetic anhydride, benzoyl chloride, methyl sulphate, and phenylcarbimide is indicated. When the Grignard action is applied, unchanged anil is obtained at temperatures below 30°; above 40°, the red variety is transformed by the Grignard reagent, but the yellow variety is not. The same relationships with regard to Grignard's reagent hold with salicylaldehydeanil; it is known only in the yellow form, and does not interact, whereas its methyl ether does.

The picrate obtained from the yellow form differs in tint from that obtained from the red form.

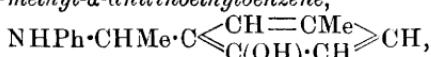
The conclusion is drawn that all yellow anils have a similar structure, whereas the red anil in question has the configuration of its ether. Crystallographic measurements also confirmed this view.

The crystalline form of salicylaldehydeanil differs from that of anisaldehyde.

The *acetyl* derivatives of *o-hydroxy-m-methylbenzylideneaniline*, C₁₈H₁₉O₄N,
separates from light petroleum in needles, m. p. 101°.

o-Hydroxy-m-methylbenzylideneaniline, C₁₅H₁₅ON, prepared by the action of methyl sulphate at 40° on the anil, separates from light petroleum in yellow needles, m. p. 70°.

o-Hydroxy-m-methyl-a-anilinoethylbenzene,



obtained by the action of magnesium methyl iodide on the anil, separates from light petroleum in colourless, rectangular leaflets, m. p. 98°.

o-Methoxy-m-methyl-a-anilinoethylbenzene, $C_{16}H_{19}ON$, obtained from magnesium methyl iodide and the methylated anil, separates from light petroleum in glistening crystals, m. p. 78°.

o-Hydroxy-m-methyl-a-acetylaniinoethylbenzene, $C_{17}H_{19}O_2N$, separates from light petroleum in nodular crystals, m. p. 123°.

o-Methoxy-m-methyl-a-acetylaniinoethylbenzene, $C_{18}H_{21}O_2N$, is a syrup.

a-Anilino-o-ethylanisole, $C_{15}H_{17}ON$, separates from light petroleum in pyramids, m. p. 46°.

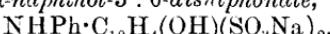
A. McK.

Preparation of Aminonaphthols. FRANZ SACHS (D. R.-P. 181333).—The aminonaphthols can be obtained by heating the naphthols or their alkali derivatives with sodamide at 200—210°. The use of the latter compounds reduces the proportion of sodamide required. Naphthalene, quinoline, paraffin, and other heavy hydrocarbons are employed as diluents. Under these conditions, β -naphthol furnishes 5-amino- β -naphthol, whilst α -naphthol yields 5-amino- α -naphthol (compare Abstr., 1906, i, 829 and 949).

G. T. M.

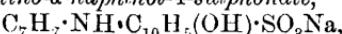
Preparation of 8-Arylamino- α -naphtholsulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 181929).—The 8-amino- α -naphtholsulphonic acids when heated with aromatic amines and their dry hydrochlorides give rise only to tarry products, but when these acids or their alkali salts are heated with aromatic amines in the presence of water, the hitherto unknown 8-arylamino- α -naphtholsulphonic acids are obtained.

Sodium 8-anilino- α -naphthol-3 : 6-disulphonate,



produced by heating sodium 8-amino- α -naphthol-3 : 6-disulphonate with aniline and water at 120° for forty-eight hours, crystallises from water in spherical aggregates of white needles; the *sodium hydrogen* salt separates in felted, white needles.

Sodium 8-p-tolylamino- α -naphthol-4-sulphonate,



prepared in a similar manner from sodium 8-amino- α -naphthol-4-sulphonate, *p*-toluidine, and water, crystallises in needles; the free *acid* separates in felted, white needles. The patent contains a tabulated description of ten 8-arylamino- α -naphtholsulphonic acids and other sodium salts.

G. T. M.

1 : 2-Methylnaphtha- ψ -quinol. GUIDO BARGELLINI and S. SILVESTRI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 255—261. Compare this vol., i, 862).—1-Methyl- β -naphthol, when oxidised in acetic acid solution with chromic acid, yields 1 : 2-methylnaphtha- ψ -quinol (compare Fries and Hübner, Abstr., 1906, i, 190).

6-Bromo-2-methoxy-1-methylnaphthalene, $C_{10}H_5BrMe \cdot OMe$, crystallises from acetic acid in white needles, m. p. 65—66° (Fries and Hübner, *loc. cit.*).

2-Benzeneazo-1-methylnaphthalene, $C_6H_4\begin{array}{c} \text{CMe:C(N}_2\text{Ph)} \\ \swarrow \quad \searrow \\ \text{CH}=\text{CH} \end{array}$, prepared by the action of phenylhydrazine on 1 : 2-methylnaphtha- ψ -quinol, crystallises from alcohol in orange-red scales, m. p. 79—80° (decomp.), is soluble in ether, ethyl acetate, chloroform, or acetone, and dissolves in concentrated hydrochloric or sulphuric acid to a red solution.

Methylnaphthylazocarbonamide, $C_6H_4\begin{array}{c} \text{CMe:C-N}_2\text{-CO-NH}_2 \\ \swarrow \quad \searrow \\ \text{CH}=\text{CH} \end{array}$, prepared by the action of semicarbazide on 1 : 2-methylnaphtha- ψ -quinol, crystallises from water in orange needles, m. p. 143—144° (decomp.), is readily soluble in ether, acetic acid, or chloroform, and dissolves in concentrated hydrochloric or sulphuric acid giving a green coloration which rapidly turns red.

1 : 2-Methylnaphtha- ψ -quinoloxime, $C_{10}H_6\text{Me(OH):NOH}$, separates from ethyl acetate in crystals, m. p. 140° (decomp.), and dissolves readily in chloroform, benzene, carbon disulphide, or alcohol, and sparingly in light petroleum. By acetic acid, it is decomposed probably in similar manner to the oxime of dimethylnaphtha- ψ -quinol (compare Cannizzaro and Andreucci, Abstr., 1896, i, 488), yielding 2-nitroso-1-methylnaphthalene. Reduction of the oxime by means of zinc dust and acetic acid yields 1-methyl-2-naphthylamine and its acetyl derivative (compare Fries and Hübner, *loc. cit.*). **1-Methyl-2-naphthylamine hydrochloride** separates in shining scales, m. p. 245° (decomp.). T. H. P.

Condensation Products of Formaldehyde. J. BRESLAUER and AMÉ PICTET (*Ber.*, 1907, 40, 3784—3786).—Methylphthalimide is formed on heating phthalimide with a 40% solution of formaldehyde in a sealed tube at 150—160°; similarly, methylenedisuccinimide (Bechert, *Abstr.*, 1894, i, 488) is obtained from formaldehyde and succinimide.

Methylene phenyl methyl ether, $\text{OPh}\cdot\text{CH}_2\cdot\text{OMe}$, is produced by the interaction of phenol and formaldehyde in the presence of sulphuric acid, and by the action of monochloromethyl ether on potassium phenoxide. It is a colourless liquid, b. p. 197—200°, D_{12}^{12} 1·0814, and yields with bromine water a dibromo-derivative, $C_8H_8O_2Br_2$, which crystallises in colourless, silky needles, m. p. 112—113°.

The action of formaldehyde on α -naphthol in the presence of potassium carbonate results in the formation of a substance, $C_{23}H_{16}O_3$, obtained as a dark brown, amorphous, infusible powder. This on distillation yields a substance, $C_{22}H_{16}O$, which forms small, pale yellow crystals, m. p. 79—80°, and gives a deep blue coloration with ferric chloride.

W. H. G.

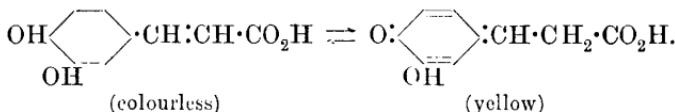
Action of Benzyl Chloride on Resorcinol and Catechol. MARUSSIA BAKUNIN and P. ALFANO (*Gazzetta*, 1907, 37, ii, 250—252).—The interaction of benzyl chloride and resorcinol in benzene solution in presence of zinc yields: (1) a compound, $C_{13}H_{12}O_2$, crystallising from carbon tetrachloride in slender, white needles, m. p. 74—76°; (2) a hydrocarbon crystallising in nacreous laminae, m. p. 203—206°, and containing 96% of carbon; (3) an oily compound, $C_6H_4O_2(CH_2Ph)_2$.

Similarly, benzyl chloride and catechol yield a crystalline compound, m. p. 100°, the nature of which has not yet been determined.

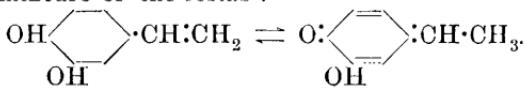
T. H. P.

Cyclic Carbonic Esters of Vinylcatechol. HERMANN PAULY and KARL NEUKAM (*Ber.*, 1907, 40, 3488—3498).—Pauly has lately shown (this vol., i, 709) that the cyclic esters of catechols are suitable for the isolation of the latter and that protocatechualdehyde carbonate, $\text{CHO}\cdot\text{C}_6\text{H}_3\begin{array}{c} \text{O} \\ \swarrow \quad \searrow \\ \text{O} \end{array}\text{CO}$, is suitable for the carrying out of syntheses in the catechol group.

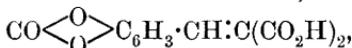
Vinylcatechol carbonate, $\text{CO}\text{C}_6\text{H}_3\text{OCH}=\text{CH}_2$, is now described, it being obtained from protocatechualdehyde carbonate by means of the corresponding benzylidene malonic acid. The latter compound (colourless) is converted by aqueous pyridine into caffeic acid (yellow), thus : $\text{CO}\text{C}_6\text{H}_3\text{OCH}=\text{CHC}(\text{CO}_2\text{H})_2 + \text{H}_2\text{O} = \text{C}_6\text{H}_3(\text{OH})_2\text{CH}=\text{CHCO}_2\text{H} + 2\text{CO}_2$. The yellow tint of the latter acid is attributed to its partly undergoing the transformation :



Evidence is submitted to show that the free vinylcatechol is an equilibrium mixture of the forms:



3 : 4-Dioxybenzylidenemalonic acid carbonate,



obtained by heating protocatechualdehyde carbonate, malonic acid, and anhydrous formic acid for nine to ten hours at about 65° in the absence of moisture, separates from glacial acetic acid in colourless needles, m. p. 197° (corr., decomp.), and is sparingly soluble in cold water; its aqueous solution exhibits a violet fluorescence; its solution in concentrated sulphuric acid is lemon-yellow. When boiled with acetic anhydride, it evolves carbon dioxide vigorously and gives a compound, m. p. about 245° . On account of the sensitiveness of the CO_3 group, the acid could not be further characterised by means of its salts.

Vinylcatechol carbonate, prepared by the dry distillation of the preceding acid in an apparatus which is described in detail, separates from a mixture of light petroleum and ether in colourless, glistening prisms, m. p. 65–66°; it has a very intense odour. Although it decolorises a solution of bromine in carbon disulphide almost immediately, a dibromide could not be obtained on account of the ease with which hydrogen bromide is eliminated after the addition. It gives a brownish-yellow coloration with ferric chloride and a violet-brown

coloration with sodium carbonate; its solution in concentrated sulphuric acid is reddish-orange. Its solution in alkalis is dark yellow.

A. McK.

Reduction of Safrole and *iso*Safrole. J. TH. HENRARD (*Chem. Weekblad*, 1907, 4, 630—632. Compare Klages, Abstr., 1899, i, 585; Ciamician and Silber, Abstr., 1890, 965, 966, 1294; Eylman, Abstr., 1890, 244; and Jacobsen, Abstr., 1878, 732).—The author has reduced safrole and *isosafrole* with nickel and hydrogen by Sabatier and Senderens's method. The reduction was never quantitative, the product always containing unchanged safrole or *isosafrole*. The reaction product was agitated with dilute sodium hydroxide, and the residual oil, containing unchanged safrole and *isosafrole* along with the dihydro-product, fractionated, the bulk distilling at 228°. The alkaline liquid contained *m*-propylphenol, formed by reduction of the dihydrosafrole with elimination of the para-hydrogen atom. The *m*-propylphenol could not be obtained crystalline, although Jacobsen gives its m. p. as 26°.

A. J. W.

Formation of *s*-Dihydroxydiphenylmethanes. KARL AUWERS [and, in part, FR. JESCHECK and C. KIPKE] (*Annalen*, 1907, 356, 124—151).—It has been shown previously that hydroxybenzyl bromides and their transformation products readily undergo reactions leading to the formation of substances formulated at first as derivatives of stilbene, but later considered to be derivatives of diphenylmethane (Abstr., 1903, i, 631; 1904, i, 487). The constitution of only one of these derivatives, 3:5:3':5'-tetrabromo-4:4'-dihydroxydiphenylmethane formed from 3:5-dibromo-4-hydroxybenzyl bromide, has been definitely established. As some of these derivatives decompose into compounds containing a single benzene nucleus, and that with an ease not to be expected of derivatives of diphenylmethane, it was necessary to establish the constitution also of one of these comparatively unstable products. This has been achieved now in the case of the product obtained from 3-bromo-4-hydroxy-2:5-dimethylbenzyl bromide, already shown (*loc. cit.*) not to be identical with 4:4'-dihydroxytetramethylstilbene. It is now found identical with 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane,



prepared by diazotisation of 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane, $\text{CH}_2(\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NH}_2)_2$, which is obtained by transformation of methylenedi-*p*-xylylamine, $\text{CH}_2(\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2)_2$.

Methylenedi-*p*-xylylamine, $\text{C}_{17}\text{H}_{22}\text{N}_2$, prepared by shaking *p*-xylidine with formaldehyde in aqueous solution, crystallises in glistening needles, m. p. 67—68°, and when heated with 2 mols. of *p*-xylidine hydrochloride and $\frac{1}{2}$ mol. of *p*-xylidine in a reflux apparatus on the water-bath, is transformed into 4:4'-diamino-2:5:2':5'-tetramethyldiphenylmethane, $\text{C}_{17}\text{H}_{22}\text{N}_2$, which separates from benzene as a colourless, crystalline powder, m. p. 138—139°. When diazotised with sodium nitrite and boiled in hydrochloric acid solution, this yields 4:4'-dihydroxy-2:5:2':5'-tetramethyldiphenylmethane, m. p. 181°.

The following substances were prepared in the course of endeavours

to synthesise dihydroxytetramethyldiphenylmethane by other reactions.

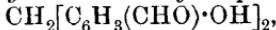
3 : 5-Dibromo-4-methoxybenzyl bromide, $C_8H_7OBr_3$, prepared by the action of hydrogen bromide on 3 : 5-dibromo-4-methoxybenzyl methyl ether in glacial acetic acid solution, crystallises in yellow needles, m. p. 66—67°. *4 : 4'-Dimethoxybenzophenone*, m. p. 143—144°, is readily obtained by the action of carbonyl chloride on anisole in carbon tetrachloride solution in presence of aluminium chloride. The action of methylal on *p*-xylene in glacial acetic-sulphuric acid solution leads to the formation of a substance, $C_{17}H_{20}$, m. p. 149°; the comparatively high temperature at which this melts makes it probable that it is not dixylylmethane. On treatment with cold fuming nitric acid, it yields a yellow, crystalline derivative, m. p. 183°.

The product from 3-bromo-4-hydroxy-2 : 5-dimethylbenzyl bromide having been shown to be 4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane, analogous constitutions must be ascribed to the products obtained similarly from other benzyl bromides. Thus the substance, m. p. 234°, described previously as tetrabromodihydroxytetramethylstilbene (Abstr., 1896, i, 150), must be 2 : 5 : 2' : 5'-tetrabromo-4 : 4'-dihydroxy-3 : 6 : 3' : 6'-tetramethyldiphenylmethane; the *diacetate*, $C_{21}H_{20}O_4Br_4$, crystallises in needles, m. p. 224—225°. The constitution of this tetrabromo-compound is confirmed by its reduction by means of sodium and boiling amyl alcohol to dihydroxytetramethyldiphenylmethane. The supposed bromide, m. p. 179° (Abstr., 1896, i, 422), is now found to be tribromo-*p*-xylanol.

Similarly, the substance, m. p. 232°, described previously as tetrabromodihydroxytetramethylstilbene (Abstr., 1899, i, 33), must be 2 : 6 : 2' : 6'-tetrabromo-4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenylmethane.

The conditions under which derivatives of dihydroxydiphenylmethane are formed from hydroxybenzyl bromides and their transformation products, and the mechanism of the reactions concerned, are discussed. The following new details are given.

Whilst the action of water or alkalis on 4-hydroxy-3-aldehydo-benzyl bromide leads to the formation of hydroxymethylsalicyl-aldehyde, *4 : 4'-dihydroxy-3 : 3'-dialdehydodiphenylmethane*,



m. p. 140°, was obtained on one occasion by long exposure to moist air of the residues from the preparation of the bromide.

2 : 2'-Dihydroxy-3 : 5 : 6 : 3' : 5' : 6'-hexamethyldiphenylmethane, m. p. 170° (Zincke and Honorst, this vol., i, 614), is formed when trimethylsaligenin is boiled with slightly acidified water.

The product, m. p. 183—184°, obtained on treating dibromo-*p*-hydroxy-*p*-cumenol with sodium amalgam in alkaline solution (Auwers and Baum, Abstr., 1897, i, 34), is found to be *4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane*.

Whilst readily decomposed by acids or water, dipiperidylmethane and its compounds remain unchanged when boiled with anhydrous solvents such as toluene. When heated with carbon disulphide at 100°, the piperidine derivative of *3 : 6-dibromo-4-hydroxy-2 : 5-di-*

methylbenzyl alcohol forms the *additive* compound,
 $\text{OH} \cdot \text{C}_6\text{Me}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{C}_5\text{NH}_{10} \cdot \text{CS}_2$,

which crystallises in strongly refracting prisms, m. p. 180—181°, but if heated with ether at 100° and then shaken with carbon disulphide the piperidine derivative yields 3 : 6 : 3' : 6'-tetrabromo-4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane and the *additive* compound of carbon disulphide and dipiperidylmethane, m. p. 58°. G. Y.

Fission of Dihydroxydiphenylmethanes on Bromination: KARL AUWERS and ERICH RIETZ (*Annalen*, 1907, 356, 152—177).—Whilst hydroxybenzyl bromides readily form the corresponding dihydroxydiphenylmethanes, these tend to decompose into simple benzene derivatives. The two reactions in question differ in that, whereas the first is general, the second has been found to take place markedly only in the case of certain derivatives of dihydroxydiphenylmethane. This paper is a study of the relation of the constitution of dihydroxydiphenylmethanes to their stability on bromination. It is found that, other things being equal, the stability diminishes as the number of methyl groups in the benzene nuclei increases. Thus, on careful bromination (avoidance of an excess of bromine and dilution with a solvent), the carbon chain of 4 : 4'-dihydroxydiphenylmethane and its monomethyl derivative remains unbroken, whilst that of the dimethyl derivative is ruptured to the extent of 2%, and that of the tetramethyl derivative to the extent of 16%. Energetic bromination of the more highly methylated derivatives leads to almost complete rupture of the carbon chain. On the other hand, no decomposition takes place when 3 : 3'-dihydroxydiphenylmethane and its dimethyl derivative are brominated.

It is shown that the rupture of the carbon chain results from the action of the nascent hydrogen bromide; the chain remains intact on bromination in presence of sodium acetate or on treatment of the dihydroxydiphenylmethane with a solution of hydrogen bromide. The following details are new.

4 : 4'-Dihydroxy-3-methyldiphenylmethane, $\text{C}_{14}\text{H}_{14}\text{O}_2$, prepared by Claus' method (*Diss.*, Marburg, 1901), has m. p. 133°.

The action of boiling aqueous sodium hydroxide on the condensation product of 3 : 5-dibromo-4-hydroxy-2 : 6-dimethylbenzyl bromide with pyridine or diethylamine leads to the formation of a small amount of a yellowish-brown powder, $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_4$, m. p. 173—175°. Attempts to prepare 4 : 4'-dihydroxy-2 : 6 : 2' : 6'-tetramethyldiphenylmethane from the corresponding 4 : 4'-diamino-compound, $\text{C}_{17}\text{H}_{22}\text{N}_2$, m. p. 205—208°, were unsuccessful.

3 : 3'-Dihydroxydiphenylmethane, $\text{C}_{13}\text{H}_{12}\text{O}_2$, prepared from the 3 : 3'-diamino-compound, crystallises in needles, m. p. 103°; the *diacetate*, $\text{C}_{17}\text{H}_{16}\text{O}_4$, crystallises in white leaflets, m. p. 57.5—58.5°.

5 : 5'-Dihydroxy-2 : 2'-dimethyldiphenylmethane, prepared from the 5 : 5'-diamino-compound, forms white crystals, m. p. 159—160°.

5 : 5'-Dinitro-2 : 3 : 2' : 3'-tetramethyl- and 5 : 5'-dinitro-2 : 4 : 2' : 4'-tetramethyl-diphenylmethanes, $\text{C}_{17}\text{H}_{18}\text{O}_4\text{N}_2$, are obtained as light brown powders, m. p. 164—167° and 173—176° respectively.

The following products are obtained on bromination of the corresponding dihydroxydiphenylmethanes.

3 : 5 : 3' : 5'-Tetrabromo-4 : 4'-dihydroxydiphenylmethane, m. p. 226—227°, from 4 : 4'-dihydroxydiphenylmethane. **5 : 3' : 5'-Tribromo-4 : 4'-dihydroxy-3-methyldiphenylmethane,** m. p. 185—195°, together with traces of a substance, m. p. 42—92°, which may be a mixture of dibromo-*o*-cresol and tribromophenol, from 4 : 4'-dihydroxy-3-methyldiphenylmethane. **5 : 5'-Dibromo-4 : 4'-dihydroxydi-*m*-tolylmethane,** m. p. 173°, and dibromo-*o*-cresol from 4 : 4'-dihydroxydi-*m*-tolylmethane. **3 : 3'-Dibromo-4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane,** m. p. 172°, and dibromo-*p*-xyleneol, m. p. 79—80°, from 4 : 4'-dihydroxy-2 : 5 : 2' : 5'-tetramethyldiphenylmethane. **Dibromo-*v*-*m*-xyleneol,** m. p. 83—85°, from 4 : 4'-dihydroxy-3 : 5 : 3' : 5'-tetramethyldiphenylmethane. A mixture of tetra- and hexa-bromo-derivatives from 3 : 3'-dihydroxydiphenylmethane. The pure *hexabromo*-derivative, $C_{18}H_6O_2Br_6$, m. p. 241—244°, is formed by the action of an excess of undiluted bromine; the *diacetate*, $C_{17}H_{19}O_4Br_6$, crystallises in needles, m. p. 224°. **4 : 6 : 4' : 6'-Tetrabromo-5 : 5'-dihydroxy-2 : 2'-dimethyldiphenylmethane,** $C_{15}H_{12}O_2Br_4$, m. p. 227—228°, from 5 : 5'-dihydroxydi-*o*-tolylmethane.

G. Y.

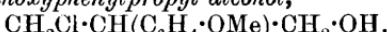
Preparation of 1 : 3-Dimethylpyrogallol Carbamate. BASLER CHEMISCHE FABRIK (D.R.-P. 181593).—1 : 3-Dimethylpyrogallol carbamate, $C_6H_3(OMe)_2 \cdot O \cdot CO \cdot NH_2$, white needles, m. p. 148—152°, has a beneficent action in tuberculosis which is greater than that of 1 : 3-dimethylpyrogallol. This is probably owing to the fact that the latter ether is too rapidly oxidised and eliminated in the form of coerulignone, whereas the carbamate is only gradually hydrolysed, so that a sustained reaction is rendered possible. The carbamate is prepared by the interaction of 1 : 3-dimethylpyrogallol and carbamic acid chloride in anhydrous ether.

G. T. M.

Preparation of Substituted Chlorohydrins. J. D. RIEDEL, AKTIEN-GESELLSCHAFT (D.R.-P. 183361).—When epichlorohydrin is subjected to the action of the magnesium derivatives of the aromatic halides, the condensation takes the normal course, and substituted chlorohydrins, $CH_2Cl \cdot CHR \cdot CH_2 \cdot OH$, are obtained, where R is an aryl or arylalkyl group.

γ -Chloro- β -phenylpropyl alcohol, $CH_2Cl \cdot CHPh \cdot CH_2 \cdot OH$, b. p. 153—154°/28 mm., results from the interaction of epichlorohydrin and magnesium phenyl bromide; it is, however, accompanied by chlorobromopropyl alcohol and phenylchloropropylene.

γ -Chloro- β -*p*-methoxyphenylpropyl alcohol,



b. p. 188—189°/25 mm., is the chief product of the interaction of magnesium *p*-methoxyphenyl bromide and epichlorohydrin. **γ -Chloro- β -benzylpropyl alcohol,** $C_6H_5 \cdot CH_2 \cdot CH(CH_2Cl) \cdot CH_2 \cdot OH$, b. p. 165—166°/22 mm., is obtained when magnesium benzyl chloride is employed.

G. T. M.

Cholesterol. III. Transformation of Cholestene. JULIUS MAUTHNER (*Monatsh.*, 1907, **28**, 1113—1124. Compare *Abstr.*, 1906, i, 579—663).—In view of the near relation of the cholesterol group to the terpenes, it appeared probable that, on addition of hydrogen chloride to cholesterol, cholesteryl chloride, and cholestene, a change might take place similar to that of pinene into camphene. This is now found to be the case with cholestene; on loss of hydrogen chloride, cholestene hydrochloride (chlorocholestan) yields a hydrocarbon different from cholestene and termed by the author ψ -cholestene.

Chlorocholestan, formed by the action of hydrogen chloride on cholestene, is obtained in two isomeric modifications, one of which crystallises in rhombic prisms, m. p. 96—97°, $[\alpha]_D^{21} + 4\cdot7^\circ$, and is the chief product of the reaction. The other crystallises in flat needles, sinters at 70°, and is melted above 80°. Both isomerides yield the same ψ -cholestene.

ψ -Cholestene, $C_{27}H_{44}$, formed by boiling chlorocholestan with sodium methoxide and potassium acetate, or by treatment of the chloro-compound with zinc dust and glacial acetic acid or alcoholic silver nitrate, crystallises in flat needles, m. p. 78—79°, $[\alpha]_D + 64\cdot86^\circ$, and gives the colour reactions of cholestene. The *dibromide*, $C_{27}H_{44}Br_2$, prepared by adding bromine dissolved in glacial acetic acid to the hydrocarbon in ethereal solution, crystallises in colourless, flat needles, m. p. 116—117°, and has $[\alpha]_D^{20} + 38\cdot7^\circ$ immediately after solution in chloroform, $[\alpha]_D^{20} + 36\cdot0^\circ$ after three hours, and $[\alpha]_D^{20} + 83\cdot4^\circ$ after four days, the solution becoming gradually reddish-yellow or dark green with slight red fluorescence, or in benzene immediately after solution $[\alpha]_D + 48\cdot0^\circ$, after twenty-four hours $[\alpha]_D + 47\cdot0^\circ$, and after forty-seven days $[\alpha]_D + 46\cdot9^\circ$, the solution remaining colourless. The mutarotation is probably connected with a *cis-trans* transformation; the initial fall in the rotatory power may result from the dissociation of molecular aggregates.

G. Y.

Phytosterol. ADOLF WINDAUS and A. HAUTH (*Ber.*, 1907, **40**, 3681—3686).—A convenient method of separating stigmasterol from phytosterol is described, and a direct comparison of sitosterol and the phytosterol so obtained confirms completely the statement that they are identical (compare this vol., i, 129).

A comparison of the behaviour of cholesterol and phytosterol towards several reagents has been made. *Dihydrophytosterol*, $C_{27}H_{48}O$, prepared by reducing phytosterol with sodium and amyl alcohol, crystallises from acetone in stout needles or rectangular plates, m. p. 175°. This substance does not give the Salkowski colour reaction. Although the substance behaves towards bromine as an unsaturated compound, repeated reduction with sodium and amyl alcohol does not alter the melting point, and therefore the substance must be regarded as a chemical entity. A molecular weight determination of the acetyl derivative shows it to correspond with $C_{29}H_{50}O_2$. *Dihydrophytosteryl chloride*, $C_{27}H_{47}Cl$, forms long, glistening prisms, m. p. 114—115°; on reduction with sodium and amyl alcohol, it yields *dihydrophytostene*, $C_{27}H_{48}$, which crystallises in rectangular leaflets, m. p. 80—81°. Both

these compounds behave as unsaturated towards bromine. This state of unsaturation must either be due to the phytosterol not being reduced but only undergoing isomeric change through the intermediary of sodium amyl oxide, or, if reduction has taken place, then phytosterol must contain at least two ethylene linkings. However, on testing phytosterol with sodium amyloxide, there was obtained, not the dihydro-phytosterol, but a ψ -phytosterol, $C_{27}H_{46}O$, which crystallises in aggregates of needles, m. p. 146—147°. It is indifferent to sodium and amyl alcohol, but it is unsaturated towards bromine, the addition taking place more slowly than with phytosterol. The conclusion is drawn that dihydrophtyosterol is a reduction product, and that phytosterol must contain two ethylene linkings, notwithstanding that only 1 mol. of bromine is absorbed.

Whereas cholesterol yields the same saturated substance with sodium amyloxide, or sodium and amyl alcohol, it is probable that it is not a reduction product, but one due to isomeric change; phytosterol, however, gives rise to two different products with these different reagents (compare this vol., i, 610).

W. R.

Migration of the Phenyl Group of Aromatic Iodohydriins by Elimination of Hydrogen and Iodine from the Same Carbon Atom. MARC. TIFFENEAU (*Compt. rend.*, 1907, 145, 593—596. Compare this vol., i, 39).—The author has previously proposed to explain the transformation of aromatic iodohydriins of the type $OH\cdot CArR\cdot CHI|R'$ into aldehydes or ketones, when deprived of hydrogen iodide, by (1) loss of hydrogen and iodine from the same carbon atom and migration of the aromatic group, followed by (2) isomeric change of the vinyl alcohol derivative at first produced, thus:



Study of the ethers of these iodohydriins affords experimental proof of the correctness of this view. Whilst the ethers of the aromatic iodohydriins react with silver nitrate, giving the aldehyde or ketone directly (owing to hydrolysis of the vinyl derivative by the liberated nitric acid), by using mercuric oxide the reaction can be stopped at the end of the first stage. When an ethereal solution of anethole ethyliodohydriin, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CHMeI$, is shaken with mercuric oxide, the *vinyl ether*, $OMe\cdot C_6H_4\cdot CMe\cdot CH\cdot OEt$, is formed. This has b. p. 269—271°, $D^{\circ} 1\cdot044$, and combines directly with bromine. Its lower homologue, $OMe\cdot C_6H_4\cdot CMe\cdot CH\cdot OMe$, has b. p. 262—263°, and $D^{\circ} 1\cdot065$. Both are easily converted by acids into *p*-methoxyhydratropaldehyde.

The author considers that the iodohydriins of the type



belong rather to the glycols than to the iodohydriins of the general type, since elimination of hydrogen iodide from the latter leaves a less resistant hydroxyl group, whilst elimination of HI or water from the two former types leaves a more resistant hydroxyl.

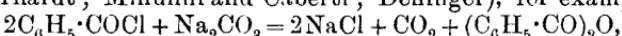
E. H.

A Product obtained in the Technical Preparation of Benzoic Acid from Coal Tar. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1907, 28, 1091—1097).—A method of preparing benzoic acid from

coal tar has been based (D.R.-P. 109122) on the observation by Krämer and Spilker (Abstr., 1890, 496) of benzonitrile in coal tar freed from phenol and bases. The present paper is an account of the examination of a product obtained together with the benzoic acid. It is found to consist of benzoic esters, chiefly 1 : 3 : 4-xylenyl benzoate, together with small amounts of free phenols and benzoic acid, and traces of coumarone. The crude material for the preparation of the benzoic acid, in spite of having been treated with alkalis, must contain 1 : 3 : 4-xylenol together with not more than traces of phenol and cresol, which on hydrolysis of the benzonitrile esterify part of the benzoic acid.

G. Y.

Hyposulphites. IV. ARTHUR BINZ and THEODOR MARX (*Ber.*, 1907, 40, 3855—3860. Compare Abstr., 1904, i, 964; 1905, ii, 521; 1906, ii, 23).—Where benzoyl chloride acts on potassium oxalate, sodium nitrite, or sodium carbonate, it forms benzoic anhydride (Gerhardt; Minunni and Caberti; Deninger), for example :



the reactions in question taking place with great ease in the presence of pyridine. The action of benzoyl chloride on sodium hyposulphite is similar, benzoic anhydride resulting either in the presence or absence of pyridine. Three additional products are, however, obtained ; from benzoyl chloride alone, benzoyl disulphide is produced ; from benzoyl chloride and pyridine, in addition to benzoyl disulphide, a red base of the probable formula $C_{11}H_{10}N_2S$, and a yellow compound of a high molecular weight are formed.

The behaviour of benzoyl chloride towards sodium sulphite, both in the absence and presence of pyridine, has also been studied. Benzoyl disulphide is not formed in this case. The change $2C_6H_5\cdot COCl + Na_2SO_3 = 2NaCl + (C_6H_5\cdot CO)_2O + SO_2$ is accompanied by the formation of the red and yellow compounds already mentioned. The latter compounds are also formed by the action of sulphur dioxide on a mixture of benzoyl chloride and pyridine.

The yellow compound, to which the formula $C_{23}H_{16}O_6N_4S_4$ is provisionally assigned, is either not dissolved by the ordinary solvents or is transformed into the red base, $C_{11}H_{10}N_2S$, which forms ruby-red needles, m. p. 259°. The molecular weight of the latter compound was determined by the cryoscopic method.

A. McK.

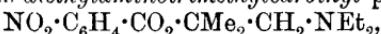
Preparation of the Alkylamino-esters of *p*-Aminobenzoic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 179627, 180291, 180292).—The esters of aromatic acids are known to possess anaesthetic properties, but only in a few cases is this action of any practical importance, owing to the circumstance that it is somewhat transient and is accompanied by irritant after-effects. It has now been found that the soluble hydrochlorides of the alkylamino-esters of *p*-aminobenzoic acid produce a well-sustained anaesthesia without any disagreeable irritation.

Chloroethyl p-nitrobenzoate, $NO_2\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Cl$, white needles, m. p. 56°, is produced by heating equal quantities of chlorhydrin and *p*-nitrobenzoyl chloride at 120—125°; when heated with

piperidine it furnishes *piperidinoethyl p-nitrobenzoate*, m. p. 61—62°. *Piperidinoethyl p-aminobenzoate*, m. p. 90°, results from the reduction of the preceding ester; its hydrochloride, m. p. 213°, crystallises in white needles.

Diethylaminoethyl p-nitrobenzoate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, a viscid oil, is produced by the interaction of chloroethyl *p*-nitrobenzoate and diethylamine. *Diethylaminoethyl p-aminonitrobenzoate*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, m. p. 51°, crystallises from dilute alcohol with $2\text{H}_2\text{O}$; hydrochloride, m. p. 156°.

Diethylaminotrimethylcarbinol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, b. p. 55°/11 mm., obtained by the action of magnesium methyl iodide on diethylaminoacetone, yields *diethylaminotrimethylcarbinyl p-nitrobenzoate*,



m. p. 47—48°, on treatment with *p*-nitrobenzoyl chloride. *Diethylaminotrimethylcarbinyl p-aminobenzoate*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, a viscid oil, gives a crystalline hydrochloride, m. p. 183—184°. The patent contains a list of eighteen of these alkylamino-esters of *p*-nitrobenzoic acid with the corresponding esters of *p*-aminobenzoic acid and their hydrochlorides.

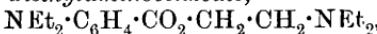
Piperidylethyl p-aminobenzoate, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$, was obtained by dissolving hydroxyethylpiperidine and *p*-aminobenzoic acid in cold concentrated sulphuric acid. The solution was subsequently heated to 90—100°, poured into ice-water, and rendered ammoniacal; the base, m. p. 90°, which is obtained from its crystalline hydrochloride, m. p. 213°, crystallises from light petroleum in needles.

Piperidylethyl p-dimethylaminobenzoate,



m. p. 45°, was obtained from hydroxyethylpiperidine and *p*-dimethylaminobenzoyl chloride in benzene solution; its hydrochloride, m. p. 205°, is readily soluble in water to a neutral solution. The ester may also be prepared by heating hydroxyethylpiperidine with *p*-dimethylamino-benzoic acid and concentrated hydrochloric acid or by warming this base with *p*-dimethylaminobenzoic anhydride.

The following esters and their hydrochlorides were also prepared : *diethylaminoethyl p-diethylaminobenzoate*,



oily ; hydrochloride, white needles, m. p. 162—163° : *diethylaminoethyl p-aminobenzoate*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NEt}_2$, m. p. 51° ; hydrochloride, m. p. 156° : *diethylaminoethyl p-methylaminobenzoate*, oily ; hydrochloride, m. p. 106—109° : *piperidylethyl p-methylaminobenzoate*, oily ; hydrochloride, m. p. 145—147° : *diethylaminoethyl p-ethylaminobenzoate*, oily ; hydrochloride, m. p. 119—121°.

These esters, which have important anaesthetic properties, can also be prepared by alkylating *p*-azobenzoic acid or its chloride with the amino-alcohols and then reducing the products.

Piperidylethyl p-azobenzoate, m. p. 118—119°, separates in brick-red needles ; *diethylaminoethyl p-azobenzoate*, m. p. 82°, forms yellowish-red leaflets.

G. T. M.

Preparation of Alkylaminohexyl Benzoates. CHEMISCHE FABRIK AUF AKTIEN, VORM. E. SCHERING (D.R.-P. 181287).—The

alkylaminohexyl alcohols on benzylation furnish a series of complex esters having the general formula $\text{NRR}'\text{CMe}_2\text{CH}_2\text{CHMe}\cdot\text{OBz}$, where R is an alkyl group and R' either a hydrogen atom or another alkyl group. These compounds are less toxic than the anaesthetics of the stovaine series, and as their hydrochlorides react as neutral substances, even in concentrated solutions, they are devoid of any irritating action.

γ -Methylamino- α -dimethylbutyl benzoate,



is an oily substance produced by treating γ -methylamino- α -dimethylbutyl alcohol with benzoic anhydride in the presence of water on the water-bath; hydrochloride, needles, m. p. 161—162°.

γ -Ethylamino- α -dimethylbutyl benzoate,



oil, prepared from γ -methylamino- α -dimethylbutyl alcohol hydrochloride and benzoyl chloride, yields a hydrochloride forming small needles, m. p. 172—173°.

γ -Dimethylamino- α -dimethylbutyl benzoate,

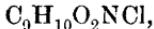


and *γ -diethylamino- α -dimethylbutyl benzoate* are oils; their hydrochlorides melt at 153—154° and 164—167° respectively.

G. T. M.

Methyl *m*-Amino-*p*-dimethylaminobenzoate. FRÉDÉRIC REVERDIN (*Ber.*, 1907, 40, 3686—3691; *Arch. sci. phys. nat.*, 1907, 24, 248—256; *Bull. Soc. Chim.*, [iv], 1, 995—1001).—It has been discovered that during the reduction of methyl nitrodimethylaminobenzoate, the ester is very easily hydrolysed, and accordingly the following compounds must be deleted from the literature. Methylaminodimethylaminobenzoate hydrochloride, m. p. 228°, the acetate, m. p. 232°, the condensation product with chlorodinitrobenzene, m. p. 253—254°, and the methyl hydroxy-*p*-dimethylaminobenzoate of m. p. 176°, and its barium salt (*Abstr.*, 1906, i, 273).

The re-investigation has resulted in the preparation of *3-acetylamino-4-dimethylaminobenzoic acid*, $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}_2$, which forms glistening leaflets, m. p. 246—247°; the *diacetyl* compound, lamillæ, m. p. 194°; the *picrate*, m. p. 199—200°. *3-Chloro-4-dimethylaminobenzoic acid*,



forms long prisms, m. p. 178—179°; the corresponding *iodo*-compound has m. p. 190—191°, and crystallises in white needles. The *methyl* ester was obtained from the acid, and by reduction of the nitro-derivative with sodium hyposulphite in the cold; it forms prisms, m. p. 56°; the *monacetyl* compound, $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$, has m. p. 103—104°, and the *picrate*, m. p. 187°.

W. R.

Naphtholmonosulphonates of Ethyl *p*-Aminobenzoate. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 181324).—The naphtholmonosulphonates of ethyl *p*-aminobenzoate possess the powerful anaesthetic properties of the amino-ester, and are distinguished from the salts of this substance with the mineral acids by their greater stability and solubility, and also by their neutral character. They are prepared either by the direct interaction of their

components or by double decomposition between a metallic naphthol-monosulphonate and ethyl *p*-aminobenzoate hydrochloride.

Ethyl p-aminobenzoate β-naphthol-6-sulphonate,



is moderately soluble in hot water, less so in the cold solvent.

G. T. M.

p-Aminocinnamylideneacetic Acid. HERMANN FECHT (*Ber.*, 1907, 40, 3891—3893. Compare following abstract).—*p-Aminocinnamylideneacetic acid* is obtained by the reduction of the nitro-compound by a ferrous salt in ammoniacal solution. In addition to the acid, there is produced an amorphous, dark red substance, insoluble in water, which may be an abnormal ammonium salt. From *o*-aminocinnamylidenemalonic acid, the reddish-yellow hydrogen ammonium salt ($2\text{H}_2\text{O}$) can be prepared, the aqueous solution of which is decolorised by a few drops of acetic acid or of ammonium hydroxide.

p-Aminocinnamylideneacetic acid, and also methyl *p*-dimethylaminocinnamylideneacetate, form dark red solutions in acetic acid or alcoholic hydrogen chloride, whereas in hydrochloric acid a yellow solution is obtained, from which red crystals of a hydrochloride are isolated; the aqueous solution is decolorised by the addition of hydroxylamine hydrochloride, with the separation of the colourless hydrochloride of an isomeric acid containing $2\text{H}_2\text{O}$. When the solution of this hydrochloride is boiled in the absence of excess of hydrochloric acid, the yellow, isomeric amino-acid is obtained, which is called the β -acid, in contradistinction to the original *p*-aminocinnamylideneacetic acid, which is called the α -acid. The β -acid forms yellow solutions in alkalis or acetic acid, and colourless solutions in mineral acids. A hydrochloric acid solution in the cold deposits anhydrous colourless crystals of a hydrochloride, but by boiling the solution the red hydrochloride of the α -acid is obtained.

The conversion of the α - into the β -acid is promoted by phenylhydrazine, aminoguanidine, or semicarbazide, as well as by hydroxylamine.

Both the α - and β -acid give the same colourless *acetyl* derivative, m. p. 265° (decomp.).

C. S.

Quinone Formation. Constitution of Triphenylmethane Dyes. HERMANN FECHT (*Ber.*, 1907, 40, 3893—3903. Compare preceding abstract).—To the coloured salts of the *p*-aminocinnamylidene derivatives of acetic and malonic acids, the author ascribes quinonoid formulæ, $\text{NH}_2\text{Cl}:\text{C}_6\text{H}_4:\text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and



The carboxyl group in these acids has very little auxochromic influence. The pronounced difference in colour which exists between the salts of the two acids in alkaline solution disappears on acidification, because the group $\text{C} \begin{array}{l} \text{CO} \\ \swarrow \\ \text{CO} \end{array}$, which endows the dicarboxylic acid with its deeper colour, no longer exists in the quinonoid salts which are formed in

α -p-Aminocinnamylideneacetic acid,

m. p. 200° (decomp.), separates from water or alcohol in brownish-yellow needles. The β -acid, m. p. 200° (decomp.), forms yellow crystals. They are regarded as stereoisomerides. The red hydrochloride of the α -acid has m. p. 260° (decomp.), and the colourless hydrochloride of the β -acid decomposes at $250-260^\circ$. The methyl esters of the α - and β -acids, obtained by the action of diazomethane, both have m. p. $145-146^\circ$. The α -ester in benzene solution yields with alcoholic hydrogen chloride bluish-red needles of the hydrochloride, while the β -ester, which is turned red by cold hydrochloric acid, only yields a colourless hydrochloride in the presence of hydroxylamine. The tertiary base, $\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}$, m. p. 142° , obtained from the α -ester and methyl iodide, has the same colour as the non-methylated amino-acid.

 α -Aminocinnamylidenemalonic acid,

m. p. 175° , forms orange-yellow needles, and does not yield coloured salts in acid solution; the para-isomeride, m. p. 190° , crystallises in brown needles.

as-Dimethylaminodiphenylethylene, $\text{CH}_2 \cdot \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, m. p. 56° , is obtained from *p*-dimethylaminobenzophenone and magnesium methyl iodide, the intermediately-formed carbinol, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CPhMeOH}$, has b. p. $202^\circ/14$ mm., and loses water at 130° , yielding the preceding compound. Michler's ketone and magnesium methyl iodide yield the carbinol, $\text{OH} \cdot \text{CMe}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, m. p. 152° , which crystallises in colourless needles and loses water on heating, forming as-tetramethyl-diaminodiphenylethylene, $\text{CH}_2 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$, m. p. 124° , b. p. $250^\circ/12$ mm., which, like the carbinol, gives a blue solution in acetic acid and yellow solutions in mineral acids.

Benzylidene-p-dimethylaminoacetophenone, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} \cdot \text{CHPh}$, m. p. 165° , prepared from cinnamanilide, dimethylaniline, and phosphorus oxychloride, crystallises in yellow needles, dissolves in acetic or mineral acids with a yellow colour, and forms a red solution with alcoholic hydrogen chloride.

C. S.

Sodium Salicylate. WILHELM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1907, 651-652).—When water is added, drop by drop, to a weighed quantity of sodium salicylate until this just dissolves, it is found that 1 part of the salt dissolves in 1.55 parts of water or 6.45 parts in 10 c.c. In two out of eight experiments made in the reverse way, 6.57 and 6.60 parts of the salt dissolved in 10 c.c. of water, whence it is concluded that this salt shows some tendency to form supersaturated solutions. The specific gravities of a series of solutions of sodium salicylate are given in the original. T. A. H.

Behaviour of Very Weak Acids and Pseudo-acids towards Ammonia. ARTHUR HANTZSCH [and, in part, Miss EDITH MORGAN and HERBERT GORKE] (*Ber.*, 1907, 40, 3798-3805).—Although simple phenols and naphthols, such as thymol, ψ -cuminol, mesitol, α -naphthol, and β -naphthol, are almost completely converted into ammonium salts when exposed in an atmosphere of ammonia, those

phenols and naphthols which contain the "negative" group $-CO_2R$, ortho to the hydroxyl group, such as ethyl salicylate, ethyl α -naphthol-2-carboxylate, and ethyl β -naphthol-1-carboxylate, are practically indifferent towards ammonia at the ordinary temperature. The same retarding effect is produced by an acetyl or benzoyl group in the position ortho to the hydroxyl group. These phenols consequently belong to the group of "cryptophenols" (Auwers, Abstr., 1906, i, 838). Salol (phenyl salicylate) differs somewhat from ethyl salicylate, since it slowly absorbs ammonia to form an ammonium salt. The ammonium salt of ethyl salicylate is formed, however, when ammonia is passed into a solution of the ester in light petroleum or toluene at -40° . Salicylaldehyde, ethyl *m*-hydroxybenzoate, and ethyl *p*-hydroxybenzoate absorb ammonia to form salts. Salicylic acid absorbs only 1 mol. of ammonia.

A new method for ascertaining whether a compound combines with ammonia in an indifferent solvent to form a salt is described. A known weight of the substance to be examined is dissolved in benzene and the depression of the freezing point observed; the calculated quantity of ammonia in the form of a *N*/10 solution in benzene is then added and the depression again noted. If an ammonium salt is formed, the mol. wt. obtained from the total depression of the freezing point of the benzene will correspond with the mol. wt. of the salt. If no combination has taken place, the value obtained will be the mean of the mol. wts. of ammonia and the substance. When the observed value lies between this mean value and the mol. wt. of the ammonium salt, it denotes the partial formation of an ammonium salt.

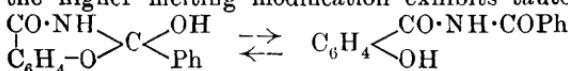
It is stated, in conclusion, that the apparent slow precipitation of the ammonium salts of various compounds recorded by Hantzsch and Dollfus (Abstr., 1902, i, 223) on passing ammonia into solutions of these compounds in benzene is due in some cases to supersaturation, whilst, in others, the crystals of the ammonium salt which separate out at first are so small that they can only be detected by illuminating the solution with a beam of light. The slow precipitation of an ammonium salt in benzene does not therefore indicate the presence of a pseudo-acid.

W. H. G.

Acyl Derivatives of Salicylamide and Allied Compounds.
KARL AUWERS (*Ber.*, 1907, 40, 3506—3514).—The author has pointed out previously (Abstr., 1905, i, 894) that the isomeric benzoates of salicylamide described by Titherley and Hicks (*Trans.*, 1905, 87, 1207) are not desmotropic in the sense of the formulæ:

$OBz \cdot C_6H_4 \cdot CO \cdot NH_2$
(m. p. 144° , labile) and $OBz \cdot C_6H_4 \cdot C(OH) \cdot NH$ (m. p. 208° , stable), and that the compound with the higher melting point is the *N*-benzoate, $OH \cdot C_6H_4 \cdot CO \cdot NH \cdot Bz$.

The present paper is a discussion of the more recent work of McConnan and Titherley (*Trans.*, 1906, 89, 1318); the latter authors are not in agreement with the author's conclusions, and suggest that the higher melting modification exhibits tautomerism in the sense:



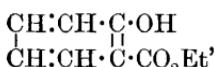
p-Hydroxybenzamide O-benzoate, $C_{14}H_{11}O_3N$, separates from glacial acetic acid in colourless needles, m. p. $218-220^\circ$.

Determinations of the molecular weights of acetyl benzamide, *N*-acetylsalicylamide, and *O*-benzoylsalicylamide respectively in *p*-dibromobenzene solutions are submitted in support of the views advocated.

o-Benzoyloxyphenylacetamide, $OBz \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot NH_2$, obtained by benzoylating *o*-hydroxyphenylacetamide, separates from alcohol in glistening leaflets, m. p. $162-164^\circ$. It is insoluble in alkali and is converted by cold concentrated sulphuric acid into the original substance; it is accordingly an *O*-ester. The constitution was proved still further by conversion of the compound into *o*-benzoyloxybenzyl cyanide, $C_{15}H_{11}O_2N$, by means of phosphoric oxide; the latter compound separates from light petroleum in needles, m. p. 50° , and, when hydrolysed, forms *o*-hydroxybenzyl cyanide, which separates from a mixture of light petroleum and benzene in colourless needles, m. p. $117-119^\circ$.

A. McK.

Phenylhydrazone of Salicylic Acid. HUGO SCHRÖTTER AND JOSEF FLOOH (*Monatsh.*, 1907, 28, 1099—1106. Compare Madsen, this vol., i, 423).—The resemblance of the enolic formula of ethyl acetoacetate, $\begin{matrix} CMe \cdot OH \\ || \\ CH \cdot CO_2Et \end{matrix}$, to the formula of ethyl salicylate,



suggested that the latter or its ketonic form should undergo condensations similar to those of ethyl acetoacetate. This view has led the authors to investigate the action of phenylhydrazine on methyl salicylate.

When heated with 2 mols. of freshly distilled phenylhydrazine and a few drops of piperidine in a reflux apparatus on a water-bath, methyl salicylate forms *salicylic acid-phenylhydrazone*, $C_{13}H_{12}O_2N_2$, in a 10% yield. This crystallises in white leaflets, m. p. 130° , gives a violet coloration when heated with aqueous, or in the cold with aqueous-alcoholic, ferric chloride, reduces ammoniacal silver, platinum chloride, and Fehling's solutions, dissolves in aqueous alkali carbonates, and can be recrystallised from concentrated sulphuric acid. It must have the annexed constitution. The ammonium salt exists only in solution; the *potassium*, *sodium*, *calcium*, and *barium* salts readily decompose on recrystallisation or on evaporation of their aqueous solutions. The *piperidine* salt, $C_{18}H_{12}O_2N_2C_5H_{11}N$, is obtained in a 55—60% yield by heating methyl salicylate and phenylhydrazine with an excess of piperidine; it crystallises in nacreous leaflets, m. p. 162° , is neutral in cold, but alkaline in hot, aqueous solution, and is decomposed slowly at 100° or by prolonged action of steam, or more quickly by aqueous alkalis.

G. Y.

Synthesis of Iodogorgonic Acid. HENRY L. WHEELER (*Am. Chem. J.*, 1907, 38, 356—358).—Henze (this vol., i, 370) has referred to the iodogorgonic acid prepared by Wheeler and Jamieson (Abstr.,

1905, i, 350) as *l*-di-iodotyrosine. It has now been found that the supposed *l*-tyrosine, which, on treatment with iodine, yielded iodo-gorgonic acid, was really the inactive variety, and that the iodo-gorgonic acid (di-iodotyrosine) produced was also inactive and identical in every respect with the natural acid.

E. G.

***m*-Hydroxytritanolactone.** HANS VON LIEBIG and PAUL KEIM (*J. pr. Chem.*, 1907, [ii], 76, 275—277. Compare Abstr., 1905, i, 781; this vol., i, 45).—The condensation of benzil with phenol in presence of zinc chloride leads to the formation of a substance, crystallising in colourless needles, m. p. 239°, and *m*-hydroxytritanolactone, $C_{20}H_{14}O_2$, which crystallises in rhombic leaflets, m. p. 120°. The sodium, $C_{20}H_{15}O_3Na$, disodium, $C_{20}H_{14}O_3Na_2$, potassium, and dipotassium salts have been analysed. Whilst *m*-hydroxytritanolactone remains unchanged on evaporation of its solutions, the alkali salts decompose forming diphenylmethane. *Bromo-m*-hydroxytritanolactone, $C_{20}H_{13}O_2Br$, forms colourless, rhombic leaflets, m. p. 129°.

***m*-Methoxytritanic acid,** $C_{21}H_{18}O_3$, prepared by hydrolysis of the methyl ester, crystallises in rhombic leaflets, m. p. 235°, and loses carbon dioxide at about 280°. The potassium salt, $C_{21}H_{17}O_3K \cdot 2H_2O$, crystallises in needles. The methyl ester, $C_{22}H_{20}O_3$, forms stout prisms, m. p. 134°.

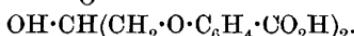
***m*-Ethoxytritanic acid,** $C_{22}H_{20}O_3$, crystallises in needles, m. p. 264°, boils slightly above its m. p. in a vacuum, and loses carbon dioxide when heated under atmospheric pressure. The potassium salt, $C_{22}H_{19}O_3K$, was analysed. The ethyl ester, $C_{24}H_{24}O_3$, forms rhombohedra, m. p. 84°.

***m*-Methoxytritanol,** $C_{20}H_{18}O_2$, prepared by the action of concentrated sulphuric acid or of lead dioxide and glacial acetic acid on *m*-methoxytritanic acid, remains unchanged when heated at 360° or when boiled with ethereal or alcoholic hydrogen chloride. ***m*-Methoxytritane,** $C_{20}H_{18}O$, formed by heating *m*-methoxytritanic acid, separates from alcohol in small, rhombic crystals, m. p. 116°. ***m*-Ethoxytritane** crystallises in large prisms, m. p. 68°. ***m*-Hydroxytritane,** $C_{19}H_{16}O$, formed by heating the methyl ether or methoxytritanol or ethoxytritane with hydrogen iodide and glacial acetic acid, crystallises in hexagonal leaflets, m. p. 124°. These tritanic acids and tritanol derivatives give a violet coloration with concentrated sulphuric acid; the tritane derivatives give a yellow coloration. Only *m*-hydroxytritanolactone does not give a coloration.

G. Y.

The Condensation of Salicylic Acid with Epichlorohydrin or the Dichlorohydrins. MARTIN LANGE (D.R.-P. 184382).—Salicylic acid, when condensed in sodium hydroxide solution with epichlorohydrin or α - or β -dichlorohydrin, gives rise to the soluble sodium salt of a condensation product which corresponds with either

of the following formulae: $\text{CH}_2\begin{array}{c} \text{O} \\ | \\ \text{O} \end{array}>\text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ or



The free acid, m. p. 167°, crystallises from dilute alcohol in aggregates

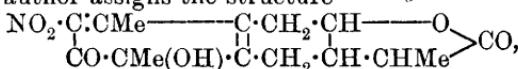
of white needles. It is not decomposed by boiling with aqueous acids or alkalis.

G. T. M.

Polymerisation of Ethyl Phenylpropiolate. PAUL PFEIFFER and W. MÖLLER (*Ber.*, 1907, 40, 3839—3844). Compare Stobbe, this vol., i, 769).—Ethyl phenylpropiolate is converted when heated in a sealed tube at 210° for ten to twelve hours into *diethyl 1-phenyl-naphthalene-2 : 3-dicarboxylate*, m. p. 127—128°, identical with the compound described wrongly by Lanser as triethyl triphenyltrimesate (*Abstr.*, 1899, i, 916). Only one of the carbethoxy-groups is hydrolysed by an aqueous or alcoholic solution of potassium hydroxide; the *ester acid*, m. p. 202—203°, so formed, probably has the formula $\text{C}_6\text{H}_4 < \begin{matrix} \text{CPh:C:CO}_2\text{Et} \\ \text{CH=C:CO}_2\text{H} \end{matrix}$, and is identical with the compound wrongly described by Lanser and Halversen (*Abstr.*, 1902, i, 458) as monoethyl diphenyltrenecarboxylate. It crystallises with 4H₂O, which are driven off on heating the substance; the *sodium salt*, C₂₀H₁₅O₄Na, 6H₂O, crystallises in small, silvery leaflets; the *calcium salt*, (C₂₀H₁₅O₄)₂Ca, forms small, slender needles; the *pyridinium salt*, C₂₀H₁₅O₄, C₅H₅NH, forms brilliant, quadratic plates, m. p. 150—152°. A mixture of the calcium salt and calcium hydroxide yields, on distillation at 325°, a substance which crystallises in brilliant, brownish-yellow needles, m. p. 157°, and is probably *allochrysoketone* (compare Stobbe, this vol., i, 765).

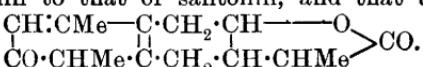
W. H. G.

ψ-Quinol Derivatives of the Santonin Group. GUIDO BARGELINI (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 262—265).—Since the desmotroposantonins and the santonous acids contain the same ring, $\begin{matrix} \cdot\text{C:CMe:C:OH} \\ \cdot\text{C:CMe:CH} \end{matrix}$, as is present in 1:4-dimethyl-β-naphthol, the author has investigated the oxidation of these compounds to ascertain if they also yield derivatives of the ψ-quinol type (compare this vol., i, 914). Desmotroposantonous acid gives a ψ-quinol which is apparently isomeric with santoninic acid and yields an azo-compound when treated with phenylhydrazine. From desmotroposantonin has been prepared, not the corresponding ψ-quinol or hydroxysantonin, but its nitro-derivative which was obtained by Andreucci (*Abstr.*, 1898, i, 266), and to which the author assigns the structure



as it forms an acetyl compound. The corresponding quinitrole, $\begin{matrix} \text{NO}_2\cdot\text{C:CMe} & \text{---} & \text{C}\cdot\text{CH}_2\cdot\text{CH} & \text{---} & \text{O} \\ & & \parallel & & >\text{CO}, \\ & & \text{CO}\cdot\text{CMe}(\text{NO}_2) & \cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe} & \end{matrix}$, has also been prepared.

This capacity of the aromatic ring of desmotroposantonin and desmotroposantonous acid of becoming alicyclic in the transformation of these compounds into ψ-quinols would indicate that the type changes from that of desmotroposantonin to that of santonin, and that the latter should have the formula:



T. H. P.

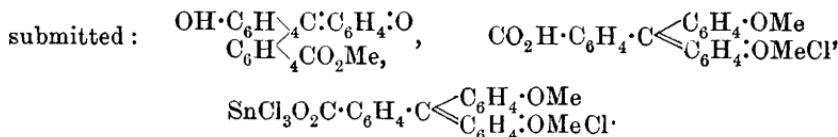
Constitution of Phthalein Salts. RICHARD MEYER and KARL MARX (*Ber.*, 1907, 40, 3603—3605).—An intensely yellow *diethyl* quinonoid derivative of phenolphthalein, m. p. 98—104°, similar to the quinonoid derivative of tetrabromophenolphthalein (this vol., i, 421), has been prepared by the action of ethyl iodide on the solid potassium salt; on recrystallisation, it is transformed into the stable lactone ether, m. p. 118—120°.

The absorption spectra of the alkali salts of phenolphthalein, quinolphthalein, and fluorescein are compared. If the wave-lengths of the absorbed light are taken as a function of the concentration of the solutions, the three spectra give similar curves. That the curve for fluorescein, although differing in position, is similar in shape to those for phenolphthalein and quinolphthalein, which lie close together, shows that the difference between these three substances is one of degree and not fundamental.

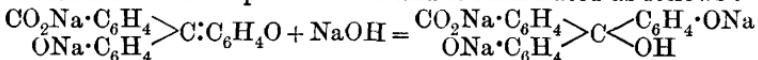
G. Y.

Halochromism of Phenolphthalein and its Esters. KURT H. MEYER and ARTHUR HANTZSCH (*Ber.*, 1907, 40, 3479—3488).—Whilst the behaviour of phenolphthalein towards alkalis and the constitution of its alkali salts have been frequently investigated, its basic properties and its power of forming salts with acids have been comparatively little studied. The authors have accordingly found that phenolphthalein forms a red salt with hydrogen chloride at —30°, but the salt could not be isolated; on the other hand, brilliant red compounds were obtained with aluminium chloride and stannic chloride respectively. The lactoid dimethyl ether of phenolphthalein exhibits a similar behaviour towards these chlorides.

The authors confirm the results of Green and King (*Abstr.*, 1906, i, 670) with regard to the quinonoid methyl ester of phenolphthalein and agree with their theoretical conclusions. This compound also forms double salts. Since the alkali salts of phenolphthalein have the same colour as those of the quinonoid ester, the quinonoid formula is assigned to the former. The following formulæ are accordingly



The fact that the red colour of phenolphthalein in alkaline solution is discharged by excess of alkali is not due to the formation of the colourless sodium salt of phenolphthalein, as is often supposed; the decolorisation is a time phenomenon and is formulated as follows :

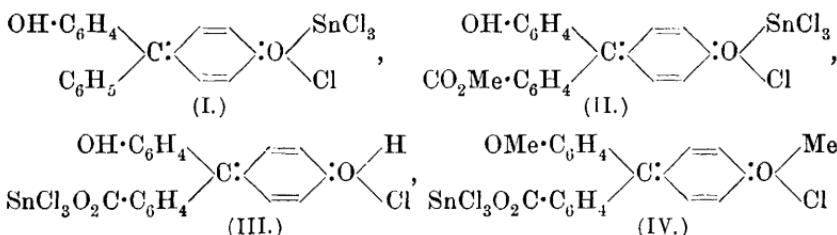


The quinonoid monomethyl ester of phenolphthalein also forms red double salts with stannic chloride and aluminium chloride; these salts are undoubtedly of quinonoid structure.

The double salts of phenolphthalein and its lactoid dimethyl ether have, not only the same colour when solid, namely, cinnabar-red, but in solution have almost the same absorption spectra as the salts of the

quinonoid ester, exhibiting a characteristic green band. The conclusion is drawn that the salts of the lactoid ether are quinonoid, in fact, *all salts of phenolphthalein with acids are quinonoid*.

The tin double salts of benzaurin (I), the quinonoid ester (II), phenolphthalein (III), and the lactoid dimethyl ether (IV) are respectively represented as follows:



When hydrogen chloride is passed over dry phenolphthalein at the ordinary temperature, there is no change, but at -30° addition of from 1—2 mols. of the acid takes place, the salt being red; on rise of temperature, however, all the hydrogen chloride is eliminated.

The salt, $C_{20}H_{14}O_4AlCl_3$, obtained by adding the calculated amount of a solution of aluminium chloride in nitrobenzene to a solution of phenolphthalein in nitrobenzene and then pouring the mixture into carbon disulphide, is a cinnabar-red powder, which chars on being heated. The salt, $C_{20}H_{14}O_4C_6H_5NO_2SnCl_4$, obtained from stannic chloride in a similar manner, is a red, hygroscopic powder. The salt, $C_{22}H_{18}O_4AlCl_3$, obtained from the lactoid dimethyl ether, is a cinnabar-red powder. The salt, $C_{22}H_{18}O_4SnCl_4$, forms red crystals, m. p. 128—129°; its solution in chloroform is red; its alcoholic solution orange-yellow.

Quinonoid phenolphthalein methyl ester (methyl benzaurin-carboxylate), obtained by the action of methyl sulphate on phenolphthalein (compare Green and King, *loc. cit.*), is a red, amorphous powder melting indefinitely between 127° and 130°. Its concentrated solutions are red, but become yellow on dilution; its solution in liquid ammonia is reddish-violet. It undergoes saponification with great ease. It forms the salt, $C_{21}H_{16}O_4 \cdot AlCl_3$, which is a cinnabar-red powder. The salt, $C_{21}H_{16}O_4 \cdot SnCl_4$, forms red flakes.

The absorption spectra of the tin double salts prepared are described.

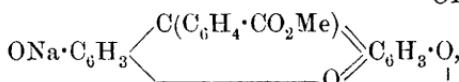
The red solutions of phenolphthalein alkali salts require such a large excess of alkali in order to be decolorised that the reaction cannot be clearly followed by conductivity measurements. Tetrabromophenolphthalein was, however, examined from this standpoint. A. MCK.

Constitution of the Phenolphthalein and Quinolphthalein Salts. II. ARTHUR G. GREEN and PERCY E. KING (*Ber.*, 1907, 40, 3724—3734. Compare *Abstr.*, 1906, i, 670*).—The scarlet compound described previously as the quinonoid methyl ester of phenolphthalein is found to be the hydrochloride of the ester. The *ester*, which is much

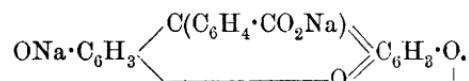
* See also Proc., 1907, 23, 228.

more stable than its hydrochloride, is obtained best by passing dry hydrogen chloride into a solution of phenolphthalein in methyl alcohol and 100% sulphuric acid, and, after keeping overnight, pouring the solution into ammonium hydroxide at 0°. After purification, it crystallises in orange, prismatic needles, and in alcoholic solution yields with hydrochloric acid a scarlet solution of the chloride which gradually loses its colour and yields phenolphthalein. The ester forms a violet-red solution in alkali hydroxides, from which the unchanged methyl ester is obtained by immediate acidification and phenolphthalein by postponed acidification. The methyl ester of quinolphthalein in the form of its chloride exhibits precisely analogous behaviour, and forms a bluish-purple solution in alkalies.

For these coloured alkali salts of the esters, the authors recommend the formulæ: $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}) \cdot \text{C}_6\text{H}_4 \cdot \text{O} \begin{array}{l} \text{H} \\ \swarrow \\ \text{OH} \end{array}$ and



and from analogy the coloured salts of phenol- and of quinol-phthaleins must be represented by $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Na}) \cdot \text{C}_6\text{H}_4 \cdot \text{O} \begin{array}{l} \text{H} \\ \swarrow \\ \text{OH} \end{array}$ and

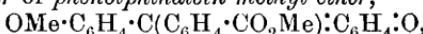


These conclusions, which accord with the behaviour of the salts of the phthaleins and their esters with excess of potassium hydroxide and with alcohol, the salts of the esters remaining coloured, are confirmed by a study of the lactonoid methyl and dimethyl ethers of phenolphthalein and quinolphthalein (Meyer and Spengler, Abstr., 1905, i, 440). The methyl ethers represented by the preceding quinonoid structures would not contain a phenolic hydroxyl group, and consequently should not form coloured alkali salts, and should yield esters insoluble in alkalies. This is actually the case. Phenolphthalein methyl ether has a double m. p. initially at 148—149°, and after resolidification at 80°; in alkalies, it yields a faintly red solution, the colour of which is weaker the purer the ether (Meyer and Spengler: m. p. 141—142°, red solution in alkalies). This solution probably contains the colourless carbinol salt,

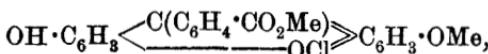


Quinolphthalein methyl ether separates from benzene in colourless prisms, m. p. 118—122°, and after removal of the benzene of crystallisation, m. p. 107—109°; it dissolves in alkalies forming a colourless solution of the carbinol salt (compare Nietzki and Burckhardt, Abstr., 1897, i, 225).

The methyl ester of phenolphthalein methyl ether,

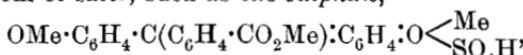


obtained from the lactonoid methyl ether in a similar manner to the methyl ester of phenolphthalein, is an orange substance insoluble in alkalies; the hydrolysed compound yields the original lactonoid ether by acidification. The methyl ester of quinolphthalein methyl ether is obtained in the form of the chloride,



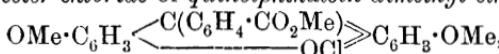
when dry hydrogen chloride is passed into a methyl-alcoholic solution of the lactonoid ether; it forms red plates, readily loses methyl chloride, is insoluble in aqueous alkalis, and yields the lactonoid ether by hydrolysis. The *chloride*, $\text{OH}\cdot\text{C}_6\text{H}_3 \xleftarrow[\text{OCl}]{\text{C}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})} \text{C}_6\text{H}_3\cdot\text{OMe}$, is prepared by passing hydrogen chloride into a glacial acetic acid solution of quinolphthalein methyl ether; it forms dark red, glistening crystals, and is instantaneously decomposed by water or moist ether.

The esters of dimethylated phenol- or quinol-phthalein are obtained only in the form of salts, such as the *sulphate*,



which is an unstable, scarlet substance. More stable is the red double salt, $2[\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me})\cdot\text{C}_6\text{H}_4\cdot\text{OMeCl}],\text{SnOCl}_2$, which is decolorised by water, alcohol, or alkalis with regeneration of the lactonoid ether.

The *methyl ester chloride of quinolphthalein dimethyl ether*,



is isolated in the form of the double salt, $2\text{C}_{22}\text{H}_{19}\text{O}_5\text{Cl},\text{ZnCl}_2$, which is C. S.

Preparation of *o*-Carboxyphenylthioglycollic Acid. KALLE & Co. (D.R.-P. 181658).—When diazotised anthranilic acid is treated with sodium monosulphide, a poor yield of thiosalicylic and salicylic acids is obtained, but when sodium polysulphide is employed a new sulphur derivative is obtained, which, unlike thiosalicylic acid, is insoluble in alcohol, and yields *o*-carboxyphenylthioglycollic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, on treatment with an alkaline solution of sodium chloroacetate.

G. T. M.

Nitration of Benzoylvanillin. JOAN POPOVICI (*Ber.*, 1907, 40, 3504—3506).—When benzoylvanillin is nitrated by cold concentrated nitric acid, one nitro-group only enters into the ring. It takes up the ortho-position relatively to the aldehyde group; this was proved by comparing the compound obtained with that resulting from the action of benzoyl chloride on (*vic*)-*o*-nitrovanillin; the phenylhydrazones are also identical.

Benzoylvanillinphenylhydrazone separates from glacial acetic acid in prisms, m. p. 209—210° (corr.).

(*vic*)-*o*-*Nitrobenzoylvanillin*, $\text{CHO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)(\text{OMe})\cdot\text{OBz}$ (1:2:3:4), separates from glacial acetic in colourless prisms, m. p. 97°. Its *phenylhydrazone* separates from glacial acetic acid in golden-yellow plates, m. p. 192°.

A. McK.

cycloButanone. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 922—925. Compare *Abstr.*, 1905, i, 355).—Further details are given for the preparation of pure cyclobutanone together with fresh determinations of some physical constants. *cycloButanone*, b. p. 98.5—99°/745 mm.; D_0^0 0.9548; D_b^{16} 0.9382; n_b^{16} 1.4220. The

semicarbazone of *cyclo*-butanone has m. p. 201° (decomp.). When boiled with lead oxide and water, 1 : 1-dibromocyclobutane is converted into cyclobutanone and an unsaturated bromide, probably $\text{CH}_2 < \begin{matrix} \text{CH}_2 \\ \diagup \\ \text{CH} \end{matrix} \geqslant \text{CBr}$, b. p. 93—95°.

Z. K.

cycloNonanone. RICHARD WILLSTÄTTER and TOKUHEI KAMETAKA (*Ber.*, 1907, 40, 3876).—The authors confirm the observations of Zelinsky (this vol., i, 780) regarding the formation of *cyclonanonanone* from sebacic acid.

A. McK.

Terpenes and Ethereal Oils. LXXXVII. Nopinone. OTTO WALLACH and ARNOLD BLUMANN (*Annalen*, 1907, 356, 227—249).—Nopinone (Baeyer and Villiger, *Abstr.*, 1896, i, 622) has been prepared previously in such small amounts that only its b. p. has been determined. It was desirable therefore to attempt the preparation of larger quantities.

Nopic acid, m. p. 126°, $[\alpha]_D - 15\cdot64^\circ$, is best isolated from the oxidation product of turpentine oil by conversion into its sparingly soluble sodium salt. Much better yields are obtained from dextro-rotatory American than from laevorotatory French turpentine oil.

Nopinone, $\text{C}_9\text{H}_{14}\text{O}$, is obtained in good yields by adding potassium permanganate and concentrated sulphuric acid to a hot aqueous solution of sodium nopalate. It solidifies in a freezing mixture to a crystalline mass, m. p. slightly above 0°, b. p. 209°, D 0·981, $n_D^{20} 1\cdot4787$, $[\alpha]_D + 18\cdot48^\circ$ when undiluted, $+37\cdot27^\circ - +38\cdot04^\circ$ in alcohol, $+11\cdot02^\circ$ in ether, or $+10\cdot79^\circ - +10\cdot95^\circ$ in benzene. When treated with hydrogen chloride in alcoholic solution, it condenses, forming the trichloride, $\text{C}_{18}\text{H}_{29}\text{OCl}_3$, which crystallises in stout prisms, decomp. 148° (evolving gas), and on prolonged boiling in solution or digestion with 1 mol. of sodium ethoxide is converted into the dichloride, $\text{C}_{18}\text{H}_{28}\text{OCl}_2$, crystallising in needles, m. p. 125—126°. The trichloride is again formed on treating the dichloride with hydrogen chloride in alcoholic solution; the ease with which it is formed together with its sparing solubility makes the trichloride suitable for the recognition of nopinone. On prolonged boiling with dilute sulphuric acid, nopinone is transformed into 1-*isopropyl*- Δ^2 -cyclohexene-4-one (*Abstr.*, 1906, i, 195).

Reduction of nopinone with sodium in moist ethereal solution leads to the formation of two nopinols, probably *cis*- and *trans*-isomerides. α -*Nopinol*, $\text{C}_9\text{H}_{15}\cdot\text{OH}$, sublimes in white needles, m. p. 102°, b. p. 204—205°, $[\alpha]_D - 5\cdot32^\circ$, remains unchanged in contact with dilute sulphuric acid, and forms a *phenylurethane*, $\text{NHPh}\cdot\text{CO}_2\cdot\text{C}_9\text{H}_{15}$, m. p. 131—132°. β -*Nopinol* is obtained as a viscous mass, $[\alpha]_D 15\cdot03^\circ$, forms a *phenylurethane*, m. p. 95—96°, and when heated with zinc chloride yields a small amount of nopinonene, C_9H_{14} , b. p. 157—160°.

Reduction of nopinone by means of sodium in alcoholic solution leads to the formation of the *pinacone*, $\text{C}_{18}\text{H}_{30}\text{O}_2$, which is obtained in crystals, m. p. 106—107°, b. p. 195—200°/11 mm.

Homonopinol (*methylnopinol*, *pinene hydrate*), $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$, prepared by the action of magnesium methyl iodide on nopinone, crystallises in needles, m. p. 58—59°, b. p. 204—205°, $[\alpha]_D - 4\cdot99^\circ$, has an odour resembling camphor, is stable towards permanganate, and yields *cis*-

terpin hydrate when shaken with 5% sulphuric acid, or in less amount when treated with cold saturated oxalic acid. The action of formic acid on homonopinol leads to the formation of a mixture of products resulting probably from the primary formation of terpin and the further transformation of this into dipentene, terpinol, terpinene, and terpineol. Dipentene dihydrochloride is formed by the action of hydrogen chloride on homonopinol in glacial acetic acid solution.

When heated with zinc chloride, homonopinol yields polymerisation products together with small amounts of hydrocarbons, which boil chiefly at 170—180°, are volatile with steam, and have an odour of limonene. The action of potassium hydrogen sulphate on homonopinol at 130° leads to the formation of a *hydrocarbon*, $C_{10}H_{16}$, b. p. 163—164°.

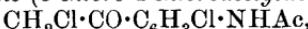
On treatment with phosphorus pentachloride in light petroleum, homonopinol yields a chloride, $C_{10}H_{17}Cl$, b. p. 95—105°/13 mm. or 200—205°/760 mm. evolving hydrogen chloride, which is isomeric with the chloride obtained by the action of hydrogen chloride on pinene, and on treatment with hydrogen chloride in glacial acetic acid solution yields dipentene dihydrochloride. The action of amyl nitrite and nitric acid on the chloride leads to the formation of a *nitrosate* containing chlorine; when treated with aniline, the chloride yields dipentene. This chloride may be formed as an intermediate product in the formation of dipentene by the action of hydrogen chloride on moist pinene.

G. Y.

[**Alkylation of ψ -Ionone.**] HAARMANN and REIMER (D.R.-P. 183855).— ψ -Ionone, when mixed with five parts of methyl sulphate and the solution subsequently warmed at 40°, yields an alkylated product which is separated by distillation in steam. The alkyl derivative when freed from ionone by sodium hydrogen sulphite has the following properties: b. p. 135°/12 mm., D^{20} 0·945, n_D 1·5150. It is, however, a mixture, the ketonic constituent of which when separated by means of semicarbazone has b. p. 120—128°/12 mm., D^{20} 0·940, n_D 1·491—1·494. A semicarbazide, $C_{13}H_{21}ON_3$, was obtained, m. p. 182—183°. These results point to the production of a new methyl-ionone.

G. T. M.

1-Chloroacetyl-2-chloro-4-aminobenzene [ω -2-Dichloro-4-aminoacetophenone] and its Derivatives. FRANZ KUNCKELL and A. RICHARTZ (*Ber.*, 1907, 40, 3394—3397).— ω -2-Dichloro-4-acetylaminoacetophenone (3-chloro-4-chloroacetylacetanilide),



obtained by Friedel-Craft's synthesis from chloroacetyl chloride and *m*-chloroacetanilide in the presence of carbon disulphide, crystallises from benzene and melts at 146—147°.

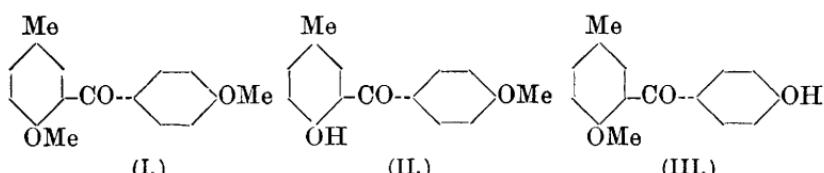
When oxidised with acidified permanganate, the ketone yields 1-chloro-2-acetylaminobenzoic acid, $C_9H_8O_3NCl$, m. p. 206—207°, and this on hydrolysis yields Tiemann's 2-chloro-4-aminobenzoic acid (Abstr., 1891, 704).

ω -2-Dichloro-4-aminoacetophenone, obtained by hydrolysing the acetyl derivative, yields a *hydrochloride*, $CH_2Cl\cdot CO\cdot C_6H_3Cl\cdot NH_2\cdot HCl$, in the form of yellowish-red needles, m. p. 278° (decomp.). The free amine melts at 95—97°.

J. J. S.

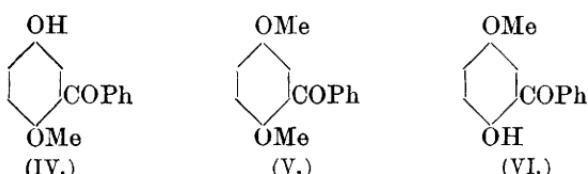
Saponifiability of Ethers of Aromatic Hydroxy-ketones.—KARL AUWERS and ERICH RIETZ (*Ber.*, 1907, 40, 3514—3521).—It has been pointed out by Auwers (*Abstr.*, 1904, i, 67) that, by the condensation of phenetole with *p*-nitrobenzoyl chloride in the presence of aluminium chloride, small amounts of 4'-nitro-2-hydroxybenzophenone, , are formed in addition to the normal product, 4'-nitro-4-ethoxybenzophenone. The conclusion was drawn that the ethers of aromatic *o*-hydroxyketones are more readily saponified than the isomeric para-derivatives.

In support of this view, the authors have studied the behaviour of the ketone (I) on saponification with aluminium chloride; a mono-



methylated compound is formed which is not attacked by aluminium chloride even at 220°. The other methyl group, on the other hand, is eliminated with remarkable ease; in the synthesis of the dimethyl ether from *p*-cresol methyl ether and anisic chloride, the monomethyl ether is formed in about the same amount of the dimethyl ether. That the product of the partial saponification has the formula (II) was proved by the fact that the isomeric ether (III) is produced by the condensation of *p*-cresol methyl ether with *p*-nitrobenzoyl chloride and subsequent displacement of the nitro- by the hydroxy-group. The latter compound is saponified with great ease.

Kauffmann ascribed the formula (IV) to the substance obtained



by the partial saponification of the compound (V). The authors conclude that the correct formula is (VI), since cryoscopic determinations in *p*-dibromobenzene solutions give normal values.

Similar results were obtained with ethers of another series of dihydroxy-ketones.

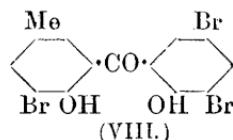
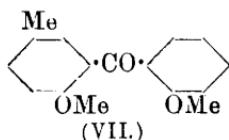
2:4'-Dimethoxy-5-methylbenzophenone, C₁₆H₁₈O₃, separates from light petroleum in colourless needles, m. p. 69—70°. *2-Hydroxy-4'-methoxy-5-methylbenzophenone*, C₁₅H₁₄O₃, separates from dilute alcohol in yellow leaflets, m. p. 108—109°. Its *dibromo-derivative*, C₁₅H₁₂O₃Br₂, crystallises from glacial acetic acid in yellow needles, m. p. 168—169°.

4'-Nitro-2-methoxy-5-methylbenzophenone, C₁₅H₁₈O₄N, separates from light petroleum in golden, glistening leaflets, m. p. 101—102°.

4'-Amino-2-methoxy-5-methylbenzophenone, $C_{15}H_{15}O_2N$, obtained by the reduction of the preceding compound with ammonium sulphide, separates from benzene in tiny needles, m. p. 152° . *4'-Amino-2-hydroxy-5-methylbenzophenone*, $C_{14}H_{13}O_2N$, separates from dilute acetic acid in leaflets, m. p. 137° .

4'-Hydroxy-2-methoxy-5-methylbenzophenone, $C_{15}H_{14}O_2$, obtained from *4'-amino-2-methoxy-5-methylbenzophenone* by replacing the amino- by the hydroxy-group, crystallises from benzene in glistening leaflets, m. p. 160° . When saponified, it forms *2 : 4'-dihydroxy-5-methylbenzophenone*, $C_{14}H_{12}O_3$, which crystallises from benzene in tiny, yellow needles, m. p. $150-151^\circ$. The latter compound forms a *tribromo-derivative*, $C_{14}H_9O_3Br_3$, crystallising from glacial acetic acid in yellow needles, m. p. $211.5-202.5^\circ$.

The ketone (VII), obtained from *o*-methoxybenzoyl chloride and

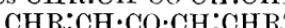


p-cresol methyl ether, was saponified at 100° with aluminium chloride and the product brominated, when the *tribromo-compound* (VIII) was obtained; it separates from glacial acetic acid in yellow crystals, melting indefinitely at 190° .

A. McK.

Dinitro- and Dibromo-*2 : 2'-dihydroxydibenzylideneacetone*.

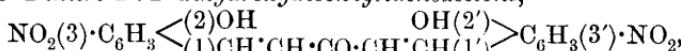
RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1907, 40, 3455—3461).—Compounds of the types $CHR:CH\cdot CO\cdot CH:CHR$ and



have already been studied by Claisen and others; the authors have been interested in the effect of the substitution of nitro- or bromine groups on the behaviour as dyes of those types which possess the complex chromophore $C:C\cdot CO\cdot C:C$, are symmetrically constituted, and in which the two hydrogen atoms in the ortho-positions in each ring are substituted by hydroxyl groups.

It has been previously shown by Fabinyi (D.R.-P. 110521) that salicylaldehyde and acetone interact in alcoholic solution in the presence of concentrated sodium hydroxide to form the sodium salt of *2 : 2'-dihydroxydibenzylideneacetone*, from which the latter compound itself is isolated when dilute mineral acid is added.

3 : 3'-Dinitro-2 : 2'-dihydroxydibenzylideneacetone,



obtained from *m*-(*vic*-)nitrosalicylaldehyde in an analogous manner, separates from alcohol in yellow needles, m. p. $231-232^\circ$ (decomp.). Its solution in concentrated sulphuric acid is yellowish-red and becomes colourless on the addition of water. The sodium salt forms glistening ruby-red crystals. The *diacetyl* derivative separates from glacial acetic acid in yellow crystals, m. p. $228-230^\circ$ (decomp.); the *dibenzoyl* derivative separates from nitrobenzene in tiny, yellow crystals, m. p. $235-238^\circ$ (decomp.).

5 : 5'-Dinitro-2 : 2'-dihydroxydibenzylideneacetone, obtained from *m-(as-)nitrosalicylaldehyde*, separates from alcohol in orange-yellow crystals, m. p. 212—214° (decomp.); its solution in concentrated sulphuric acid is orange-red; its sodium salt is reddish-brown. Its *diacetyl* derivative separates from glacial acetic acid in yellow scales, m. p. 203°.

4 : 4'-Dinitro-2 : 2'-dihydroxydibenzylideneacetone, obtained by the direct nitration of *2 : 2'-dihydroxydibenzylideneacetone*, separates from alcohol in tiny needles, m. p. about 204° (decomp.); its solution in concentrated sulphuric acid is orange-red; its solution in alkali, cherry-red; its sodium salt is dark red. Its *diacetyl* derivative separates from glacial acetic acid in tiny leaflets, m. p. 196° (decomp.).

By the action of concentrated nitric acid on *2 : 2'-dihydroxydibenzylideneacetone*, the more highly nitrated compound, *tetranitro-2 : 2'-dihydroxydibenzylideneacetone*, $\text{CO}[\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{OH}]_2$, may be obtained under the conditions quoted; it separates from nitrobenzene in yellow needles; its solution in concentrated sulphuric acid is orange-coloured; it begins to decompose at 240°.

5 : 5'-Dibromo-2 : 2'-dihydroxydibenzylideneacetone, obtained from *5-bromosalicylaldehyde*, crystallises from alcohol in yellow needles, m. p. 188° (decomp.); its solution in dilute aqueous sodium hydroxide is red, and the sodium salt is reddish-brown. Its solution in concentrated sulphuric acid is cherry-red; its solution in concentrated aqueous sodium hydroxide is bluish-violet. Its *diacetyl* derivative crystallises from glacial acetic acid in tiny, yellow needles, m. p. 187—188° (decomp.). The *dimethoxy*-derivative, obtained by the action of methyl iodide on the sodium salt, crystallises from alcohol in yellow leaflets, m. p. 137°; the *diethoxy*-derivative forms yellow leaflets, m. p. 131°. The *dibenzoyl* derivative crystallises from benzene in yellow crystals, m. p. 221° (decomp.).

2 : 2'-Diacetoxydibenzylideneacetone crystallises from glacial acetic acid or alcohol in yellow needles, m. p. 128°. *2 : 2'-Dimethoxydibenzylideneacetone* separates from alcohol in glistening yellow leaflets, m. p. 124°. *2 : 2'-Diethoxydibenzylideneacetone* forms glistening yellow leaflets, m. p. 89°. *2 : 2'-Dibenzoyloxydibenzylideneacetone* forms yellowish-white crystals, m. p. 135°.

A. McK.

Duplobenzylidenethioacetone and the Oxonium Theory.
HANS VON LIEBIG (*J. pr. Chem.*, 1907, [ii], 76, 277—280).—A criticism of Fromm and Höller's views as the constitution of the additive compounds of duplobenzylidenethioacetone (this vol., i, 710) from the standpoint of the present author's view of the nature of oxonium salts (this vol., i, 45).

G. Y.

Acetalation of Aldehydes and Ketones. LUDWIG CLAISEN (*Ber.*, 1907, 40, 3903—3914).—In consequence of the criticisms of many investigators, the author publishes the details of his process for obtaining acetals in nearly quantitative yield from aldehydes or ketones by means of ethyl orthoformate. The aldehyde, or ketone (1 mol.), and ethyl orthoformate (1·1 mols.) are dissolved in alcohol (not less than 3 mols.) and the mixture, in the presence of a catalyst, such as a

mineral acid, ferric chloride, or ammonium chloride, is kept at the ordinary temperature or is gently warmed.

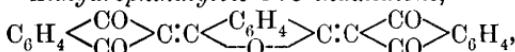
o-Ethers of β -diketones and of the esters of ketonic acids are also obtained by this method. Benzoylacetone yields the *ether*, $\text{COPh}\cdot\text{CH}(\text{CMe})\cdot\text{OEt}$, b. p. 162–164°, $D^{15} 1.058$, which is converted by hydroxylamine into *3-phenyl-5-methylisooxazole*, m. p. 42–43°.

If too large a quantity of the catalyst is used in the process, or if the time is unduly prolonged, the yield of the acetal may diminish to zero.

Arbusoff's experiments on the acetalation of acetone and acetophenone by ethyl orthoformate and alcohol without a catalyst (this vol., i, 749) have been repeated, and not a trace of the acetal has been obtained.

C. S.

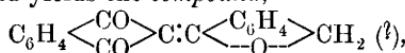
Condensation of Diketohydrindene [1:3-Indandione] with Phthalic Anhydride. CARMELO MARCHESE (*Gazzetta*, 1907, 37, ii, 303–309).—*Anhydrophtalylbis-1:3-indandione*,



prepared by the condensation of phthalic anhydride with 1:3-indandione or ethyl 2-sodio-1:3-diketohydrindene-2-carboxylate in presence of acetic anhydride, crystallises from xylene or nitrobenzene in yellow needles, m. p. 325°, and dissolves in alkali hydroxides, giving intensely red solutions.

Phtalylbis-1:3-indandione, $\text{C}_6\text{H}_4[\text{CO}\cdot\text{CH}(\text{CO})_2\cdot\text{C}_6\text{H}_4]_2$, obtained by boiling the preceding compound with alcoholic potassium hydroxide solution, separates from ethyl acetate in faintly yellow, shining crystals, m. p. 198°, and dissolves readily in nitrobenzene and sparingly in alcohol, benzene, xylene, or acetic acid. The salts of the alkali metals and of calcium are intensely red and readily soluble in water; the *barium* salt, $\text{C}_{26}\text{H}_{12}\text{O}_6\text{Ba}, 11\text{H}_2\text{O}$, was analysed.

Reduction of anhydrophtalylbis-1:3-indandione by means of zinc dust and acetic acid yields the *compound*,



m. p. 275°, which dissolves in acetic acid or ethyl acetate and, to a slight extent, in alcohol, water, benzene, or xylene.

An attempt to condense camphoric anhydride with 1:3-indandione in presence of acetic anhydride yielded 2-acetyl-1:3-indandione (compare Schwerin, Abstr., 1894, i, 194).

T. H. P.

New Anthraquinone Derivatives. EDUARD LAUBÉ (*Ber.*, 1907, 40, 3562–3567).—1-*p*-Bromoanilinoanthraquinone, prepared by condensing aminoanthraquinone with *p*-dibromobenzene in presence of potassium carbonate and copper powder, is a dark red powder, m. p. 308°, dissolving in concentrated sulphuric acid with a green coloration which changes to a scarlet-red on the addition of a drop of dichromate. *p*-Phenylenebis-1-aminoanthraquinone, obtained at the same time as the above compound, separates from chloroform as a blackish violet powder giving a violet, metallic, glistening mark on porcelain, m. p. above 320°. 2-*p*-Bromoanilinoanthraquinone forms ball-like, scarlet-

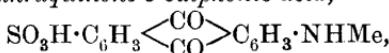
red crystals, m. p. 242°, dissolving in sulphuric acid with a cornflower-blue coloration. *p-Phenylenabis-2-aminoanthraquinone* is a dark brown powder, m. p. 300°, giving a greenish-blue coloration with sulphuric acid.

1-Iodoanthraquinone reacts more easily with carbazole and with diphenylamine than the corresponding chloro-compound. *N-Anthraquinonylcarbazole* crystallises in well-formed, ruby-red crystals, m. p. 252—254°, dissolving in sulphuric acid with an emerald-green coloration which, on warming, changes through olive-green to brown. It gives rise to a yellowish-red solution with green fluorescence when reduced with zinc and acetic acid. *1-Diphenylaminoanthraquinone* is a blackish-red powder, dissolving with an olive-green coloration in sulphuric acid.

E. F. A.

[Preparation of Amino-, Alkylamino-, and Arylamino-derivatives of Anthraquinone.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 181722). Compare this vol., i, 224).—The sulphonic groups in 1:5- and 1:8-anthraquinonedisulphonic acids may be partially or completely replaced by amino-, alkylamino-, or arylamino-groups by heating the alkali salts of these acids with ammonia, an alkylamine, or an aromatic amine.

1-Methylaminoanthraquinone-5-sulphonic acid,



is produced together with a small amount of *s*-dimethyl-1:5-diaminoanthraquinone, $\text{NHMe} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CO} \\ \swarrow \quad \searrow \\ \text{CO} \end{array} \text{C}_6\text{H}_3 \cdot \text{NHMe}$, by heating potassium 1:5-anthraquinonedisulphonate with aqueous methylamine at 150°; the potassium salt crystallises from water in violet-brown needles.

1-Methylaminoanthraquinone-8-sulphonic acid, 1-aminoanthraquinone-5-sulphonic acid, and 1-aminoanthraquinone-8-sulphonic acid are similarly obtained, and their tinctorial properties are described in the patent.

s-1:5-*p*-Ditolylaminoanthraquinone may be prepared from 1:5-anthraquinonedisulphonic acid and *p*-toluidine. G. T. M.

Preparation of Trichloroanthraflavic Acid. R. WEDEKIND (D.R.-P. 181659).—The chlorine additive product of anthraflavic acid (“hexachloroanthraflavic acid”), when heated with phenol or some other solvent of high boiling point, such as xylene or nitrobenzene, loses hydrogen chloride and furnishes a *trichloroanthraflavic acid*, which separates in lustrous, yellow needles. This compound, which is employed in the preparation of dyes of the anthracene series, is insoluble in water, and yields a sparingly soluble sodium salt.

G. T. M.

Preparation of Dianthraquinonyl and its Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 184495).—The following is an alternative method of preparing dianthraquinonyl and its derivatives. 1-Amino-2-methylanthraquinone is diazotised in sulphuric acid and the dry diazo-sulphate suspended in acetic anhydride

and treated with copper powder, when 2:2'-dimethyl-1:1'-dianthraquinonyl is obtained (compare this vol., i, 539). G. T. M.

Preparation of a Chlorine Additive Compound of Anthraflavic Acid. R. WEDEKIND (D.R.-P. 179916).—Anthraflavic acid does not absorb chlorine in acidified water at 100°, but, when the boiling temperature is raised by the addition of sulphuric acid, substitution occurs with the formation of the dichloro-derivatives; when, however, this acid is suspended in concentrated calcium or magnesium chloride solution and treated at 110° with a mixture of sodium chlorate and hydrochloric acid, a yellow substance having the composition of a hexachlorodihydroxyanthraquinone is obtained. This compound is moderately stable towards acids, but is decomposed by aniline and dilute alkalis. When heated in phenol or cresol, this additive product loses hydrogen chloride and a well-defined trichloroanthraflavic acid is produced. G. T. M.

Benzanthrone Derivatives of the Naphthanthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 181176). Compare Abstr., 1906, i, 889, and this vol., i, 324).—Naphthanthraquinone resembles anthraquinone in reacting with glycerol to yield benzanthrone derivatives, which on heating with alkali hydroxides furnish blue colouring matters suitable for vat dyeing.

Benzonaphthanthrone, C₂₁H₁₂O, m. p. 186—188°, was prepared in the following ways: (1) by heating naphthanthraquinone with glycerol, aniline sulphate, and concentrated sulphuric acid at 150°, or by warming its dihydro-derivative with these reagents at 110°; (2) by heating the quinone or naphthanthranol with glycerol and zinc chloride at 200 to 210°. G. T. M.

Linalool is a Tertiary Alcohol. ROURE-BERTRAND FILS (*Chem. Zentr.*, 1907, ii, 464; from *Wiss. u. ind. Ber. Roure-Bertrand Fils*, [ii], 5, 3—5).—Experiments on the formation of esters of geraniol and linalool have shown that linalool is a tertiary alcohol. The alcohols were mixed with acetic acid (6 mols.) and kept at a constant temperature. The quantities which had entered into combination after different periods are given below:

	hours.		days.					months.	
	6.	24.	3.	10.	15.	24.	45.	5.	12.
Geraniol	2·7	5·5	12·6	29·2	35·7	45·0	62·3	85·6	90·0%
Linalool	—	0·4	—	0·6	—	1·1	—	3·9	5·3%

E. W. W.

Terpenes and Ethereal Oils. LXXXVI. Compounds of the Terpinene Series. OTTO WALLACH and FRIEDRICH BOEDECKER [and, in part, FRITZ MEISTER] (*Annalen*, 1907, 356, 197—226. Compare this vol., i, 64).—This paper contains a further account of the compounds of the terpinene series and their relationships to other terpenes. Part of the details have been already published (this vol., i, 227, 228, 229); the following are new.

In addition to the methods of preparation described previously, terpinene dihydrochloride, m. p. 52°, has now been formed from terpineneterpin, from the saturated alcohol, $C_{10}H_{17}\cdot OH$, from sabinene hydrate, and from the monohydrochloride.

Terpinene monohydrochloride, $C_{10}H_{17}Cl$, b. p. 85—95°/11 mm., prepared by the action of hydrogen chloride on the terpinene in carbon disulphide solution, forms the dihydrochloride when treated with hydrogen chloride in glacial acetic acid. The monohydrochloride obtained from sabinene (this vol., i, 229) does not solidify in a mixture of solid carbon dioxide and ether, and is more stable towards potassium hydroxide than is limonene monohydrochloride.

The terpin, *terpineneterpin*, $C_{10}H_{18}(OH)_2$ (this vol., i, 229), is prepared by shaking thujene or terpineol with sulphuric acid. Terpineol is formed as an intermediate product in the preparation of the terpin from sabinene. The terpin crystallises and sublimes in white leaflets, m. p. 137—138°, b. p. 250° (slight decomp.), is markedly volatile with steam, is more readily soluble than *cis*-terpin hydrate, forms mixed crystals, m. p. about 108°, with anhydrous *cis*-terpin, and with hydrogen chloride in glacial acetic acid forms terpinene dihydrochloride.

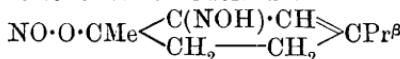
When distilled with a saturated solution of oxalic acid, terpineneterpin yields terpineol and *terpinene-cineol*, which is obtained as a colourless oil, b. p. 172—173°, D 0.897, n_D^{20} 1.4485, has an odour resembling cineol, does not solidify in a mixture of solid carbon dioxide and ether, and is volatile with steam. On treatment with hydrogen bromide in light petroleum solution, it forms terpinene dihydrobromide, gives a light red, crystalline precipitate with bromine in light petroleum, and on oxidation yields products different from those obtained from cineol.

The terpineol obtained from cardamom and majorana oils must have the constitution $CMe\begin{array}{c} CH_2\cdot CH_2 \\ \swarrow \quad \searrow \\ O \\ \backslash \quad / \\ CH_2\cdot CH_2 \end{array} CPr^8\cdot OH$, since the trihydroxyterpane, m. p. 114—116°, obtained on oxidation with potassium permanganate, yields carvenone when heated with hydrochloric acid. The trihydroxyterpane, $OH\cdot CMe\begin{array}{c} CH(OH)\cdot CH_2 \\ \swarrow \quad \searrow \\ CH_2 \quad CH_2 \\ \backslash \quad / \\ CH_2 \end{array} CPr^8\cdot OH$, on oxidation with chromic acid, yields a small amount of a ketone which forms a semicarbazone, $C_{10}H_{19}ON_3$, m. p. 146°, and may be thujaketone. The trihydroxyterpane is oxidised by potassium permanganate in alkaline solution, forming two isomeric acids. The acid, $C_{10}H_{18}O_6$, m. p. 205—206°, which is the main product, loses water when heated or when boiled with acids, forming a lactone, $C_{10}H_{14}O_4$, m. p. 63—64°. This is volatile with steam, and on treatment with alkalis again forms the acid, m. p. 205—206°. The isomeric acid, m. p. 188—189°, yields a lactone, $C_{10}H_{14}O_4$, m. p. 72—73°, from which it is regenerated by the action of alkalis.

The terpineol from sabinene has $[\alpha]_D + 2504'$, and on oxidation yields a trihydroxyterpane, $[\alpha]_D + 21021'$. Optically inactive terpineol, which on oxidation yields the acid, m. p. 188—189°, is obtained from terpinene dihydrochloride and from the fractions of commercial terpineol boiling at low temperatures. The terpineol from terpinene-

terpin is oxidised to the acid, m. p. 188—189°, and probably contains small amounts of Δ^4 -menthene-1-ol together with the Δ^1 -menthene-4-ol.

The reduction of terpinene nitrosite in alkaline solution leads to the formation of a mixture of carvenone and tetrahydrocarvenone (compare Wallach and Laufer, Abstr., 1901, i, 89; Amenomiya, Abstr., 1905, i, 603). The constitutional formula



is ascribed to the nitrosite, which, however, in view of its chemical behaviour and in spite of the results of molecular weight determinations, is considered to be bimolecular.

The paper concludes with a discussion of the constitution of terpinene.

G. Y.

Sesquiterpenes. I. Caryophyllene. ERNST DEUSSEN and ARNOLD LEWINSOHN (*Annalen*, 1907, 356, 1—23).—A study of caryophyllene was undertaken in continuation of the investigation of West Indian sandalwood oil (Abstr., 1900, ii, 579; 1902, i, 552).

Caryophyllene nitrosochloride (m. p. 161—163°: Wallach and Walker, Abstr., 1893, i, 101; 158—160°: Schreiner and Kremers, Abstr., 1900, i, 106) is found to be a mixture; on extraction with alcohol containing 10% of ethyl acetate, α -caryophyllene nitrosochloride remains unchanged, and on recrystallisation from chloroform separates in glistening crystals, m. p. 177° if slowly or 179° if quickly heated; it is optically inactive, is stable, remaining unchanged when boiled with concentrated hydrochloric or nitric acids, and forms solutions in chloroform and benzene which are colourless at the ordinary temperature and become blue when heated. The alcohol-ethyl acetate extract contains β -caryophyllene nitrosochloride, which crystallises in needles, m. p. 159°, $[\alpha]_D - 98\cdot07^\circ$, is moderately soluble in hot light petroleum, and may be bimolecular, and a substance, $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$, which crystallises in prismatic needles, m. p. 162·5—163·5°, $[\alpha]_D + 217\cdot2^\circ$, is sparingly soluble in light petroleum, and decolorises bromine, but does not react with benzylamine. α -Caryophyllene nitrosochloride reacts with benzylamine forming Schreiner and Kremers' β -base, m. p. 126—128° (*loc. cit.*), which therefore is α -caryophyllenenitrolbenzylamine. The hydrochloride, $\text{NO}\cdot\text{C}_{15}\text{H}_{24}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}\cdot\text{HCl}$, crystallises in glistening leaflets, m. p. 195°, and is optically inactive. β -Caryophyllenenitrolbenzylamine, Schreiner and Kremers' α -base, m. p. 167°, is formed by the action of benzylamine on the β -nitrosochloride; it crystallises from chloroform and alcohol in needles, m. p. 172—173°, $[\alpha]_D^{16} + 217\cdot87^\circ$, and yields a laevorotatory hydrochloride.

α -Nitrosocaryophyllene, $\text{C}_{15}\text{H}_{23}\text{ON}$, formed by reducing the α -nitrosochloride with sodium and methyl alcohol, crystallises in rhomboids, m. p. 116°, is optically inactive, and yields a crystalline additive compound with bromine.

β -Nitrosocaryophyllene, formed by reduction of the nitrosochlorides, crystallises in needles, m. p. 120—121°, $[\alpha]_D + 61\cdot77^\circ$.

The blue caryophyllene nitrosite, m. p. 115°, $[\alpha]_D + 102\cdot95^\circ$, when treated successively with potassium hydroxide and acetic acid in

alcoholic solution, is converted into a unimolecular *isomeride*, which crystallises in colourless needles, m. p. 139—139·5°, $[\alpha]_D^{18} + 120\cdot0^\circ$, forms greenish-blue solutions in glacial acetic acid or alcohol, decolorises bromine in glacial acetic acid solution, and if heated with glacial acetic acid forms a crystalline *substance* resembling nitrocaryophyllene.

If the solution of the blue nitrosite in alcoholic potassium hydroxide is acidified with acetic acid only after four hours, it yields *d-nitrosocaryophyllene*, $C_{15}H_{23}ON$, crystallising in needles, m. p. 162—163°, $[\alpha]_D^{18} + 209\cdot2^\circ$; this substance is unimolecular, and decolorises bromine in glacial acetic acid solution or more slowly in carbon tetrachloride solution.

When the blue nitrosite is boiled with light petroleum in a current of carbon dioxide, the solution becomes green and finally yellow, evolves nitric oxide, and deposits a voluminous precipitate containing (a) a *substance*, $C_{15}H_{23}O_6N_4$ or $C_{15}H_{23}O_7N_3$, which crystallises from acetone on addition of light petroleum in silky needles, m. p. 159° (decomp.), and dissolves in aqueous potassium hydroxide, but is optically inactive and does not decolorise bromine, and (b) a *nitrosite*, $C_{15}H_{22}O_4N_2$, which crystallises in flat needles, m. p. 130·5°, decolorises bromine in glacial acetic acid solution, and is optically inactive.

The action of boiling alcohol on the blue nitrosite leads to the formation of a *substance* crystallising in needles, m. p. 128°.

A new *sesquiterpene*, $C_{15}H_{24}$, is obtained from the light petroleum mother-liquor from the preparation of blue caryophyllene nitrosite as an oil, b. p. 123—124°/14·5 mm., $[\alpha]_D - 25\cdot03^\circ$, $D^{20} 0\cdot8990$, $n_D^{20} 1\cdot49617$, and with nitrosonyl chloride forms a *nitrosochloride*, m. p. 122°, together with traces of α -caryophyllene nitrosochloride, derived probably from a small admixture of caryophyllene, and an oil, $[\alpha]_D - 17^\circ$, which distils in a current of steam. Whether the new sesquiterpene is formed during the preparation of the nitrosite or is present originally in the caryophyllene remains undecided.

The resemblance of the reactions of α -caryophyllene nitrosochloride to those of caryophyllene alcohol suggests that these substances are closely related in their constitutions.

G. Y.

Components of Ethereal Oils. Sesquiterpene Cedrene. FRIEDRICH W. SEMMLER and ALFRED HOFFMANN (*Ber.*, 1907, 40, 3521—3528. Compare Rousset, *Abstr.*, 1898, i, 595).—Cedrene, b. p. 124—126°/12 mm., $D^{15} 0\cdot9354$, $\alpha_D - 55^\circ$ (100 mm. tube), $n_1 1\cdot50233$, yields, on oxidation with potassium permanganate, *cedreneglycol*, $C_{15}H_{26}O_2$, which separates from acetone in centimetre-long columnar prisms, m. p. 160°, b. p. 186—187°/11 mm., $D^{15} 1\cdot053$; it is very resistant towards permanganate and only reacts very slowly with acetic anhydride. Another product of the oxidation is *cedrene-keto-aldehyde* or *diketone*, $C_{15}H_{24}O_2$, b. p. 165°/10 mm., $D^{15} 1\cdot055$, the *disemicarbazone* of which has m. p. 234°. The chief product is *cedrene-ketonic acid*, $C_{15}H_{24}O_3$, b. p. 215—222°/11 mm.; the *semicarbazone* has m. p. 245°; the *oxime*, m. p. about 60°, whilst the *methyl ester*, b. p. 160—165°/8 mm., $D^{15} 1\cdot054$, $n_D 1\cdot484$, forms a *semicarbazone*, m. p. 180°. *Methyl cedrenedicarboxylate* has b. p. 165—173°, $n_D 1\cdot47936$, $D^{15} 1\cdot081$.

Cedrone, $C_{15}H_{22}O$, formed by oxidation of cedrene with chromic acid, is a slightly yellow oil with an intense odour of cedarwood, b. p. $147-150^\circ$, $D^{12.5} 1.011$, $n_D 1.51202$, $a_D -91^\circ 30'$ (100 mm. tube), and forms a semicarbazone, m. p. $242-243^\circ$. The reduction product, *dihydroisocedrol*, $C_{15}H_{26}O$, shows b. p. $148-151^\circ/9.5$ mm., $D^{18} 1.007$, $n_D 1.51202$, $[a]_D -20^\circ 30'$. In addition to cedrone, another ketone is formed, b. p. $148-152^\circ/10$ mm., $D^{16} 1.005$, $a_D -40^\circ$. Crude cedrone forms an *oxime*, b. p. $160-180^\circ/11$ mm., and this gives rise to an *amine*, b. p. $145-150^\circ$, $D^{15} 0.979$, $n_D 1.5097$, $a_D -20^\circ 36'$.

Dihydrocedrene, $C_{15}H_{23}$, has b. p. $116-122^\circ/10$ mm., $D^{15} 0.9052$, $n_D 1.48721$.
E. F. A.

First Runnings from Finnish Turpentine Oil. OSSIAN ASCHAN (*Zeitsch. angew. Chem.*, 1907, 20, 1811—1816. Compare Atterberg, *Abstr.*, 1880, 663; Harries, *Abstr.*, 1898, i, 232; Aschan, *Abstr.*, 1906, i, 442, 686).—The yellowish-brown colour and characteristic suffocating odour of the turpentine oil obtained by the distillation of the roots of Finnish pines and firs, *Pinus abies* and *P. sylvestris*, is chiefly due to the presence of diacetyl and its homologues, and the quinones derived from these compounds by condensation. In addition to these compounds, the fraction, b. p. $20-160^\circ$, obtained from Finnish turpentine oil, was found on investigation to contain simple aldehydes, furan, sylvan, benzene, toluene, *m*-xylene, methyl esters of fatty acids, furfuraldehyde, unsaturated compounds (probably hydrocarbons), and probably 2:5-dimethylfuran. The fraction, b. p. $100-105^\circ$, obtained from the fraction, b. p. $20-160^\circ$, gave a red coloration with a pine shaving moistened with hydrochloric acid similar to that obtained with pyrrole. However, the fraction contains no nitrogen, so that this reaction cannot be employed as a test for pyrrole in distillation products obtained from wood. W. H. G.

American Colophony. PAUL LEVY (*Ber.*, 1907, 40, 3658—3660).—The statement made that the abietin obtained by the distillation of abietic chloride (*Abstr.*, 1906, i, 870) is identical with Kraemer and Spilker's substance from colophony (*Abstr.*, 1900, i, 150) has been confirmed by a careful fractionation of the crude oil from the dry distillation of American colophony.

Abietic acid is indifferent to molten alkali and to the usual reducing agents, although it forms with hydrogen bromide an additive product pointing to this acid containing two ethylenic linkings.

W. R.

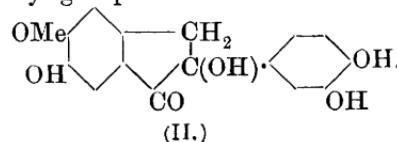
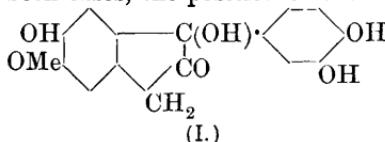
Chemical Examination of Eriodictyon Glutinosum. II. GUSTAV MOSSLER (*Monatsh.*, 1907, 28, 1029—1039. Compare Power and Tutin, *Abstr.*, 1906, ii, 885; *Trans.*, 1907, 91, 887).—Eriodictyonone has $[a]_D^{20} -28.21^\circ$. It is now found that eriodictyonone tetra-acetate does not form an additive compound with bromine, and, further, that the supposed tetrabromide is a *dibromo*-derivative, $C_{16}H_{12}O_6Br_2$; hence eriodictyonone cannot contain an ethylene linking. The presence of a carbonyl group is confirmed by the formation in alcoholic-acetic acid solution of a *phenylhydrazone*, $C_{16}H_{14}O_5:N_2HPh$, which separates in yellow crystals, m. p. $184-186^\circ$. Neither eriodictyonone nor its tetra-acetate is oxidised by potassium per-

manganate in neutral solution; in presence of an alkali, there is obtained the resin formed by the action of alkalis alone.

When heated with fuming hydrochloric acid in a sealed tube at 120°, eriodictyonone yields catechol and an oil, which gives a green coloration with alcoholic ferric chloride, and is probably an impure homocatechol, $C_6H_8Me(OH)_2$.

The action of diazomethane on eriodictyonone leads to the formation of a methyl ether, $C_{15}H_{10}O_4(OMe)_2$, which crystallises in prisms, m. p. 160°, reduces ammoniacal silver solution, forms a red resin when heated with aqueous alkalis, and gives a red coloration with alcoholic ferric chloride. On further treatment with an excess of diazomethane, this ether yields the tetramethyl ether, $C_{15}H_8O_2(OMe)_4$, which crystallises in yellow needles, m. p. 162°, is insoluble in aqueous alkalis, and does not give a coloration with ferric chloride. When fused with potassium hydroxide, the tetramethyl ether forms protocatechuic acid.

In the light of these results, it is considered that the constitution of eriodictyonone must be represented by the formula I or II. In both cases, the position of the methoxyl group remains undecided.



(see also Power and Tutin, Proc., 23, 243).

G. Y.

Spectrophotometry of the Chlorophyllins and the Energies of Chlorophyll. M. TSVETT (*Ber. deut. bot. Ges.*, 1907, 25, 388—397. Compare this vol., i, 787).—Results obtained with an alcoholic solution of chlorophyllin show that the absorption is greater in the blue portion of the spectrum than in the red. The band λ 460—475 can be distinguished in solutions so diluted that the band in the red portion is no longer visible.

N. H. J. M.

Phylloxyanthin. M. TSVETT (*Biochem. Zeitsch.*, 1907, 6, 373—378).—A reply to Marchlewski's criticism (this vol., i, 867) of the conclusions drawn by the author (this vol., i, 787). The spectrum of phylloxyanthin is very similar to that of β -chlorophyllan; neither substance can be transformed into phylloxyanin.

G. B.

New Method of Preparing Azophenin. VLADIMIR SCHAPOSCHNIKOFF (*Zeitsch. Farb.-Ind.*, 1907, 6, 289—291).—Details are given for preparing quinonedichlorodi-imine by the action of a solution of bleaching powder on *p*-phenylenediamine or its hydrochloride; by the method used, a pure white product is readily obtained. It is best converted into azophenin by adding aniline to its solution in benzene; other substances are also formed, but azophenin is the principal product (2·8 grams of azophenin from 3·5 grams of quinonedichlorodi-imine), and can be easily separated in a pure state.

W. A. D.

Oxidation of Aromatic Amines by Means of Manganese Salt with Formation of Dyes. FRITZ CRONER (*Chem. Zeit.*, 1907, 31, 948—949).—If 10 c.c. of a 0·2% aqueous solution of atoxyl

[monosodium *p*-aminophenylarsonate] are treated with 10 drops of an 8% manganese chloride solution free from iron and three drops of 20% ammonia, and the resulting precipitate dissolved by addition of a moderate excess of sulphuric acid to the mixture, there is obtained an intense red solution. The red substance is not extracted by shaking with amyl alcohol. The coloration is not produced if the precipitate and reaction liquid are treated with acid separately. Colorations are obtained in the same manner with primary or secondary aromatic amines, but not with tertiary amines, nitroamines, or acylamines. These results confirm Ehrlich and Bertheim's formula for atoxyl (this vol., i, 812). Descriptions are given of the colorations obtained with numerous aromatic amino- and diamino-compounds; where the resulting substance is soluble in amyl alcohol, the colour of the extract is also given.

The amount of dye formed is proportional to the manganese salt and not to the alkali added. The colour reaction takes place in presence of mercuric chloride or arsenious acid, but is diminished in intensity by addition of small amounts of hydrogen cyanide or thiocyanate, and is suppressed completely when these are present in molecular proportion to the manganese salt. Similar colour reactions are obtained in this manner, but only in isolated cases with ferrous chloride; nickel, chromium, and copper salts do not give colorations. G. V.

G. V.

Methylfurfurantialdoxime. Correction. WILHELM MEIGEN (*Ber.*, 1907, **40**, 3567—3568. Compare this vol., i, 232).—The compound, m. p. 51—52°, previously regarded as a mixture of the *syn-* and *anti-* forms of the oxime, is now shown to be pure methylfurfurantialdoxime. E. F. A.

E. F. A.

Hydroperbromides of Negatively-Substituted 4-Pyrones.
FRANZ FEIST (*Ber.*, 1907, 40, 3647—3652. Compare *Abstr.*, 1905, i, 914; 1906, i, 974).—Contrary to Hantzsch and Denstorff's view that only oxides having relatively strong basic properties are capable of forming hydroperbromides, crystalline, more or less stable hydroperbromides have been prepared from 4-pyrones with feeble or no basic properties.

Hydroperbromides of bromo- and dibromo-2:6-dimethyl-4-pyrone were shown previously to exist in the crude product of the action of undiluted bromine on 2:6-dimethyl-4-pyrone; the composition of this crude product is found now to have undergone little change in two years. The pure hydroperbromides are prepared by the action of bromine and hydrogen bromide on bromo- and dibromo-2:6-dimethyl-4-pyrone.

3-Bromo-2:6-dimethyl-4-pyrone hydroperbromide,
 $(C_7H_7O_2Br)_2HBr, Br_2$,
 forms a yellow, crystalline powder, decomp. 150°.

3 : 5-Dibromo-2 : 6-dimethyl-4-pyrone hydroperbromide,
 $(C_7H_6O_2Br_2)_2HBr, Br_2$

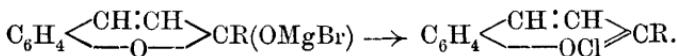
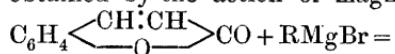
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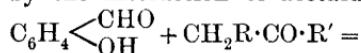
the ordinary temperature, and can be recrystallised repeatedly from chloroform containing traces of bromine, from which it separates in glistening crystals.

Ethyl chelidonate and ethyl dibromochelidonate form *hydroperbromides*, $C_{11}H_{12}O_6$, HBr, Br₇ and $C_{11}H_{10}OHBr_2$, HBr, Br₅, respectively, which crystallise in reddish-brown needles or prisms, but are less stable than the hydroperbromides of the brominated dimethylpyrones, decomposing when washed with ether or light petroleum or on exposure to air, evolving fumes of bromine and hydrogen bromide. G. Y.

Synthesis of Benzopyrylium Derivatives. HERMAN DECKER and THEODOR VON FELLENBURG (*Ber.*, 1907, 40, 3815—3818).—Benzopyrylium derivatives may be prepared by the method employed by Bünzly and Decker (*Abstr.*, 1904, i, 912) in the synthesis of xanthonium compounds; thus, 2-substituted benzopyrylium compounds are obtained by the action of magnesium alkyl bromides on coumarin:



They also result from the ring-condensation of the products obtained by the interaction of acetaldehyde or ketones and salicylaldehyde:

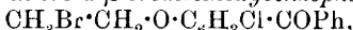


Hydrogen chloride passed into a mixture of resorcytaldehyde, and acetophenone precipitates 7-hydroxy-2-phenylbenzopyrylium chloride, OH·C₆H₃·C₆H₄·CH:CH·OCl·CPh, identical with the compound obtained by Bülow and Sicherer (*Abstr.*, 1902, i, 113) from benzoylacetaldehyde and resorcinol. The compounds obtained by Bülow (*Abstr.*, 1901, i, 400, 559; 1902, i, 113) from 1:3-diketones and dihydroxybenzenes are therefore hydroxybenzopyrylium salts. The formulae of these compounds must consequently contain 1 mol. of water less than is present in the formulae assigned to them by Bülow; this mol. of water is really present as water of crystallisation.

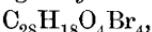
7-Hydroxy-2-phenylbenzopyrylium picrate loses its water of crystallisation at 100° without undergoing decomposition as stated by Bülow and Sicherer (*loc. cit.*). W. H. G.

Synthesis of Leuco-coumaranketones. STANISLAUS VON KOSTANECKI, VICTOR LAMPE, and CH. MARSCHALK (*Ber.*, 1907, 40, 3660—3669).—The synthesis of *p*-benzoylcoumarans was attempted in order to throw further light on the constitution of catechin (compare this vol., i, 73). Two methods were tried: (1) the conversion of *p*-hydroxybenzophenone into the corresponding coumaran derivative, (2) interaction of aromatic acid chlorides in the presence of aluminium chloride

on coumaran and its substitution derivatives. The first method did not yield the desired result. By the condensation of 3-chloro-4-hydroxybenzophenone and ethylene dibromide in the presence of sodium methoxide, *3-chloro-4-β-bromoethoxybenzophenone*,



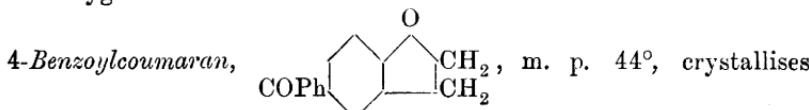
is formed as chief product. It crystallises in small, white plates, m. p. 79—80°. There is also formed the sparingly soluble *4:4"-ethylenedioxy-bis-3-chlorobenzophenone*, $\text{C}_2\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{COPh})_2$, crystallising in white needles, m. p. 224—226°. All attempts, however, to close the coumaran ring by the Wurtz reaction were unsuccessful, and the same remark applies to the bromo-derivatives. *3-Bromo-4-β-bromoethoxybenzophenone*, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}_2$, crystallises in white leaflets from dilute alcohol, m. p. 96—97°; the *4:4"-ethylenedioxy-bis-3 bromobenzophenone*, $\text{C}_{28}\text{H}_{20}\text{O}_4\text{Br}_2$, m. p. 229—230°. *3:5-Dibromo-4-β-bromoethoxybenzophenone*, $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Br}_3$, crystallises in white plates, m. p. 106—107°; the corresponding *ethylenedioxy-derivative*,



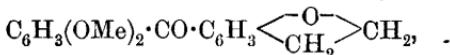
has m. p. 217—218°.

4-β-Bromoethoxybenzophenone, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{Br}$, which crystallises in prisms from alcohol, m. p. 72°, does not yield *p-benzoylcoumaran* on treatment with aluminium chloride; the product obtained is *p-benzoylphenol*. The corresponding *ethylenedioxy-compound*, $\text{C}_{28}\text{H}_{22}\text{O}_4$, has m. p. 195°.

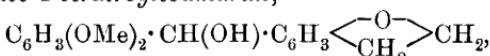
Coumaran itself reacts easily with aromatic acid chlorides in the presence of aluminium chloride and from analogy to the phenol ethers, the conclusion is drawn that substitution occurs in the para-position to the oxygen atom.



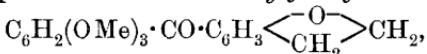
from light petroleum in the triclinic system [$a:b:c = 1.4568:1:1.8354$; $\alpha 101^\circ 32'$, $\beta 109^\circ 45'$, $\gamma 103^\circ 9'$]. By reduction of an alcoholic solution, the *leuco-p-benzoylcoumaran* was obtained as a viscous oil; it is conjectured to be the parent substance of catechin. *4-Veratroylcoumaran*,



crystallises in stout, white prisms, m. p. 136—137°, and gives on reduction *leuco-4-veratroylcoumaran*,



stout prisms, m. p. 97—98°. *2-Trimethylgalloylcoumaran*,



forms needles, m. p. 110—111°, and its *leuco-compound*, $\text{C}_{18}\text{H}_{20}\text{O}_3$, forms leaflets, m. p. 108—109°.

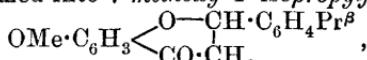
Chroman also combines with acid chlorides to form similar derivatives. *6-Benzoylchroman*, $\text{C}_{16}\text{H}_{14}\text{O}_2$, is an oil, b. p. 365°/710 mm., solidifying to a crystalline mass in a cold mixture. *6-Veratroyl-*

chroman, $\text{C}_6\text{H}_8(\text{OMe})_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{O} - \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, crystallises in white needles, m. p. $103-104^\circ$; its *leuco*-compound, $\text{C}_{18}\text{H}_{20}\text{O}_4$, forms prisms, m. p. $115-116^\circ$.

The following compounds are also described: *p-veratroyl-o-ethyl-anisole*, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Et} \cdot \text{OMe}$, which crystallises in white needles, m. p. $103-104^\circ$, and its *leuco*-derivative, $\text{C}_{18}\text{H}_{22}\text{O}_4$, white needles, m. p. $84-85^\circ$; *p-trimethylgalloyl-o-ethylanisole*, $\text{C}_{19}\text{H}_{22}\text{O}_5$, m. p. 105° , the *leuco*-compound has m. p. $86-88^\circ$.
W. R.

Further Synthesis in the Flavone Group. STANISLAUS VON KOSTANECKI (*Ber.*, 1907, 40, 3669-3677).—[With M. KOLKER.]—*6-Hydroxy-4'-isopropylflavone*, $\text{C}_{19}\text{H}_{20}\text{O}_3$, prepared by the interaction of quinacetophenone monomethyl ether, cumenol, and sodium hydroxide, crystallises from alcohol in colourless leaflets, m. p. 90° . *3-Bromo-6-methoxy-4'-isopropylflavanone*, $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{O} - \text{CH} \cdot \text{C}_6\text{H}_4\text{Pr}^\beta \\ || \\ \text{CO} \cdot \text{CHBr} \end{array}$, obtained by brominating the corresponding methoxyisopropylflavanone in carbon disulphide, forms white needles, m. p. $125-127^\circ$. Like all 3-bromoflavanones when treated with concentrated potassium hydroxide in alcoholic solution, hydrogen bromide is eliminated and *6-methoxy-4'-isopropylflavone*, $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{O} - \text{C}_6\text{H}_4\text{Pr}^\beta \\ || \\ \text{CO} \cdot \text{CH} \end{array}$, is obtained; it crystallises from dilute alcohol in white leaflets, m. p. 135° . On heating with hydriodic acid, *6-hydroxy-4'-isopropylflavone*, $\text{C}_{18}\text{H}_{16}\text{O}_3$, is formed, and from alcohol gives pale yellow needles, m. p. $182-183^\circ$.

[With A. TOBLER.]—*2'-Hydroxy-4'-methoxy-4-isopropylchalkone*, $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Pr}^\beta$, prepared by condensing cumenol with paeonol, crystallises from alcohol in yellow leaflets, m. p. 104° . When an alcoholic solution of this compound is heated with dilute hydrochloric acid for twenty-four hours, it is transformed into *7-methoxy-4'-isopropylflavanone*,



which crystallises in prisms, m. p. 75° . Amyl nitrite and hydrochloric acid convert the flavanone into the *isonitroso*-derivative, which, however, is unstable, and there results *7-methoxy-4'-isopropylflavanol*, $\text{OMe} \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{O} - \text{C}_6\text{H}_4\text{Pr}^\beta \\ || \\ \text{CO} \cdot \text{C} \cdot \text{OH} \end{array}$; it crystallises in pale yellow,

glistening leaflets, m. p. 201° . Like all flavanols, the yellow *sodium salt* is sparingly soluble; the *acetate*, $\text{C}_{21}\text{H}_{20}\text{O}_5$, has m. p. $163-164^\circ$. Reduction of the methoxyisopropylflavanol with hydriodic acid gives rise to *7-hydroxy-4'-isopropylflavanol*, $\text{C}_{18}\text{H}_{16}\text{O}_4$, which forms almost colourless leaflets, m. p. 243° ; the *diacetate*, $\text{C}_{22}\text{H}_{20}\text{O}_6$, crystallises in white needles, m. p. 124° .

[With H. RABINOWITSCH.]—*2'-Hydroxy-3':4'-dimethoxy-4-isopropyl-chalkone*, $\text{OH} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4\text{Pr}^\beta$, prepared from gallacetophenone dimethyl ether and cumenol in the presence of

50% sodium hydroxide, crystallises in yellow leaflets, m. p. 114°, and forms the starting point for the preparation of the 7:8-dihydroxyisopropylflavanol in a similar manner to that of the 7-hydroxy-compound.

7:8-Dimethoxy-4'-isopropylflavanone, $C_{20}H_{22}O_4$, forms small, white, granular crystals, m. p. 92°. The isonitroso-derivative, $C_{20}H_{21}O_5N$, is stable and has m. p. 173°.

7:8-Dimethoxy-4'-isopropylflavanol, $C_{20}H_{20}O_5$, forms pale yellow needles, m. p. 162°, and yields an intensely yellow sodium salt; the acetate, $C_{22}H_{22}O_6$, white needles, m. p. 152°.

7:8-Dihydroxy-4'-isopropylflavanol, $C_{18}H_{16}O_5$, crystallises in glistening leaflets, m. p. 265°; the diacetate, $C_{24}H_{22}O_8$, forms white needles, m. p. 152°.

[With G. STENZEL.]—*2-Cumenylideneaceto-1-naphthol*,
 $O\cdot H \cdot C_{13}H_6 \cdot CO \cdot CH \cdot CH \cdot C_6H_4Pr^\beta$,

prepared from cumenol and 2-aceto-1-naphthol under similar conditions to the benzylidene compound (compare Abstr., 1898, i, 369), crystallises from alcohol in orange-red prisms, m. p. 98°; the acetate, $C_{24}H_{22}O_3$, is pale yellow, m. p. 88—89°. *4'-isoPropyl-a-naphthalanone* (annexed formula) forms colourless prisms, m. p. 134—135°; the corresponding *flavanol*, $C_{22}H_{18}O_3$, crystallises in pale yellow needles, m. p. 211—212°; the acetate, $C_{24}H_{20}O_4$, is white, m. p. 157°.

W. R.

Preparation of Santaryl Esters. CHEMISCHE FABRIK VON HEYDEN (AKTIEN-GESELLSCHAFT) (D.R.-P. 182627). Compare Abstr., 1906, i, 972).—The santaryl esters of the higher fatty acids from valeric acid onwards do not possess the unpleasant odour and irritating properties of free santalol and its esters with acetic acid and its immediate homologues.

Santaryl stearate, a clear yellow oil, is prepared by mixing santalol and stearyl chloride and completing the reaction on the water-bath; it separates on the addition of alcohol.

Santaryl valerate and *santaryl oleate* resemble the preceding compound, and are prepared respectively in a similar manner from valeryl and oleyl chlorides and santalol.

G. T. M.

Preparation of Thionaphthen Derivatives. KALLE & Co. (D.R.-P. 184469).—*o-Aminophenylthioglycollic acid*, prepared from *o-thioaniline* and chloroacetic acid, when diazotised and treated with potassium cuprocyanide furnishes *o-cyanophenylthioglycollic acid*, yellowish needles, m. p. 142°. This substance on hydrolysis with aqueous sodium hydroxide yields *3-amino-(1)-thionaphthen-2-carboxylic acid*, which on further treatment with alkali gives rise to *3-hydroxy-*

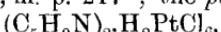
(1)-thionaphthen-2-carboxylic acid and 3-hydroxy-(1)-thionaphthen,
 $\text{C}_6\text{H}_4 < \begin{matrix} \text{S} \\ \diagdown \\ \text{CO} \end{matrix} > \text{CH}_2$

G. T. M.

Some New Alkaloids from Plants. AMÉ PICTET and G. COURT (*Ber.*, 1907, 40, 3771—3783; *Bull. Soc. chim.*, 1907, [iv], 1, 1001—1016).—The hypothesis put forward by Pictet (*Abstr.*, 1905, i, 541) receives support from the fact that alkaloids of simple structure are obtained by steam distillation from plants which have been treated with dilute sodium carbonate solution.

The concentrated aqueous extract of tobacco leaves (“raw nicotine”) yields, when distilled at 80—120°, an alkaline distillate from which pyrrolidine and 1-methylpyrroline were isolated and identified by means of their auri- and platini-chlorides. *1-Methylpyrroline picrolonate* crystallises in yellow prisms, m. p. 222° (decomp.).

Black pepper yields a distillate which does not contain piperidine as stated by Johnstone (*Abstr.*, 1889, 298), but a *base* which is probably a *C*-methylpyrroline, $\text{C}_5\text{H}_9\text{N}$; the *aurichloride*, $\text{C}_5\text{H}_9\text{N},\text{HAuCl}_4$, crystallises in yellow leaflets or flat needles, m. p. 182°; the *picrolonate* is a yellow, crystalline powder, m. p. 217°; the *platinichloride*,



m. p. 203°, forms microscopic, orange prisms.

The distillate from carrot leaves was found to contain pyrrolidine and a new base, *daucine*, $\text{C}_{11}\text{H}_{18}\text{N}_2$, a colourless, oily liquid with a nicotine-like odour, b. p. 240—250°, $[\alpha]_D + 7.74^\circ$ in ether. The *hydrochloride* forms long needles; no precipitate is produced on adding auric, platinic, or mercuric chloride to a solution of the hydrochloride. The hydrochloride when heated with zinc dust does not give a coloration with a pine shaving. The *base* obtained from carrot seeds is not identical with daucine, since it gives the pyrrole reaction and its *aurichloride*, m. p. 172—175° (decomp.), is insoluble.

The leaves of parsley yield a *base*, the crystalline *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust; no precipitate is obtained on adding auric or platinic chloride to a solution of the hydrochloride; the *picrolonate* forms yellow, microscopic needles, m. p. 210°.

Coca leaves yield a *base*, the *hydrochloride* of which gives the pyrrole reaction when heated with zinc dust. No precipitate is formed on adding picric acid, auric or platinic chloride to a solution of the hydrochloride; picrolonic acid produces a yellow, flocculent precipitate.

The authors consider that, since the above bases, with the exception of daucine, belong to the pyrrole group, they are probably derived from the plant albumin.

W. H. G.

Cinchona Alkaloids. VII. A New Oxidation Product of Cinchonine. PAUL RABE [with ERNST ACKERMANN and W. SCHNEIDER] (*Ber.*, 1907, 40, 3655—3658).—An intermediate product of the oxidation of cinchonine by chromic acid in either sulphuric acid or glacial acetic acid has been isolated in small quantity. It is a *base*,

$C_{19}H_{20}ON_2$, containing two atoms of hydrogen less than cinchonine, and crystallises in pale yellow needles, m. p. $126-127^\circ$, $[\alpha]_D^{20} + 68.8^\circ$ in 3.3% alcoholic solution. Although a strong base, it also dissolves in aqueous alkali hydroxides, from which it is precipitated by carbon dioxide. It is oxidised by chromic acid to cinchonic acid and meroquinine; potassium permanganate and bromine are, however, without action. The *hydrochloride*, $C_{19}H_{20}ON_2 \cdot HCl$, crystallises in white needles, m. p. $245-247^\circ$; the *methiodide*, has m. p. $232-233^\circ$, and the *dihydroiodide* is oily. The base combines with hydroxylamine.

W. R.

True and False (Pseudo-) Commercial Tannates of Quinine.

PIETRO BIGINELLI (*Gazzetta*, 1907, 37, ii, 205-226).—Tannic acid is capable of forming, with the ordinary salts of quinine, additive compounds which are usually yellow. Such compounds, containing variable proportions of tannic acid, are always obtained when solutions of tannic acid act on quinine salts. Many of the commercial quinine tannates are compounds of this nature, retaining some of the qualities of the quinine salts from which they have been prepared, and are hence termed pseudo- or false tannates. Quinine pseudo-tannates of constant composition can be prepared under constant conditions. The percentage of quinine in these compounds varies from 18 to 39. Tannic acid is not capable of displacing sulphuric or hydrochloric acid from its combination with quinine. True quinine tannates can only be prepared by mixing solutions of the base and acid in proportions varying according to the tannate required.

The following compounds have been prepared and analysed.

- (1) True quinine tannates : $C_{20}H_{24}O_2N_2 \cdot C_{14}H_{10}O_9 \cdot 3H_2O$;
 $C_{20}H_{24}O_2N_2 \cdot 2C_{14}H_{10}O_9 \cdot 6H_2O$; $C_{20}H_{24}O_2N_2 \cdot 3C_{14}H_{10}O_9 \cdot 10H_2O$.
- (2) False or pseudo-tannates : $4(C_{20}H_{24}O_2N_2 \cdot H_2SO_4) \cdot 5C_{14}H_{10}O_9 \cdot 13H_2O$;
 $2(C_{20}H_{24}O_2N_2 \cdot H_2SO_4) \cdot 5C_{14}H_{10}O_9 \cdot 20H_2O$;
 $2(C_{20}H_{24}O_2N_2 \cdot H_2SO_4) \cdot 7C_{14}H_{10}O_9 \cdot 25H_2O$;
 $2C_{20}H_{24}O_2N_2 \cdot H_2SO_4 \cdot 5C_{14}H_{10}O_9 \cdot 20H_2O$;
 $2(C_{20}H_{24}O_2N_2 \cdot 2HCl) \cdot 5C_{14}H_{10}O_9 \cdot 13H_2O$;
 $C_{20}H_{24}O_2N_2 \cdot 2HCl \cdot 5C_{14}H_{10}O_9 \cdot xH_2O$. T. H. P.

A Base Obtained in the Working Up of the Alkaloids Occurring with Cocaine. CARL LIEBERMANN (*Ber.*, 1907, 40, 3602-3603).—Anhydroecgonine ethyl ester (Einhorn, *Abstr.*, 1887, 741; Willstätter, *Abstr.*, 1901, i, 649) has been found in the ecgonine residues obtained in the separation of the subsidiary alkaloids of crude cocaine. It is formed probably by esterification of anhydroecgonine during the process of separation. The ethyl ester, b. p. $130-132^\circ/11$ mm., $[\alpha]_D - 51^\circ 33'$, is hydrolysed by boiling hydrochloric acid, D 1.125, forming anhydroecgonine. The *picrate*, $C_{11}H_{17}O_2N \cdot C_6H_3O_7N_3$, crystallises in yellow leaflets, m. p. 168° ; the *platinichloride*, m. p. 217° (211° : Einhorn, *loc. cit.*); the *aurichloride*, $C_{11}H_{17}O_2N \cdot HAuCl_4$, forms lemon-yellow granules, m. p. 124° .

G. Y.

isoConiine. ALBERT LADENBURG (*Ber.*, 1907, **40**, 3734—3736. Compare *Abstr.*, 1906, i, 692).—In consequence of Löffler's suggestion that the high rotatory power of synthetic coniine is due to the presence of allylpiperidine, the author has attempted to prepare the alkaloid by a method which excludes the formation of the unsaturated base. Methylpicolylalkine is reduced by hydriodic acid and amorphous phosphorus at 125°, the product treated with zinc dust and cold water, and the resulting propylpyridine reduced by sodium and alcohol to propylpiperidine, which is resolved by tartaric acid. The liberated base is pure *isoconiine*, and has $[\alpha]_D^{18.5} + 17.85^\circ$. C. S.

Morphine. XIV. allo- ψ -Codeine, a New Isomeride of Codeine. LUDWIG KNORR, HEINRICH HÖRLEIN, and CLEMENS GRIMME (*Ber.*, 1907, **40**, 3844—3851).—It has been lately pointed out by Knorr and Hörlein (this vol., i, 789) that, of the two compounds, ψ -codeine and *isocodeine*, quoted in the literature as being isomeric with codeine, ψ -codeine is a structural isomeride of codeine. Uncertainty exists, however, regarding Schryver and Lees' "isocodeine" (*Trans.*, 1901, **79**, 576), which is a mixture containing appreciable amounts of ψ -codeine, the presence of the latter doubtless accounting for the ψ -codeinone obtained by the oxidation of "isocodeine." In attempting to prepare pure *isocodeine*, the authors have obtained a new base, isomeric with codeine; crude *isocodeine* appears to contain *isocodeine*, ψ -codeine, and small amounts of this new base, which, for the present, is termed *allo- ψ -codeine*. When this new base is oxidised with chromic acid in sulphuric acid solution, it forms ψ -codeinone, and accordingly contains the alcoholic hydroxyl group in position 8.

The melting points and specific rotations of the isomeric morphines, codeines, and methylmorphimethines are quoted in tabular form, and also the melting points and specific rotations of the corresponding methiodides.

From the products of the hydrolysis of chloromorphide, γ -*isomorphine*, a new isomeride of morphine, has been isolated. This compound has m. p. 278°, $[\alpha]_D^{15^\circ} - 94^\circ$ (solvent not stated), and its methiodide has m. p. 295° and $[\alpha]_D^{15^\circ} - 51^\circ$; when methylated, it forms ψ -codeine [compare, however, Lees (*Trans.*, 1907, **91**, 1408), who has also lately studied the hydrolysis of chloromorphide and obtained, as one of the products, *neoisomorphine*, which seems to be identical with the above-mentioned γ -*isomorphine*].

allo- ψ -Codeine is possibly identical with Lees' β -*isocodeine*. It is prepared as follows from the mixture of bases obtained by the method of Schryver and Lees by the hydrolysis of bromocodeide. Potassium iodide is added to the solution of this crude *isocodeine* in dilute acetic acid, when a mixture of ψ -codeine and *allo- ψ -codeine* hydriodides gradually separates and may be separated by means of absolute alcohol. As an alternative method, crude *isocodeine* is acetylated by means of boiling acetic anhydride and the mixture of acetyl derivatives separated by means of absolute alcohol, in which acetyl *allo- ψ -codeine* is soluble with difficulty, and separates in tiny needles, m. p. 194—195°.

allo- ψ -Codeine, obtained either from the hydriodide or the acetyl derivative, is an oil with a bluish-violet fluorescence; it has not yet been obtained crystalline. In absolute alcohol, it has $[\alpha]_D^{15} - 228^\circ$ ($c = 4.5$). Its *hydriodide* separates from water in spear-shaped crystals decomposing at $280-285^\circ$; in aqueous solution, it has $[\alpha]_D^{15} - 153^\circ$ ($c = 1.967$). It differs from ψ -codeine hydriodide, which crystallises from water in glistening leaflets, contains $1H_2O$, has m. p. $260-265^\circ$ (decomp.), and $[\alpha]_D^{15} - 57^\circ$.

When *allo- ψ -codeine* is oxidised, it forms ψ -codeinone.

Acetylallo- ψ -codeine crystallises from absolute alcohol in needles, m. p. $194-195^\circ$, and differs from acetyl- ψ -codeine, which is an oil, and from acetylcodeine, which has m. p. 133.5° . Its *methiodide*, $C_{20}H_{22}O_4N, MeI, EtOH$, separates from absolute alcohol in leaflets, m. p. about 260° (decomp.).

allo- ψ -Codeine methiodide, $C_{18}H_{21}O_3N, MeI$, crystallises from methyl alcohol in rectangular leaflets, m. p. about 215° (decomp.). In aqueous solution, it has $[\alpha]_D^{15} - 142^\circ$ ($c = 1.728$). When boiled with sodium hydroxide, it forms a methine base which, for the present, is termed ζ -*methylmorphimethine*; it is apparently related to ϵ -methyl-morphimethine in the same manner as *allo- ψ -codeine* is related to ψ -codeine. The new base has $[\alpha]_D^{15} - 174^\circ$ ($c = 8.91$) in alcoholic solution (after treatment with alcoholic potassium hydroxide); when dried until constant in weight, it gave $[\alpha]_D^{15} - 178^\circ$ ($c = 10.955$) in alcoholic solution. Its *methiodide*, $C_{19}H_{23}O_3N, MeI$, is a colourless powder, m. p. about 180° (indefinite); in aqueous solution, it has $[\alpha]_D^{15} - 148^\circ$ ($c = 2.486$).

A. McK.

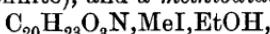
Morphine. XV. Deoxycodeine and Deoxydihydrocodeine.
LUDWIG KNORR and RUDOLF WAENTIG (*Ber.*, 1907, 40, 3860—3868).—In continuation of the work of Knorr and Hörlein (this vol., i, 235), it is found that deoxycodeine is best prepared by the reduction of bromocodeide or chlorocodeide with zinc dust and alcohol in the absence of acid. The reduction product, obtained by means of sodium and alcohol, is, however, not identical, as was formerly supposed, with the product obtained by the action of zinc and hydrochloric acid or of zinc dust and alcohol; it is laevorotatory, whereas the other products are dextrorotatory.

From the dextrorotatory deoxycodeine of Knorr and Hörlein, the laevorotatory base, deoxydihydrocodeine, is obtained by the action of sodium and alcohol.

Deoxycodeine melts at about 126° and crystallises from dilute methyl alcohol in glistening, hexagonal or rhombic leaflets. In alcoholic solution, it has $[\alpha]_D^{15} + 119-121^\circ$ ($c = 4.9215$).

Deoxycodeine hydrochloride, $C_{18}H_{21}O_2N, HCl, EtOH$, crystallises from absolute alcohol in glistening prisms, which soften at about 165° , and have m. p. about 270° (decomp.); in aqueous solution, it has $[\alpha]_D^{15} + 84-87^\circ$. The *hydriodide*, $C_{18}H_{21}O_2N, HI$, separates from water in needles, m. p. about 265° (decomp.). The *benzoate* crystallises from water in tiny, prismatic needles, m. p. about 188° ; in absolute alcohol, it has $[\alpha]_D^{15} + 106^\circ$ ($c = 5.53$). The *acetyl* derivative is an oil, and forms

an *hydriodide*, $C_{20}H_{23}O_3N\cdot HI$, which separates from water in silky needles, m. p. 230° (indefinite), and a *methiodide*,



which crystallises from absolute alcohol in yellow needles, m. p. about 270° .

Deoxycodeine forms a glassy methiodide, from the aqueous solution of which a brown oil separates on boiling with sodium hydroxide; when this oil is crystallised from absolute alcohol, it forms yellow prisms, m. p. $162-164^\circ$, and is the methine base of deoxycodeine. It is readily oxidised even at the ordinary temperature by the air; its *nitrate*, $C_{19}H_{23}O_2N\cdot HNO_3$, is, however, more stable and separates from acetic acid in silky needles, m. p. 202° .

Methyldeoxycodeine methiodide, $C_{19}H_{23}O_2N\cdot MeI$, obtained by the methylation of deoxycodeine in alkaline solution with methyl sulphate and interaction of the product with potassium iodide, crystallises in glistening leaflets, m. p. $251-252^\circ$, with preliminary softening. It has $[\alpha]_D^{15} + 108^\circ$ ($c = 2.290$) in alcoholic solution.

When the aqueous solution of methyldeoxycodeine methiodide is boiled with sodium hydroxide, an oil separates, which is very unstable; it decomposes in hydrochloric acid solution giving dimethylmorphol.

Deoxydihydrocodeine, $C_{18}H_{23}O_2N\cdot \frac{1}{2}H_2O$, crystallises from dilute methyl alcohol in glistening leaflets, m. p. about 132° ; the anhydrous compound has $[\alpha]_D^{15} - 24^\circ$ ($c = 5.171$) in absolute alcoholic solution. Its *hydrochloride*, $C_{18}H_{23}O_2N\cdot HCl\cdot EtOH$, has m. p. about 155° (decomp.), and $[\alpha]_D^{15} - 17^\circ$ ($c = 5.289$) in aqueous solution. The *benzoate* separates from ethyl acetate in tetrahedra, m. p. about 180° , and has $[\alpha]_D^{15} - 9^\circ$ ($c = 5.145$).

Methyldeoxydihydrocodeine methiodide, $C_{19}H_{25}O_2N\cdot MeI$, obtained by methylating deoxydihydrocodeine with methyl sulphate and then causing the product to react with potassium iodide, separates from water in leaflets and from alcohol in needles, m. p. $248-249^\circ$ (indefinite), and has $[\alpha]_D^{15} - 12^\circ$ ($c = 2.773$) in 99% alcoholic solution.

A. McK.

Preparation of Narceine and Homonarceine Derivatives. KNOLL & Co. (D.R.-P. 183589. Compare this vol., i, 236).—Narceine and homonarceine were formerly alkylated by treatment with alkyl sulphates, and it is now found that the same derivatives are obtained by the action of alkyl iodides, methyl phosphate, and methyl nitrate.

Ethylnarceine hydrochloride, m. p. 231° , may be obtained from the product of the interaction of ethyl bromide on the potassium derivative of narceine.

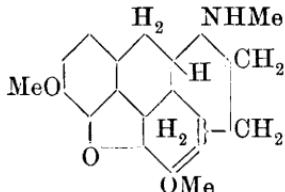
Methylnarceine hydrochloride, m. p. 243° , is produced by treating the potassium derivative of narceine with methyl phosphate and combining the resulting base with hydrochloric acid.

G. T. M.

The Action of Ozone on Thebaine. ROBERT PSCHORR and HANS EINBECK (Ber., 1907, 40, 3652-3654).—Morphine bases are converted into phenanthrene derivatives by treatment with ozone,

the side-ring containing nitrogen undergoing rupture. Thebaine, however, behaves differently, the nitrogen ring remains intact, a 60% yield of *α*-thebaizone, $C_{19}H_{21}O_5N$, leaflets, m. p. 125—126° (corr.), is obtained containing two atoms of oxygen more than thebaine. This new compound contains two methoxyl groups like thebaine, and the presence of a carbonyl group is shown by the formation of a *mono-semicarbazone*, $C_{20}H_{24}O_5N_4$, which crystallises in flat rods, m. p. 202° (corr.).

On dissolution of the thebaizone in dilute sodium hydroxide solution, hydrolysis of one methoxyl group occurs, and the conclusion is drawn that one of the methoxy-groups exists as the ester. The fifth oxygen atom is indifferent. These results, taken in conjunction with those already known about thebaine, lead to the constitution annexed,



the grouping $\cdot C(OMe)\cdot C\cdot$ being converted into that represented by $CO_2Me\cdot C\cdot O$.

W. R.

A New Base from the Solanaceæ. RICHARD WILLSTÄTTER and WOLFGANG HEUBNER (*Ber.*, 1907, 40, 3869—3875)—The new *alkaloid*, $C_8H_{20}N_2$, obtained from *Hyoscyamus muticus* in addition to hyoscyamine and other products, is a colourless liquid, b. p. 169° (corr.), and with D^{15} 0.7941; it is miscible with water in all proportions, has a strongly alkaline reaction, and is easily volatile with steam. It exhibits the behaviour of a saturated, tertiary base. It is quite stable towards permanganate in cold sulphuric acid solution, and does not react with benzenesulphonic chloride and alkali. In moderate doses, it has no poisonous action. The *hydrochloride*, $C_8H_{20}N_2 \cdot 2HCl$, crystallises in triangular prisms, m. p. 273° (decomp.), is deliquescent, and very readily soluble in water. Its *platinichloride*,

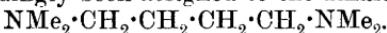


has m. p. 234° (decomp.); its *aurichloride* decomposes at 206—207°.

The compound, $C_4H_8(NMe_3)_2$, forms hygroscopic leaflets or tiny needles, m. p. 305—308° (decomp.). By the distillation of the ammonium base, obtained from the iodide by means of silver oxide, an aqueous distillate was obtained and a gas, which was identified as butadiene by means of the sparingly soluble *α*-bromide, m. p. 117°, and the more easily soluble bromide, m. p. 39°. The aqueous distillate contained, in addition to trimethylamine, tetramethyldiaminobutane, which was identified by means of its aurichloride.

The preparation of 1:4-diaminobutane from succinaldoxime is described, the method used being a modification of the method of Ciamician and Zanetti. The methylation of 1:4-diaminobutane is described, hexamethyltetramethylenediammonium chloride being obtained. When the latter compound is distilled, the main product is the monoamine, 1-methylpyrrolidine. 1-Methylpyrrolidine methiodide, $C_6H_{14}NI$, crystallises in prisms, which decompose above 300°; the *aurichloride*, $C_6H_{14}NCl_4Au$, crystallises in hexagonal prisms with pyramidal ends, m. p. 286° (decomp.).

The product of the methylation of tetramethylenediamine, in the form of its chloride, aurichloride, platinichloride, and picrate, was compared with the quaternary derivatives of the solanaceous base investigated, the agreement being complete. The following constitution has accordingly been assigned to the alkaloid :

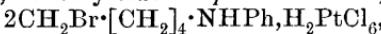


Hexamethyltetramethylenediammonium chloride, $\text{C}_4\text{H}_8(\text{NMe}_3)_2\text{Cl}_2$, crystallises from alcohol in prisms; its *picrate* has m. p. 285° (decomp.); its *platinichloride* has m. p. 279° (decomp.); its *aurichloride* decomposes at $304-309^\circ$.

A. McK.

Rupture of Cyclic Bases by Cyanogen Bromide. JULIUS VON BRAUN (*Ber.*, 1907, 40, 3914—3933).—The action of cyanogen bromide on cyclic bases either breaks the ring (*Abstr.*, 1900, i, 430) or replaces the alkyl or aryl group attached to the nitrogen atom by the cyanogen group (*Abstr.*, 1902, i, 365). A third alternative is represented by the scheme $\text{X}\triangleleft\text{N}\cdot\text{R} + \text{Br}\cdot\text{CN} = \text{Br}\cdot\text{X}\cdot\text{NR}\cdot\text{CN}$. The improved methods for the preparation of $\alpha\delta$ -dibromobutane and $\alpha\epsilon$ -dibromopentane (*Abstr.*, 1904, i, 841) have enabled the author to prepare numerous derivatives of pyrrolidine and piperidine, by means of which he has shown that the rupture of a cyclic base is more easily accomplished by cyanogen bromide than by any other method, a brominated cyanamide being formed in accordance with the preceding scheme.

The reaction between 1-phenylpiperidine and cyanogen bromide leads, after several hours, to the formation of *phenyl- ω -bromoamylcyanamide*, $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{NPh}\cdot\text{CN}$, and the quaternary *bromide*, $\text{C}_5\text{NH}_{10}\text{PhBr}\cdot[\text{CH}_2]_5\cdot\text{NPh}\cdot\text{CN}$. The latter is a brown oil which is identified by conversion into the *platinichloride*, $(\text{C}_{23}\text{H}_{30}\text{N}_3)_2\text{PtCl}_6$, m. p. $121-122^\circ$. The former is an oil which is soluble in concentrated acids, and by prolonged boiling with 48% hydrobromic acid is converted into the oily *ω -bromoamylaniline hydrobromide*, from an aqueous solution of which the *picrate* is obtained as a yellowish-green powder which sinters at 137° and has m. p. 141° . The *base* is a faintly-coloured, feebly-smelling oil, which yields the *platinichloride*,



m. p. $117-118^\circ$, in reddish-yellow crystals, and by warming changes quantitatively to *1-phenylpiperidine hydrobromide*, m. p. 235° . *1-Phenylpiperidine picrate* has m. p. 148° .

Piperidine in excess and phenyl- ω -bromoamylcyanamide react to form *ω -piperidinoamylphenylcyanamide*, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{NPh}\cdot\text{CN}$, b. p. $230-232^\circ/9$ mm., of which the *picrate*, m. p. 112° , forms yellow leaflets, and the *methiodide*, m. p. 101° , white leaflets.

Phenylmethylpiperidinium iodide has m. p. 146° ; distillation of the hydroxide does not cause a rupture of the ring, but regenerates 1-phenylpiperidine.

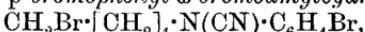
1-*p*-Tolylpiperidine, prepared from *p*-toluidine and $\alpha\epsilon$ -dibromopentane, has b. p. $268-269^\circ$ (compare Lellmann and Just, *Abstr.*, 1891, 1244; Scholtz and Wassermann, this vol., i, 339), and behaves with cyanogen bromide in a similar manner to 1-phenylpiperidine. The *bromide*, $\text{C}_7\text{H}_7\cdot\text{C}_5\text{NH}_{10}\text{Br}\cdot[\text{CH}_2]_5\cdot\text{N}(\text{C}_7\text{N}_7)\cdot\text{CN}$, m. p. $124-125^\circ$,

forms hygroscopic, white leaflets. *p-Tolyl- ω -bromoamylcyanamide*, $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{N}(\text{C}_7\text{H}_7)\cdot\text{CN}$, is an oil which reacts with an excess of *p*-toluidine to form *ω -p-toluidinoamyl-p-tolylcyanamide*,



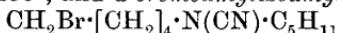
m. p. 87° , the *hydrochloride* and *hydrobromide* of which have m. p. $153-154^\circ$ and 149° respectively. The preceding cyanamide is hydrolysed by 30% sulphuric acid, yielding *s-di-p-tolylpentamethylenediamine*, $\text{C}_3\text{H}_6(\text{CH}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$, m. p. 60° , of which the *hydrochloride*, *platinichloride*, *hydrobromide*, and *sulphate* are mentioned; the *dinitroso*-derivative is a yellow, crystalline powder, m. p. $70-71^\circ$, which yields a bishydrazine derivative by reduction. *Dicyanodi-p-tolylpentamethylenediamine*, $\text{C}_3\text{H}_6[\text{CH}_2\cdot\text{N}(\text{CN})\cdot\text{C}_7\text{H}_7]_2$, prepared from the diamine and cyanogen bromide in ethereal solution, has m. p. 92° .

1-*p*-Bromophenylpiperidine reacts somewhat slowly with cyanogen bromide, and yields *p-bromophenyl- ω -bromoamylcyanamide*,



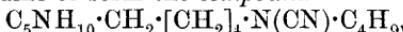
m. p. 53° , which by boiling with sodium phenoxide in alcoholic solution forms the *ether*, $\text{OPh}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{N}(\text{CN})\cdot\text{C}_6\text{H}_4\text{Br}$, m. p. 60° , b. p. $270-280/10$ mm.

1-*iso*Amylpiperidine and cyanogen bromide yield *isoamylpiperidine hydrobromide*, m. p. 255° , and *ω -bromoamylisoamylcyanamide*,



which reacts with piperidine to form *ω -piperidinoamylisoamylcyanamide*, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{N}(\text{CN})\cdot\text{C}_5\text{H}_{11}$, b. p. $213-215^\circ/12$ mm., of which the *picrate*, *platinichloride*, *aurichloride*, *methiodide*, and *methochloride* are oils: the *platinichloride* of the last-mentioned, however, forming red crystals, m. p. 145° , sintering at 137° . The preceding cyanamide is hydrolysed by heating with concentrated hydrochloric acid at 130° for fifteen to twenty hours, and yields *ω -piperidinoamylisoamylamine*, $\text{C}_5\text{NH}_{10}\cdot\text{CH}_2\cdot[\text{CH}_2]_4\cdot\text{NH}\cdot\text{C}_5\text{H}_{11}$, b. p. $170-172^\circ/9$ mm., of which the *picrate* has m. p. 152° .

1-*Butylpiperidine*, $\text{C}_5\text{NH}_{10}\cdot\text{C}_4\text{H}_9$, b. p. $175-176^\circ$, is obtained from butylamine and α -dibromopentane in 85-90% yield; the *picrate* has m. p. 132° . *Butyl- ω -bromoamylcyanamide*, $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{N}(\text{CN})\cdot\text{C}_4\text{H}_9$, reacts with piperidine to form the *compound*



b. p. $206-207/12$ mm.

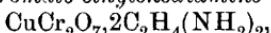
C. S.

Compounds of Dichromates of Bivalent Metals with Organic Bases. NICOLA PARRAVANO and A. PASTA (*Gazzetta*, 1907, 37, ii, 252-264).—The normal dichromates of bivalent metals, when obtainable, are unstable, but they yield with organic bases well-defined additive compounds which are stable and can be prepared relatively easily.

The compounds prepared by the authors were obtained by adding the organic base to a solution containing potassium dichromate (1 mol.) and the metallic sulphate (1 mol.), or in the case of cadmium, the nitrate.

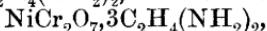
The copper dichromate pyridine compound, $\text{CuCr}_2\text{O}_7\cdot 4\text{C}_5\text{NH}_5$, forms a green, pulverulent precipitate and dissolves readily in ammonia, giving an intensely green liquid from which can be isolated: (1) the *compound*, $\text{CuCr}_2\text{O}_7\cdot 4\text{NH}_3\cdot 2\text{H}_2\text{O}$, in shining, black, prismatic crystals, and (2) the *compound*, $\text{CuCrO}_4\cdot 4\text{NH}_3$, in small, green prisms; both these compounds

are decomposed by water. The *copper dichromate aniline derivative*, $\text{CuCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$, forms a tobacco-coloured powder decomposable by water. The *copper dichromate ethylenediamine compound*,

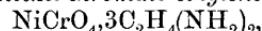


crystallises from water in chestnut-red laminae.

The *nickel dichromate pyridine compound*, $\text{NiCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$, forms pale chestnut prisms; the *aniline compound*, $\text{NiCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$, a bright red, crystalline crust decomposable by water; the *ethylenediamine compounds*, $\text{NiCr}_2\text{O}_7 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, almost black crystals, and



pale red crystals. The *nickel chromate ethylenediamine compound*,



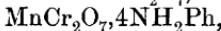
is extremely stable and forms small, dirty yellow prisms.

Cobalt dichromate forms the *compounds*: $\text{CoCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$, minute, black crystals; $\text{CoCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$, minute, brick-red crystals decomposable by water. The *compound*, $\text{CoCrO}_4 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, forms silky, golden-yellow needles.

Cadmium dichromate gives: $\text{CdCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$, forming an orange-yellow, crystalline precipitate; $\text{CdCr}_2\text{O}_7 \cdot 4\text{NH}_2\text{Ph}$, as minute, yellow crystals decomposed by water; $\text{CdCr}_2\text{O}_7 \cdot 3\text{C}_2\text{H}_4(\text{NH}_2)_2$, as minute, orange-yellow crystals.

Zinc dichromate forms: $\text{ZnCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$, which resembles the corresponding cadmium compound, but is not altered by light; $\text{ZnCr}_2\text{O}_7 \cdot 3\text{NH}_2\text{Ph.H}_2\text{O}$, which resembles the analogous cadmium derivative in appearance and properties.

Manganese dichromate yields: $\text{MnCr}_2\text{O}_7 \cdot 4\text{C}_5\text{NH}_5$ and



both forming dark chestnut crystals.

All these compounds are in accord with Werner's theory of co-ordination (*Zeitsch. anorg. Chem.*, 1893, **3**, 267; *Abstr.*, 1893, ii, 379).

The solubility of the pyridine derivatives of the dichromates increases, whilst the stability decreases, continuously in the series: copper, nickel, cobalt, cadmium, zinc, manganese. The conductivity of these compounds increases in the order: nickel, cobalt, cadmium, zinc.

T. H. P.

Diphenyldimethylhexamethyleneimine. GUIDO BARGELLINI
(*Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 344—349). Compare Harries and de Osa, *Abstr.*, 1903, i, 815).—Reduction of benzylidene-acetoxime with aluminium amalgam yields: (1) γ -amino- α -phenylbutane (Harries and de Osa, *loc. cit.*); (2) a substance, b. p. much above 238° , and (3) *4:5-diphenyl-2:7-dimethylhexamethyleneimine*, $\text{NH} < \begin{matrix} \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHPh} \\ | \\ \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHPh} \end{matrix}$, which is a colourless, mobile liquid, b. p. $235—238^\circ$, with an odour recalling that of piperidine and forming strongly alkaline solutions. Its *benzoyl derivative*, $\text{C}_{20}\text{H}_{24}\text{NBz}$, crystallises from aqueous alcohol in white needles, m. p. $101—102^\circ$, and has the normal molecular weight in freezing benzene. The *picrate*, $\text{C}_{20}\text{H}_{25}\text{N.C}_6\text{H}_3\text{O}_7\text{N}_3$, crystallises from benzene or water in yellow needles, m. p. $143—144^\circ$; the *oxalate* crystallises from alcohol in nacreous scales, or from aqueous alcohol in slender needles, m. p.

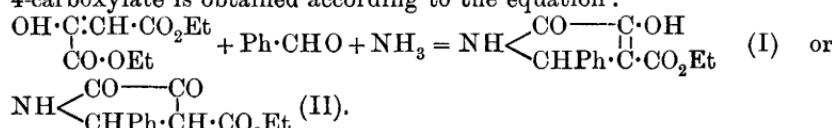
212—213°; the *hydrochloride*, $C_{20}H_{25}N \cdot HCl$, forms white needles, m. p. 154—155°; the *platinichloride*, $(C_{20}H_{25}N)_2 \cdot H_2PtCl_6$, crystallises from water in microscopic, pale yellow, rhombic plates, m. p. 185—187°, and the *aurichloride*, $C_{20}H_{25}N \cdot HAuCl_4$, crystallises from water in shining, yellow needles, m. p. 162—163°, and dissolves readily in alcohol.

T. H. P.

[Preparation of Isatin.] KALLE & Co. (D.R.-P. 184693, 184694).—*o*-Nitromandelic acid, when reduced with zinc dust in an alkaline or ammoniacal solution containing ammonium chloride and the filtered solution treated with excess of concentrated hydrochloric acid, furnishes a yellow, crystalline product, m. p. 162°, which is probably an *anhydride* of *o-hydroxylaminomandelic acid*, $OH \cdot NH \cdot C_6H_4 \cdot CH(OH) \cdot CO_2H$, and may be represented by the formula $C_6H_4 \begin{array}{c} C(OH) \cdot CO_2H \\ \swarrow \quad \searrow \\ NH \end{array}$. When this anhydride is melted either alone or preferably with a dehydrating agent, such as acetic anhydride, it gives rise to isatin or acetylisatin respectively. Isatin is also produced when the anhydride is dissolved in aqueous sodium carbonate or hydroxide and the solution subsequently acidified.

G. T. M.

Action of Ethyl Oxalacetate on Aldehydes in Presence of Ammonia and Primary Amines: a New General Reaction of Aldehydes. Louis J. SIMON and A. CONDUCHE (*Ann. Chim. Phys.*, [viii], 12, 5—58).—Ethyl oxalacetate readily condenses with aldehydes in presence of ammonia, forming derivatives of 2:3-diketopyrrolidine; thus, in the case of benzaldehyde, ethyl 2:3-diketo-5-phenylpyrrolidine-4-carboxylate is obtained according to the equation:



If a primary amine is used in place of ammonia, a compound containing the group NR instead of the NH of the pyrrolidine nucleus is obtained. Some of the substances obtained in this way have been described already (*Abstr.*, 1904, i, 521 and 812; 1905, i, 887 and 888; this vol., i, 725). The following facts are new.

The diketopyrrolidine derivatives, as liberated from their ammonium salts by adding acid, contain $1H_2O$; as this water is not present in the ammonium salts which are derived from the enolic formula (I) above, it is probably combined with the carbonyl group in position 3 in formula II, thus: $NH \begin{array}{c} CO \quad C(OH)_2 \\ \swarrow \quad \searrow \\ CHPh \cdot CH \cdot CO_2Et \end{array}$ (III). This water can be expelled by heating in a vacuum at 100°; the anhydrous substance remaining sometimes takes up water again from the atmosphere (salicylic and piperonylic derivatives), but in other cases does not do so. The substance decomposing at 185°, obtained from benzaldehyde and previously given the formula I above (*Abstr.*, 1904, i, 522), is really the hydrated substance (III); when dehydrated, it decomposes at the

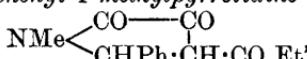
same temperature, 185°. The ammonium salt, $\text{NH} \begin{array}{c} \text{CO} \\ | \\ \text{CHPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array} \text{C}(\text{ONH}_4)$, decomposes at 175°; the analogous aniline salt melts at 160°, and the p-toluidine salt decomposes at 173°; the last two substances, when heated at 120—130°, lose the whole of the combined base, leaving the anhydrous compound (I).

The ammonium salt, $\text{NH} \begin{array}{c} \text{CO} \\ | \\ \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{array} \text{C} \cdot \text{ONH}_4$, of the compound from salicylaldehyde, ethyl oxalacetate and ammonia, decomposes at 190°; the copper salt crystallises with 4H₂O. The ammonium salt of the compound from anisaldehyde decomposes at 175°. The compound $\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} \begin{array}{c} \text{NH} \quad \text{CO} \\ | \quad || \\ \text{CH}(\text{CO}_2\text{Et}) \cdot \text{CO} \end{array}$, prepared from vanillin, crystallises in rhombic prisms with 2H₂O; the ammonium salt decomposes at 175°. The compound from piperonal gives an ammonium salt decomposing at 185°; the copper salt, (C₁₄H₁₂NO₆)₂Cu, C₂H₄O₂, forms yellowish-green needles.

Furfuraldehyde condenses with ethyl oxalacetate and ammonia to form the compound C₄OH₃·CH< $\begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \\ | \\ \text{CO} - \text{CO} \end{array}$. From acetaldehyde, the compound $\text{NH} \begin{array}{c} \text{CO} \quad \text{CO} \\ | \quad || \\ \text{CHMe} \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$ (m. p. 146°) is obtained similarly; it is anhydrous and has a definite melting point, differing in these respects from all the other compounds of a similar type; a second form of this substance (m. p. 132°), also anhydrous, is produced with it, the two compounds being probably the racemic and meso-forms which should exist owing to the presence of two asymmetric carbon atoms. The copper salt crystallises with 1H₂O.

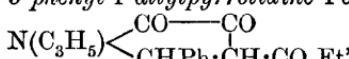
The compound $\text{NH} \begin{array}{c} \text{CO} \quad \text{CO} \\ | \quad || \\ \text{CH}(\text{C}_6\text{H}_{13}) \cdot \text{CH} \cdot \text{CO}_2\text{Et} \end{array}$ (m. p. 128°), prepared from heptaldehyde, ethyl oxalacetate, and ammonia, is also anhydrous, melts without decomposing, and appears to exist in two forms; the ammonium salt, which decomposes at 146°, the potassium, and silver salts are crystalline.

Ethyl 2:3-diketo-5-phenyl-1-methylpyrrolidine-4-carboxylate,



prepared from ethyl oxalacetate, benzaldehyde, and methylamine, crystallises in white needles, is anhydrous, decomposes at 162°, and gives a crystalline methylamine salt, C₁₄H₅O₄N.NH₂Me, which decomposes at 155°.

Ethyl 2:3-diketo-5-phenyl-1-allylpyrrolidine-4-carboxylate,



prepared similarly by using allylamine, crystallises from alcohol in slender needles, m. p. 146°; the allylamine salt forms silky prisms and decomposes at 142°.

Ethyl 2:3-diketo-5-phenyl-1-benzylpyrrolidine-4-carboxylate, prepared

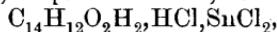
by using benzylamine, crystallises in white needles, m. p. 190° with decomposition ; the *benzylamine* salt, m. p. 140°, is crystalline.

Ethyl 2 : 3-diketo-1 : 5-diphenylpyrrolidine-4-carboxylate, obtained from ethyl oxalacetate, benzaldehyde, and aniline (compare *Abstr.*, 1904, i, 812), is also formed when ethyl oxalacetate is left at the ordinary temperature in ethereal solution with benzylideneaniline. The *potassium* salt, $C_{19}H_{16}O_4NK, 3\frac{1}{2}H_2O$, the *barium*, *copper*, and *silver* salts are described ; it does not form a salt with aniline.

In the introduction to the paper, the relationship of the substances described with compounds containing the same fundamental nucleus is discussed at length.

W. A. D.

2'- and 4'-Nitro-6'-methyl- α -stilbazole. FELIX B. AHRENS and AUGUST LUTHER (*Ber.*, 1907, 40, 3400—3406).—2'-*Nitro-6-methyl- α -stilbazole*, $C_{14}H_{12}O_2N_2$, obtained by heating *o*-nitrobenzaldehyde with 2 : 6-lutidine and zinc chloride at 180—190° for ten hours, crystallises from dilute alcohol in slender, pale yellow needles, m. p. 55—57°. The following salts have been prepared. *Hydrochloride*, $C_{14}H_{12}O_2N_2HCl$, glistening needles, m. p. 235—275° (decomp.) ; *hydrobromide*, slender, yellow needles, m. p. 240—241° (decomp.) ; *hydriodide*, yellow plates, m. p. 198—199° ; *nitrate*, pale yellow needles, m. p. 148—149° ; *picrate*, $C_{20}H_{15}O_9N_5$, m. p. 227—228° (decomp.) after sintering at 210° ; *mercurichloride*, $C_{14}H_{12}O_2N_2HCl, HgCl_2$, m. p. 147—148° ; *aurichloride*, m. p. 191—192° ; *platinichloride*, yellow plates ; *hydrogen sulphate*, yellow needles, m. p. 130—131° ; *stannichloride*,

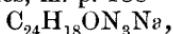


yellow needles, m. p. 225—226° ; $C_{14}H_{12}O_2N_2HCl, ZnCl_2$, m. p. 195—196° ; $C_{14}H_{12}O_2N_2HCl, BaCl_2$, long, yellow needles decomposing at 238°.

The isomeric 4'-*nitro-6-methyl- α -stilbazole* crystallises from dilute alcohol in long needles, m. p. 131—132°. The salts prepared are : *hydrochloride*, $C_{14}H_{12}O_2N_2HCl$, long yellow needles, m. p. 221—222° ; *nitrate*, pale yellow plates, m. p. 162—163° ; *platinichloride*, decomposes at 255° ; *aurichloride*, m. p. 225—226° ; *mercurichloride*, yellow needles.

When reduced with tin and hydrochloric acid, the *o*-nitro-compound yields 2'-*amino-6-methyl- α -stilbazole*, $C_{14}H_{14}N_2$, in yellow, glistening needles, m. p. 136—137°. This readily absorbs carbon dioxide from the air, yielding the *carbonate*, $(C_{14}H_{14}N_2)_2, H_2CO_3$. The *hydrochloride*, $C_{14}H_{14}N_2, 2HCl$, crystallises in pale yellow plates, m. p. 234—235° ; the *stannichloride*, $C_{14}H_{14}N_2, 2HCl, 2SnCl_2$, forms orange-coloured needles, m. p. 278°, and the *mercurichloride*, similar needles, m. p. 164°. The platinichloride has not been obtained in a crystalline form. The diazotised amino-compound yields an *azo-dye*, $C_{24}H_{18}ON_3K$, with an alkaline solution of β -naphthol ; it crystallises from alcohol in red plates, m. p. 157—158°, and dyes wool or silk.

4'-*Amino-5-methyl- α -stilbazole* forms pale brown needles, m. p. 139—140°. The *hydrochloride* decomposes at 265° ; the *mercurichloride* crystallises in reddish-brown needles, m. p. 260° (decomp.) ; the *stannichloride* forms brown needles, m. p. 188—189°. The *azo-dye*,



obtained from the diazotised base and an alkaline solution of β -naphthol, crystallises in dark reddish-brown plates, m. p. 248—249°, and dyes silk and wool red.

2'-Amino-6-methyl- α -stilbazole couples with diazotised sulphanilic acid in alkaline solution yielding a yellowish-brown dye,



which is readily reduced to sulphauilic acid and *diamino-6-methyl- α -stilbazole*, $\text{C}_{14}\text{H}_{15}\text{N}_3$, the latter of which crystallises from dilute alcohol in long needles, m. p. 148—149°. The *hydrochloride*,



forms needles, m. p. 249—250° (decomp.). The *mercurichloride*,



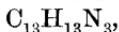
crystallises in yellow needles, m. p. 179—180°; the *stannichloride* forms glistening yellowish-brown needles, m. p. 245—246° (decomp.).

The bisdiazoo-derivative of the base couples with an alkaline solution of β -naphthol yielding a pale red dye, $\text{C}_{34}\text{H}_{23}\text{O}_2\text{N}_5\text{Na}_2$, which crystallises from alcohol in plates, m. p. 180—181°. With β -naphtholdisulphonic acid (R-acid), a brownish-red dye, $\text{C}_{34}\text{H}_{23}\text{O}_{14}\text{N}_5\text{S}_4\text{Na}_4$, is obtained; it crystallises from water in plates.

4'-Amino-6-methyl- α -stilbazole yields a dye, $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_4\text{SNa}$, with diazotised sulphanilic acid; it crystallises from alcohol in yellowish-brown plates, and dyes silk, wool, and cotton yellow. 4'-Amino- α -stilbazole and diazotised sulphanilic acid yield a yellow dye,



which can be reduced to sulphanilic acid and *diamino- α -stilbazole*,



the latter of which crystallises in long, yellow needles, m. p. 126—127°. Its *hydrochloride*, $\text{C}_{13}\text{H}_{13}\text{N}_3 \cdot 3\text{HCl}$, forms yellowish-red, glistening needles; its *mercurichloride*, red needles, and its *stannichloride*, long, red needles, m. p. 240—241°.

J. J. S.

New Process for the Preparation of Aromatic 3-Hydroxy-5-pyrazolones or Pyrazolidones. AUGUST MICHAELIS and KONRAD SCHENK (*Ber.*, 1907, 40, 3568—3569).—Malonic acid and acetylphenylhydrazine condense in presence of phosphorus trichloride to 3-hydroxy-1-phenyl-5-pyrazolone previously described by Michaelis and Burmeister (*Abstr.*, 1892, 1004). In a similar manner, dimethylmalonic acid condenses to 3-hydroxy-1-phenyl-4: 4-dimethyl-5-pyrazolone, $\text{NPh} \begin{array}{c} \text{CO} \cdot \text{CMe}_2 \\ \swarrow \\ \text{N} = \text{C} \cdot \text{OH} \end{array}$, separating in colourless crystals, m. p. 176°.

Similarly, acetyl-*p*-bromophenylhydrazine and malonic acid condense to 3-hydroxy-1-*p*-bromophenyl-5-pyrazolone, crystallising in plates, m. p. 217°, and forming a red condensation product with benzaldehyde. The method appears to be generally applicable.

E. F. A.

Thionpyrazolones. RICHARD STOERMER and D. JOHANNSEN (*Ber.*, 1907, 40, 3701—3703).—The action of phosphorus pentasulphide on pyrazolones yields thionpyrazolones and is therefore analogous to that on pyrrolidone (compare Tafel and Lawaczeck, this vol., i, 720).

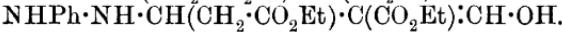
The pyrazolone, obtained from ethyl dimethylacetacetate, when

heated at 140° with phosphorus pentasulphide yields 1-*phenyl*-3 : 4 : 4-*trimethyl*-5-thionpyrazolone, NPh<_{CH:}^{N=CMe₂}CS-CMe₂, which crystallises in long, yellow prisms, m. p. 45—46°, b. p. 187—190°/12 mm. Methyl iodide gives a *dimethiodide*, m. p. 210—215°, which with silver chloride yields a *methochloride*, the *platinichloride* of which has m. p. 235—237°.

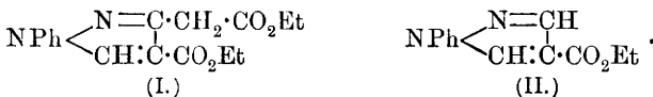
1-*Phenyl*-3-*methyl*-4 : 4-*diethyl*-5-thionpyrazolone, C₁₄H₁₈N₂S, yellow prisms, m. p. 80°, and 1-*phenyl*-3-*methyl*-5-thionpyrazolone, C₁₀H₁₀N₂S, or m. p. 103°, are best prepared in xylene solution. W. K.

Action of Phenylhydrazine on Ethyl Formylglutaconate.

WILHELM WISLICENUS and ERNST BREIT (*Annalen*, 1907, 356, 32—44). —The action of phenylhydrazine on ethyl formylglutaconate has been again studied with the object of throwing light on certain points in the reaction left indefinite by the investigations of Wislicenus and Bindemann (Abstr., 1901, i, 361) and Hesse (*Diss.*, Würzburg, 1902). The first product of the reaction is now found to be an additive compound, NHPh·NH·CH(CH₂·CO₂Et)·CH(CO₂Et)·CHO or



This condenses, forming ethyl 1-phenylpyrazole-3-acetate-4-carboxylate (I) or ethyl 1-phenylpyrazole-4-carboxylate (II), depending on the conditions. The latter product is formed when the additive compound is heated in absence of air, which explains its formation on distillation of ethyl formylacetate-phenylhydrazone (*loc. cit.*):



The additive compound, C₁₆H₂₂O₅N₂, formed by mixing ethyl formylglutaconate and phenylhydrazine in cold ethereal solution, crystallises in needles, m. p. 70°, and on exposure to air in ethereal solution forms ethyl 1-phenylpyrazole-3-acetate-4-carboxylate, m. p. 89—90°. 1-*Phenylpyrazole-3-acetic-4-carboxylic acid*, C₁₂H₁₀O₄N₂, decomp. 221°, is formed by boiling the ester with aqueous baryta, evolves carbon dioxide on prolonged heating at 140°, forming 1-phenyl-3-methylpyrazole-4-carboxylic acid, and yields the ester, m. p. 89—90°, when boiled with alcoholic hydrogen chloride. The *barium*, C₁₂H₈O₄N₂Ba, 2H₂O, and *silver*, C₁₂H₈O₄N₂Ag₂, salts were analysed.

When heated at 60—70° in presence of air, the additive compound yields a mixture of the above ester and ethyl 1-phenylpyrazole-4-carboxylate, m. p. 96—97°, together with ethyl acetate. In the absence of air, ethyl 1-phenylpyrazole-4-carboxylate and ethyl acetate only are formed.

When *p*-bromophenylhydrazine is added to an ethereal solution of ethyl formylglutaconate, the additive compound does not separate, but after some time the solution deposits *ethyl 1-p-bromophenylpyrazole-3-acetate-4-carboxylate*, C₁₆H₁₇O₄N₂Br, m. p. 128—129°, which does not give a coloration with potassium dichromate in concentrated sulphuric

acid solution. But if the ethereal solution is rapidly evaporated, the additive compound separates, and if heated at 140° in a current of carbon dioxide, loses water and ethyl acetate forming *ethyl 1-p-bromo-phenylpyrazole-4-carboxylate*, $C_{12}H_{11}O_2N_2Br$, which crystallises in needles, m. p. 133—134°.

G. Y.

The Hydrazones of Ethyl Formylacetate. WILHELM WISLICENUS and H. W. BYWATERS (*Annalen*, 1907, 356, 45—50). Compare preceding abstract; Wislicenus and Bindemann, *Abstr.*, 1901, i, 361). —The phenylhydrazone of ethyl formylacetate yields the same condensation products as are obtained from the additive compound of phenylhydrazine and ethyl formylglutaconate.

Ethyl 1-phenylpyrazole-3-acetate-4-carboxylate is formed when the phenylhydrazone is treated with hydrogen chloride in cold absolute alcoholic solution, whilst ethyl 1-phenylpyrazole-4-carboxylate is obtained on distillation of the phenylhydrazone.

The *p-bromophenylhydrazone* of ethyl formylacetate, $C_{11}H_{13}O_2N_2Br$, crystallises in slightly yellow prisms, m. p. 80—81°, is more stable than the corresponding phenylhydrazone, and gives a dark violet coloration with concentrated sulphuric acid, or a brownish-red with alcoholic ferric chloride. On treatment with hydrogen chloride in absolute alcoholic solution, it condenses, forming ethyl 1-*p*-bromo-phenylpyrazole-3-acetate-4-carboxylate (preceding abstract), which distils in a vacuum with partial decomposition, and gives the pyrazoline reaction after reduction. *1-p-Bromophenylpyrazole-3-acetic-4-carboxylic acid*, $C_{12}H_9O_4N_2Br$, crystallises in colourless needles, m. p. 229—230°; the *silver salt*, m. p. 270° (decomp.). When distilled in a vacuum, the *p*-bromophenylhydrazone of ethyl formylacetate yields ethyl 1-*p*-bromophenylpyrazole-4-carboxylate, m. p. 131—132°.

The *semicarbazone* of ethyl formylacetate, $C_6H_{11}O_3N_3$, crystallises in almost colourless prisms, m. p. 147—148°, and when heated at 160° in a sealed tube decomposes, forming alcohol, hydrazodicarbonamide, and a *resin*, which is soluble in alcohol and forms a *silver salt*.

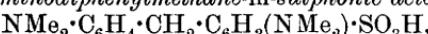
G. Y.

Preparation of a *p*-Aminodiphenylaminesulphonic Acid. ERNST ERDMANN (D.R.-P. 181179).—Although diphenylamine itself is not easily converted into a monosulphonic acid, one sulphonic group is readily introduced into the molecule of *p*-aminodiphenylamine, providing that the sulphuric acid contains a certain proportion of sulphur trioxide and that the sulphonation is effected at about 110—130°, the temperature required being dependent on the amount of trioxide present. The time required to complete the reaction varies from one to three hours. *p-Aminodiphenylaminesulphonic acid*, which is purified by dissolving in alkali and reprecipitating by mineral acid, is sparingly soluble in hot water, and crystallises from this solvent in clusters of fine needles. Its *sodium* and *potassium* salts crystallise from water, and the diazo-derivative separates as a yellow, crystalline product. The new acid differs from its isomerides in the coloration it furnishes with chromic acid and ferric chloride.

G. T. M.

Preparation of Tetra-alkyldiaminodiphenylmethanesulphonic Acids. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 183793).—The direct sulphonation of tetramethyldiaminodiphenylmethane does not lead readily to the formation of a monosulphonic acid. The product is contaminated by coloured by-products and by substances of the sulphone type. It has now been found that the monosulphonic acids of this series may be synthesised in good yield by condensing formaldehyde with dimethyl- or diethyl-aniline and dimethylaniline-*m*-sulphonic acid.

*Tetramethyldiaminodiphenylmethane-*m*-sulphonic acid,*



crystallises from aqueous solutions, and its sodium salt may be silted out in the form of slender needles.

*Dimethylaminodiethylaminodiphenylmethane-*m*-sulphonic acid,*



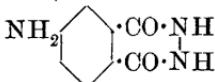
resembles its lower homologue.

G. T. M.

Action of Hydrazine Hydrate on Nitro-compounds. I. THEODOR CURTIUS (*J. pr. Chem.*, 1907, [ii], 76, 233—237).—A short account of the chief results of the study of the action of hydrazine hydrate on nitro-compounds previously unpublished or published only in dissertations.

Rothenberg showed (Abstr., 1893, i, 701) that whilst the action of hydrazine hydrate on oximes leads to substitution, *p*-nitrobenzene, *p*-nitrosodimethylaniline, and diphenylnitrosoamine are reduced by hydrazine hydrate forming aniline, *p*-aminodimethylaniline, and *α*-diphenylhydrazine respectively. It has since been found that the action of hydrazine hydrate on *p*-nitrosodimethylaniline leads also to the formation of traces of dimethylamine, whilst if the action is moderated by dilution of the hydrazine hydrate, tetramethyldiaminoazoxybenzene is formed.

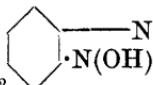
Bollenbach (*Diss.*, Heidelberg, 1902), who obtained *o*- and *p*-aminophenols by reduction of the nitrophenols with hydrazine hydrate, was unable to reduce *m*- or *p*-nitrobenzoic acid in this manner, and found that *m*-dinitrobenzene is reduced only to *m*-nitroaminobenzene. On the other hand, Hoesch (*Diss.*, Heidelberg, 1904) has obtained

β -aminophthalhydrazide,  by reduction of ethyl

β -nitrophthalate by means of hydrazine hydrate.

The action of hydrazine hydrate on ethyl 3:5-dinitrobenzoate (Reidel, *Diss.*, Heidelberg, 1902; see following abstract) leads to the formation of 3:5-dinitrobenzohydrazide, which is reduced by an excess of hydrazine hydrate forming 3-nitro-5-aminobenzohydrazide. Similarly, 3:5-dinitrobenzoic acid forms the hydrazine salts of 3:5-dinitro- and 3-nitro-5-amino-benzoic acids. The second nitro-group, as in the case of *m*-dinitrobenzene, cannot be reduced in this manner.

Bollenbach (*loc. cit.*) found that 2:4-dinitrobenzoic acid reacts in analogous manner to hydrazine hydrate, forming 2-nitro-4-aminobenzoic acid. 2:4-Dinitrophenylhydrazine, on the contrary, is not reduced by hydrazine hydrate, which functions merely as an alkali, the reaction lead-

ing to the formation of *6-nitro-1-hydroxy-1:2:3-benzotriazole*,


G. Y.

Action of Hydrazine Hydrate on Nitro-compounds. II.
Action of Hydrazine Hydrate on Ethyl 3:5-Dinitrobenzoate.
 THEODOR CURTIUS and ADOLF RIEDEL (*J. pr. Chem.*, 1907, [ii], 76, 238—263. Compare preceding abstract).—*3:5-Dinitrobenzohydrazide*, $C_6H_3(NO_2)_2 \cdot CO \cdot NH \cdot NH_2$, prepared in a 63·7—69% yield by boiling ethyl 3:5-dinitrobenzoate with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellow, prismatic needles, m. p. 158°, reduces ammoniacal silver nitrate and Fehling's solutions when heated, and forms crystalline condensation products with aldehydes and ketones. The crystalline sodium derivative,



was analysed. The *benzylidene* derivative, $C_7H_4O_5N_2 \cdot CHPh$, crystallises in slightly brown needles, m. p. 262°. The *propylidene* derivative, $C_7H_4O_5N_2 \cdot CMe_2$, forms slightly yellow needles, m. p. 213·5°. The *acetyl* derivative, $C_6H_3(NO_2)_2 \cdot CO \cdot NH \cdot NHAc$, crystallises in yellowish-white needles, m. p. 201·5°. When treated with sodium nitrite in glacial acetic acid solution, the hydrazide forms *3:5-dinitrobenzoyl-azoiimide*, $C_6H_3(NO_2)_2 \cdot CO \cdot N_3$, which is obtained in small, white crystals, detonates slightly when heated, and yields *3:5-dinitrobenzoic acid* when boiled with aqueous sodium hydroxide. *3:5-Dinitrobenzanilide*, $C_{13}H_9O_5N_3$, formed by boiling the azoimide with aniline, crystallises in brown needles, m. p. 234°. *Ethyl 3:5-dinitrophenylcarbamate*, $C_6H_3(NO_2)_2 \cdot NH \cdot CO_2Et$ (?), prepared by boiling the azoimide with absolute alcohol, is obtained as a viscid, red oil, which yields *3:5-dinitroaniline* when boiled with concentrated hydrochloric acid. *3:5-Dinitroacetanilide*, $C_8H_7O_5N_3$, crystallises in yellowish-white needles, m. p. 191°. The action of boiling methyl alcohol on the azoimide leads to the formation of methyl *3:5-dinitrobenzoate* and azoimide. *s-Bis-3:5-dinitrophenylcarbamide*, m. p. 265°, formed together with *3:5-dinitroaniline* by boiling *3:5-dinitrobenzoylazoimide* with water, is probably identical with Struve and Radenhausen's tetranitrocarbanilide (*Abstr.*, 1896, i, 35).

Bis-3:5-dinitrobenzoylhydrazide,



prepared by the action of iodine on *3:5-dinitrobenzoylhydrazide* in boiling alcoholic solution, is obtained in a 30% yield as a yellow powder, m. p. 276°, and dissolves unchanged in concentrated sulphuric acid, being reprecipitated on addition of water. When heated with alcoholic hydrogen chloride at 100° in a sealed tube, it is decomposed, yielding *m-dinitrobenzene* and hydrazine. The crystalline *disodium derivative*, $N_2Na_2[CO \cdot C_6H_3(NO_2)_2]_2$, is described.

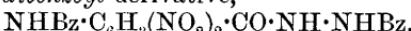
3-Nitro-5-aminobenzoylhydrazide, $NH_2 \cdot C_6H_3(NO_2) \cdot CO \cdot NH \cdot NH_2$, is formed in a 60% yield together with a reddish-grey, crystalline *powder*, m. p. 283—284°, having the composition of *bis-dinitrobenzoylhydrazide*, when ethyl *3:5-dinitrobenzoate* is boiled in concentrated alcoholic solution with an excess of hydrazine hydrate. *3-Nitro-*

5-aminobenzoylhydrazide is formed also by boiling ethyl 3-nitro-5-aminobenzoate with hydrazine hydrate in alcoholic solution. It crystallises in yellowish-red leaflets, m. p. 221°, and reduces ammoniacal silver nitrate and Fehling's solutions when heated.

Hydrazone 3 : 5-dinitrobenzoate, $C_6H_3(NO_2)_2 \cdot CO_2H \cdot N_2H_4$, formed by heating 3 : 5-dinitrobenzoic acid with a limited amount of hydrazine hydrate in alcoholic solution, crystallises in yellowish-brown needles, m. p. 168°, reduces ammoniacal silver nitrate and Fehling's solutions in the cold, yields benzaldazine and 3 : 5-dinitrobenzoic acid when shaken with benzaldehyde in aqueous solution, and is converted into ethyl 3 : 5-dinitrobenzoate when heated with alcoholic hydrogen chloride.

Hydrazone 3-nitro-5-aminobenzoate, $NH_2 \cdot C_6H_3(NO_2)_2 \cdot CO_2H \cdot N_2H_4$, prepared by boiling 3 : 5-dinitrobenzoic acid or its hydrazone salt with an excess of hydrazine hydrate in alcoholic solution, crystallises in reddish-yellow needles, m. p. 207° (decomp.), reduces ammoniacal silver nitrate and Fehling's solutions in the cold, and when shaken with benzaldehyde yields benzaldazine and 3-nitro-5-aminobenzoic acid.

The following substances derived from 3-nitro-5-aminobenzoylhydrazide are described. The *hydrochloride*, $C_7H_8O_3N_4 \cdot 2HCl$, brown crystals, m. p. 221—222°. The *benzylidene derivative*, $C_{14}H_{12}O_3N_4$, yellow, prismatic needles, m. p. 247—248°. The *m-hydroxybenzylidene derivative*, $C_{14}H_{12}O_4N_4$, reddish-brown leaflets, m. p. 242°. The *m-nitrobenzylidene derivative*, $C_{14}H_{11}O_5N_5$, yellow needles, m. p. 240°. The *propylidene derivative*, $C_{10}H_{12}O_3N_4$, golden needles, m. p. 208°. The *tri-acetyl derivative*, $NHAc \cdot C_6H_3(NO_2)_2 \cdot CO \cdot NAc \cdot NHAc$, yellow nodules, m. p. 256°. The *dibenzoyl derivative*,



slightly brown needles, m. p. 236°.

3-Nitro-5-hydroxybenzoylazoimide, $NO_2 \cdot C_6H_3(OH) \cdot CO \cdot N_3$, prepared by the action of sodium nitrite on 3-nitro-5-aminobenzoylhydrazide in acetic acid solution, is obtained as a reddish-yellow, flocculent substance, which becomes brown when dried in a desiccator and detonates when heated. It dissolves in aqueous sodium hydroxide with slight evolution of gas, forming a dark red solution, and on addition of sulphuric acid yields azoimide, *3-Nitro-5-hydroxybenzanilide*,



formed by boiling the azoimide with aniline, crystallises in white needles, m. p. 232°. The *urethane*, $NO_2 \cdot C_6H_3(OH) \cdot NH \cdot CO_2Et$, formed by boiling the azoimide with absolute alcohol, is obtained as a viscous, red oil, and, when heated with sodium hydroxide and hydrogen chloride successively, yields 3-nitro-5-aminophenol.

When heated with water, 3-nitro-5-hydroxybenzoylazoimide forms *s-di-3-nitro-5-hydroxyphenylcarbamide*, $CO[NH \cdot C_6H_3(OH) \cdot NO_2]_2$, and small amounts of 3-nitro-5-aminophenol. The carbamide is obtained as a brittle mass, decomp. 260—270°, and is decomposed by boiling concentrated sodium hydroxide forming 3-nitro-5-aminophenol.

s-Di-3-nitro-5-aminobenzoylhydrazide, $N_2H_2[CO \cdot C_6H_3(NH_2) \cdot NO_2]_2$, prepared by boiling 3-nitro-5-aminobenzoylhydrazide with iodine in alcoholic solution, is obtained as a yellow, granular powder, m. p. 263—264°, and is hydrolysed, forming hydrazine, by alcoholic hydrogen chloride at 100°.

G. Y.

Preparation of 5:5-Dialkylbarbituric Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 183628).—The dialkylbarbituric acids are obtained by heating the dialkylmalonyldiurethanes, produced from the dialkylmalonyl chlorides and alkylurethanes, either alone or in the presence of carbamide, phenyl carbonate, or a similar compound.

G. T. M.

Preparation of 5:5-Dialkylbarbituric Acids. E. MERCK (D.R.-P. 183857).—The ethyl dialkylmalonates yield 5:5-dialkylbarbituric acids when heated either with biuret or an alkyl allophanate. Ethyl dialkylmalonates, when heated with either biuret or ethyl allophanate in alcoholic sodium ethoxide, furnish 5:5-dialkylbarbituric acids (compare Abstr., 1906, i, 461). G. T. M.

Preparation of 4:6-Dioxy-2-thio-5:5-dialkylpyrimidines. EMANUEL MERCK (D.R.-P. 182764).—4:6-Dioxy-2-thio-5:5-diethylpyrimidine may be produced by heating diethylmalonyl chloride with thiocarbamide at 100°, and 4:6-dioxy-2-thio-5:5-dipropylpyrimidine is similarly prepared from dipropylmalonyl chloride. These substances are readily oxidised to the corresponding 5:5-dialkylbarbituric acids by dilute nitric acid or alkaline permanganate.

G. T. M.

Pyrimidines. XXIII. Uracil-4-carboxylic Acid. HENRY L. WHEELER (*Amer. Chem. J.*, 1907, 38, 358—366).—By the condensation of carbamide with ethyl oxalacetate, Müller (Abstr., 1897, i, 549) obtained a compound which he regarded as ethyl uracil-4-carboxylate, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \swarrow \quad \searrow \\ \text{CO} \cdot \text{CH} \end{array} \text{C} \cdot \text{CO}_2\text{Et}$.

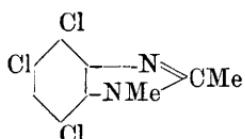
As no evidence was adduced to prove that the substance had this pyrimidine structure, it seemed possible that it might be the ester of the acid, $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \swarrow \quad \searrow \\ \text{NH} \cdot \text{CO} \end{array}$, obtained by Gabriel (Abstr., 1906, i, 636) by the action of bromine on marylureide. Müller's ester has therefore been prepared and studied, and it has been found that on hydrolysis it yields an acid, which is not identical with Gabriel's acid, and on treatment with bromine is converted into dibromobarbituric acid. It is proved, therefore, that Müller's ester has the structure originally assigned to it, that Gabriel was right in concluding that his acid was not a pyrimidine, and that marylureide has the constitution, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \swarrow \quad \searrow \\ \text{CO} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$, proposed by Guareschi (Abstr., 1877, i, 458), and not $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \swarrow \quad \searrow \\ \text{CO} \cdot \text{CH}_2 \end{array} \text{CH} \cdot \text{CO}_2\text{H}$, as suggested by Grimaux (Abstr., 1875, 752).

Uracil-4-carboxylic acid, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \swarrow \quad \searrow \\ \text{CO} \cdot \text{CH} \end{array} \text{C} \cdot \text{CO}_2\text{H}, \text{H}_2\text{O}$, m. p. 347° (decomp.), crystallises from water in prisms; the methyl ester, m. p. 230°, forms colourless needles; the potassium and barium salts are described.

An attempt to prepare ethyl uracil-4-carboxylate by treating ethyl oxalacetate with ethyl- ψ -thiocarbamide hydrobromide resulted in the formation of an additive compound, $C_{11}H_{20}O_5N_2S$, m. p. 133—134°, which crystallises in colourless needles and when boiled with hydrochloric acid yields a substance, m. p. 206—207°, which contains sulphur, but not nitrogen. When ethyl cyanoacetylacetate is treated in the same way, an additive compound, $C_{10}H_{17}O_3N_3S$, m. p. 159°, is produced, which separates from alcohol in colourless, flat prisms. Ethyl oxalomalonate, under similar conditions, yields an additive compound, $C_{17}H_{32}O_7N_4S_2$, m. p. 181° (decomp.), which crystallises from alcohol in lustrous scales.

E. G.

[Properties of Substituted Amidines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 180126).—The amidines derived from the aromatic orthodiamines may be employed as substitutes for camphor in the production of celluloid.



Methylbenziminazole, m. p. 113—115°, trichloro-2-methyl-1-ethylbenziminazole, m. p. 116—117° (from ethyl aceto-*o*-nitrotrichloroanilide), and 4:5:7-trichloro-1:2-dimethylbenziminazole, m. p. 120—121°, can be worked up with nitrocellulose in the presence of alcohol.

G. T. M.

3-Amino-2-methylquinoline. O. STARK (*Ber.*, 1907, 40, 3425—3433).—When the oxime of 3-acetyl-2-methylquinoline is heated with sulphuric acid at 180°, the Beckmann reaction occurs, followed by hydrolysis, and the elimination of the acetyl group, and the final product is 3-amino-2-methylquinoline: $C_9NH_5Me\cdot CMe\cdot NOH \rightarrow C_9NH_5Me\cdot NH\cdot COMe \rightarrow C_9NH_5Me\cdot NH_2$.

A 92% yield of 3-acetyl-2-methylquinoline may be obtained by heating an alcoholic solution of *o*-aminobenzaldehyde and acetylacetone with a few drops of piperidine. It melts at 78—79° (compare Eliasberg and Friedländer, *Abstr.*, 1892, 1106). The semicarbazone, $C_{13}H_{14}ON_4$, crystallises from alcohol in small, colourless needles, m. p. 208°.

3-Amino-2-methylquinoline crystallises from ether in long, yellow needles, m. p. 159—160°, or from light petroleum in brilliant golden needles. The hydrochloride, $C_{10}H_{10}N_2\cdot 2HCl$, obtained by passing dry hydrogen chloride into an absolute ethereal solution of the base, forms a yellowish-white, crystalline powder; the platinichloride, $2C_{10}H_{10}N_2\cdot H_2PtCl_6\cdot 2H_2O$, forms glistening golden needles, and darkens when heated to 220—230°; the picrate, $C_{10}H_{10}N_2\cdot C_6H_3O_7N_3$, also forms golden needles, and decomposes at about 235°. The acetyl derivative, $C_9NH_5Me\cdot NHAc$, crystallises from ether in needles, m. p. 164°. The solutions of the acetyl derivative do not fluoresce until hydrolysis has begun. The same acetyl derivative may also be obtained by the action of a phosphorus oxychloride solution of phosphorus pentachloride on the oxime.

When oxidised with permanganate, the aminomethylquinoline yields

water with $2\text{H}_2\text{O}$, but if a solution of the compound saturated at $60-65^\circ$ is boiled, anhydrous crystals separate. When reduced with hydrogen iodide in acetic acid solution, 3-amino-4-hydroxy-2-methylquinoline yields quinaldine (2-methylquinoline), and not aminoquinaldine as stated by Conrad, Limpach, and Eckhardt (Abstr., 1888, 1111).

J. J. S.

Fluorescence of 3-Amino-2-methylquinoline and 3-Amino-4-hydroxy-2-methylquinoline. Use of 3-Amino-2-methylquinoline as an Indicator. O. STARK (*Ber.*, 1907, 40, 3434).—Pure aqueous solutions of 3-amino-2-methylquinoline and of 3-amino-4-hydroxy-2-methylquinoline do not fluoresce even in very dilute solutions. The former compound fluoresces in acid solutions only, and the latter in both acid and alkaline solution, thus indicating the relationship between fluorescence and dissociation. A pure aqueous solution of the hydroxy-derivative is best obtained by distillation in steam; it is then non-fluorescent, but the addition of the minutest trace of acid on alkali produces fluorescence.

3-Amino-2-methylquinoline is an excellent indicator in acidimetry, and can replace methyl-orange. An alcoholic solution is the best to use.

J. J. S.

Some Methineammonium Dyes. A. PORAI-KOSCHITZ [with P. SOLODOWINKOFF and M. TROITZKI] (*Zeitsch. Farb. Ind.*, 1907, 6, 291—295. Compare Rupe and Porai-Koschitz, Abstr., 1906, i, 754; Nölting and Witte, *ibid.*, 886).—2-m-Aminostyryl-6-methylquinoline, $\text{C}_9\text{NH}_6\text{Me}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, prepared by reducing with stannous chloride and hydrochloric acid the corresponding nitro-compound prepared from *m*-nitrobenzaldehyde and 2:6-dimethylquinoline (Gasda, Abstr., 1906, i, 41), crystallises from benzene in slightly yellow needles, m. p. 160.5° , and gives a yellow hydrochloride, $\text{C}_{18}\text{H}_{16}\text{N}_2\cdot 2\text{HCl}$.

2-p-Nitrostyryl-6-methylquinoline, $\text{C}_9\text{NH}_6\text{Me}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, prepared by condensing *p*-nitrobenzaldehyde with 2:6-dimethylquinoline, crystallises from pyridine as a bright green powder, m. p. 177° ; its reduction gives 2-p-aminostyryl-6-methylquinoline, which crystallises from dilute alcohol in bright yellow leaflets, m. p. 173° after darkening at 164° ; the hydrochloride, $\text{C}_{18}\text{H}_{16}\text{N}_2\text{HCl}$, is purple-red, and the benzoyl derivative forms an orange, crystalline powder, m. p. 224° .

2-p-Dimethylaminostyryl-6-methylquinoline,
 $\text{C}_9\text{H}_6\text{MeN}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, obtained from *p*-dimethylaminobenzaldehyde and 2:6-dimethylquinoline, crystallises from dilute alcohol or pyridine in long, yellow needles, m. p. 198° ; the hydrochloride, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{HCl}$, is a purple, crystalline powder.

5-m-Aminostyrylacridine, $\text{C}_{12}\text{NH}_8\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, prepared by reducing 5-m-nitrostyrylacridine (Friedländer, Abstr., 1905, i, 829) with stannous chloride and hydrochloric acid, crystallises from pyridine in short, yellow needles, m. p. $232-234^\circ$; its salts are vermillion-red.

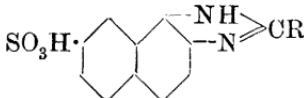
5-p-Nitrostyrylacridine, prepared by heating *p*-nitrobenzaldehyde

with 5-methylacridine and zinc chloride at 140—150°, crystallises from alcohol in small, bright yellow needles, m. p. 212°; its salts are sparingly soluble in water. 5-p-Aminostyrylacridine, obtained by reducing the foregoing, or by heating aminobenzaldehyde with 5-methylacridine and zinc chloride at 120°, crystallises from alcohol as a yellow powder, m. p. 209°. 5-p-Dimethylaminostyrylacridine, prepared by fusing *p*-dimethylbenzaldehyde with 5-methylacridine and zinc chloride during six hours at 135°, crystallises from alcohol; m. p. 238—239.5°; the hydrochloride, $C_{23}H_{20}N_2 \cdot HCl$, is blue; the dihydrochloride, yellow and unstable.

The foregoing *p*-aminobenzylidene compounds, derived from 6-methylquinaldine and 5-methylacridine, dye wool, silk, and mordanted cotton darker shades (orange to red) than the corresponding benzylidene compounds; on the other hand, the *m*-aminobenzylidene compounds either do not possess tinctorial properties or are only feebly yellow.

W. A. D.

Preparation of 2-Derivatives of 6-Hydroxy- $\alpha\beta$ -naphthiminazole-8-sulphonic Acid. AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 181178. Compare Abstr., 1906, i, 713).—



The naphthiminazole derivatives, derived from 1 : 2-diaminonaphthalene-5 : 7-disulphonic acid on fusion with alkali hydroxides, lose the sulphonic group in position 5, and become converted into

6-hydroxy- $\alpha\beta$ -naphthiminazole-8-sulphonic acids having the annexed general formula.

G. T. M.

Action of Ethylamine on Isatin. C. HASLINGER (*Ber.*, 1907, 40, 3598—3601. Compare this vol., i, 657).—Whilst the action of aromatic amines and diamines, and of pyrrole and piperidine on isatin, has been investigated exhaustively, of the aliphatic amines that of amylamine only has been studied (Schiff, *Annalen*, 1867, 144, 53). Ethylamine is now found to react with dibromoisatin yielding a yellow, a colourless, and a green product, depending on the conditions of the reaction. Under similar conditions, isatin and bromoisatin yield each only a yellow and a colourless product. All three classes of compounds dissolve in concentrated sulphuric acid, the yellow compounds forming a red to reddish-violet, the green compound forming a blue, solution from which the corresponding isatin is precipitated on addition of water; the colourless compounds form colourless solutions and are reprecipitated unchanged on dilution. With fuming hydrochloric acid, the yellow compounds form red solutions, which slowly become orange-yellow and deposit the isatin; the blue compound gives the same reaction, but more slowly, whilst the colourless compounds remain undissolved.

3-Ethyliminoisatin, $C_6H_4\begin{array}{c} N \\ \diagdown \\ C(NEt) \end{array}\begin{array}{c} \diagup \\ C \end{array} OH$, prepared by treating isatin with an equal amount of 33% alcoholic ethylamine solution, crystallises in yellow needles and intumesces at 152°, forming a violet mass which dissolves in alcohol to a reddish-violet solution.

3 : 3-Diethylamino-1-ethyl- ψ -isatin, $C_6H_4\begin{array}{c} \text{---N---} \\ | \\ \text{C}(\text{NHET})_2 \end{array}>\text{CO}$, prepared by treating isatin with four times its weight of 33% alcoholic ethylamine solution, separates from ethyl acetate in white crystals and rapidly decomposes, losing ethylamine, in solution.

5-Bromo-3-ethyliminoisatin, $C_{10}H_9\text{ON}_2\text{Br}$, forms yellow crystals and intumesces at about 167° , forming a violet mass; the potassium derivative, $C_{10}H_8\text{ON}_2\text{BrK}$, crystallises in red needles.

5 : 7-Dibromo-3-ethyliminoisatin, $C_{10}H_8\text{ON}_2\text{Br}_2$, is yellow, and decomposes about 175° .

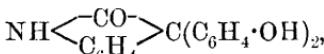
5 : 7-Dibromo-3 : 3-diethylamino-1-ethyl- ψ -isatin, $C_{14}H_{19}\text{ON}_3\text{Br}_2$, forms white needles, and is stable towards solvents.

5 : 7-Dibromo-2-ethylaminoisatin (5 : 7-dibromo-2-ethylimino- ψ -isatin), $C_6H_4\begin{array}{c} \text{---N---} \\ | \\ \text{CO} \end{array}>\text{C:NHET}$ or $C_6H_4\begin{array}{c} \text{---NH---} \\ | \\ \text{CO} \end{array}>\text{C:NET}$, prepared by prolonged action of an excess of ethylamine on dibromoisatin, forms green crystals.

Dichloroisatin yields the three corresponding derivatives with ethylamine.

G. Y.

Oxidation of Phenolisatin. CARL LIEBERMANN and N. DANAILA (*Ber.*, 1907, 40, 3588—3597).—In connexion with the study of indigotin-like colouring matters from isatin (this vol., i, 657), the authors have investigated the constitution of the dye formed by oxidation of phenolisatin. Baeyer and Lazarus (*Abstr.*, 1886, 155) showed phenolisatin to have the constitution



and considered the deep red dye formed by oxidation of this with potassium ferricyanide in alkaline solution to be aminobenzaurin,

$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\begin{array}{c} \text{---C---} \\ | \\ \text{O} \end{array}\text{H}_4$. It is found now that this dye is

2-aminoaurin, $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})\begin{array}{c} \text{---C---} \\ | \\ \text{O} \end{array}\text{H}_4$, only traces of aminobenzaurin being formed.

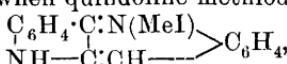
The name diphenolisatin is to be preferred to phenolisatin as more in agreement with the constitution. Diphenolisatin, m. p. 260—261° (220° : Baeyer and Lazarus, *loc. cit.*), forms stable compounds with ether, m. p. 70—80°, and chloroform, decomp. 110°. Contrary to Baeyer and Lazarus' statement, diphenolisatin forms a triacetate, $\text{C}_{20}\text{H}_{12}\text{O}_3\text{NAC}_3$, which separates from alcohol in white, microscopic crystals, m. p. 201—202°.

Halogenated diphenolisatins are prepared from halogenated isatins in the same manner as diphenolisatin from isatin. **Bromodiphenolisatin,** $\text{NH}\begin{array}{c} \text{---CO---} \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{array}>\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, crystallises in white needles, m. p. 235—236°, and forms a triacetate, $\text{C}_{20}\text{H}_{11}\text{O}_3\text{NBrAC}_3$, m. p. 217°. **Dibromodiphenolisatin,** $\text{NH}\begin{array}{c} \text{---CO---} \\ | \\ \text{C}_6\text{H}_2\text{Br}_2 \end{array}>\text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$, forms a diacetate, $\text{C}_{20}\text{H}_{11}\text{O}_3\text{NBr}_2\text{AC}_2$, m. p. 237—238°. **Chlorodiphenolisatin,** m. p. 237—238°. **Dichlorodiphenolisatin,** m. p. 276—277°.

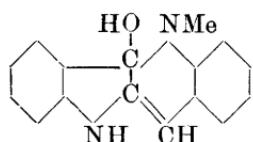
Diphenolisatins are oxidised to aminoaurins by potassium ferricyanide in alkaline solution or by potassium persulphate. The action of iodine on diphenolisation in alkaline solution leads to the formation of a bluer colour. The aminoaurins are obtained in orange, amorphous powders, insoluble in water or benzene, but readily soluble in cold alcohol or glacial acetic acid; the absorption bands in the spectra of the cherry-red, alkaline solutions lie nearer to the D line than those in the aurin spectrum. The coloration with concentrated sulphuric acid is redder with aminoaurin than with aurin.

The following aminoaurins have been analysed: 2-aminoaurin (*isatin-red*), $C_{19}H_{15}O_3N$; 5-bromo-2-aminoaurin, $C_{19}H_{14}O_3NBr$; 3:5-dibromo-2-aminoaurin, $C_{19}H_{13}O_3NBr_2$; 5-chloro-2-aminoaurin, $C_{19}H_{14}O_3NCl$; dichloro-2-aminoaurin, $C_{19}H_{13}O_3NCl_2$. G. Y.

Methylquindolanol. FRIEDRICH FICHTER and HANS PROBST (*Ber.*, 1907, 40, 3478).—It was shown by Fichter and Boehringer (this vol., i, 92) that, when quindoline methiodide,



is treated with sodium hydroxide, it forms a ψ -base, *methylquindolanol*, which, it is now found, has the annexed formula; it crystallises from methyl alcohol in tiny needles. The application of the Zeisel method showed that no methoxy-groups were present. A. McK.



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Preparation of Aromatic Monoacetyltrialamines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 183843).—The aromatic monoacetyltrialamines have hitherto not been obtained by the reduction of aromatic 2:4-dinitroacylamines owing to the resultant condensation between the contiguous amino- and acylamino-groups leading to the production of the anhydro-bases of the iminoazole series. It has now been found that reduction without condensation can be effected by the use of mild reducing agents, such as iron and dilute acetic or mineral acids.

4-Acetylamino-m-phenylenediamine, $NHAc \cdot C_6H_3(NH_2)_2$, prismatic crystals, m. p. 158—159°, results from the mild reduction of 2:4-dinitroacetanilide; when heated above its melting point or when boiled with glacial acetic acid, it loses water, forming aminomethylbenzimidazole.

2-Acetylamino-3:5-tolylenediamine, $NHAc \cdot C_6H_3Me(NH_2)_2$, yellow needles, m. p. 210—211°, is less soluble than the preceding base, and is obtained from 3:5-dinitroaceto-o-toluidide in a similar manner. Favourable results are obtained by substituting these new bases for the ordinary meta-diamines in the production of azo-dyes.

G. T. M.

[**Preparation of Triaminotriphenylethylene.**] GEORGES IMBERT and CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 180011).—Trichloro- or tribromo-ethylene or acetylene tetrachloride, or the

corresponding tetrabromide, when mixed with aniline and heated with a solution of alkali hydroxide or carbonate, furnishes an excellent yield of triaminotriphenylethylene, a base which is of use in pharmaceutical chemistry and the colour industry. G. T. M.

Oxazine Dyes. RUDOLF NIETZKI and VICTOR BECKER (*Ber.*, 1907, 40, 3397—3400).—1 : 4-Diamino-2-naphthol forms a stable *hydrochloride*, $C_{10}H_{10}ON_2 \cdot 2HCl$, which attacks the mucous membrane. The free base rapidly turns brown on exposure to the air. A blue oxazine dye, *diaminonaphthoxazone*, $NH_2 \cdot C_{10}H_5 \begin{matrix} N \\ < \\ O \end{matrix} > C_{10}H_5 \cdot NH$, is obtained when an alcoholic solution of this hydrochloride is boiled with crystallised sodium acetate while a current of air is passed through the solution. It forms well-developed, glistening crystals. A crystalline *hydrochloride*, $C_{20}H_4ON_3Cl$, is formed when the base is dissolved in phenol, precipitated with alcohol and hydrochloric acid, and dried at 100° . It dyes cotton mordanted with tannin, and its alcoholic and acetic acid solutions exhibit a brilliant red fluorescence. When the aminosulphonic acid, known as eikonogen, is used in place of the diaminonaphthol, a *disulphonic acid* derivative of the above dye is obtained.

1 : 4-Diamino- β -naphthol-6-sulphonic acid yields a *diaminonaphthoxazonedisulphonic acid*, which dyes wool in an acid-bath a blue colour. J. J. S.

Synthesis of Iminoazolylethylamine [4- β -Aminoethylglyoxaline]. ADOLF WINDAUS and W. VOGT (*Ber.*, 1907, 40, 3691—3695).—The recognition that glyoxaline radicles are contained in the alkaloid pilocarpine (Jowett, *Trans.*, 1903, 83, 438) and in substances derived from proteins like histidine (Pauly, *Abstr.*, 1904, i, 1068) has suggested the synthesis of these natural products. As a step in this direction, glyoxaline-4-propionic acid (*Abstr.*, 1905, i, 834) has been converted into 4- β -aminoethylglyoxaline, $\begin{matrix} NH \cdot CH \\ | \\ CH = N \end{matrix} \begin{matrix} NH \\ > \\ C \end{matrix} CH_2 \cdot CH_2 \cdot NH_2$, by means of Curtius' method.

Ethyl glyoxalinepropionate is a colourless oil, obtained by esterification and purification by means of the *oxalate*, which crystallises in rhombic plates, m. p. 155° ; the *picrolonate* forms light yellow needles, m. p. 226° (decomp.). The *hydrazide*, $C_6H_{10}ON_4$, obtained by the interaction of the ester and 50% hydrazine hydrate, has m. p. 142° . The *hydrochloride* of aminoethylglyoxaline is obtained in 55% yield by treating an alcoholic solution of the hydrazide with amyl nitrite and hydrochloric acid to form the azoimide, decomposing this to obtain the urethane, and finally hydrolysing the urethane. It crystallises in prisms, m. p. 240° (decomp.). No sparingly soluble salts are given by ammoniacal zinc or silver hydroxides in contradistinction to other glyoxaline compounds. The *platinichloride* is orange, blackens towards 200° , but does not melt; *picrate*, m. p. 239° (decomp.); *picrolonate* is characteristic, m. p. 266° (decomp.).

By treating the aminoethylglyoxaline with benzoyl chloride and

sodium hydroxide, the ring is ruptured and *tribenzoylbutenetriamine*, $\text{NHBz}\cdot\text{CH}\cdot\text{C}(\text{NHBz})\cdot[\text{CH}_2]_2\cdot\text{NHBz}$, is obtained as glistening needles, m. p. 191°.

W. R.

Behaviour of Hydrogen Cyanide towards Phenylcarbimide.
II. WALTER DIECKMANN and HEINRICH KÄMMERER (*Ber.*, 1907, 40, 3737—3743. Compare *Abstr.*, 1905, i, 874).—By the action of sodium ethoxide, diphenylparabanimide is converted into the isomeric *as-oxalyldiphenylguanidine*, $\text{NPh}\cdot\text{C}\begin{array}{c} \text{NPh}\cdot\text{CO} \\ \swarrow \\ \text{NH} \end{array}\text{CO}$, m. p. 225°, which forms colourless prisms, has acid properties, and is hydrolysed by concentrated hydrochloric acid yielding aniline and *phenylparabanic acid*, m. p. 209—210°. The two new compounds are also obtained by the condensation of ethyl oxalate with diphenylguanidine and phenylcarbamide respectively in the presence of sodium ethoxide.

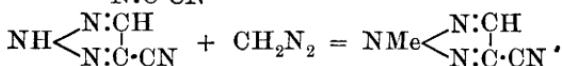
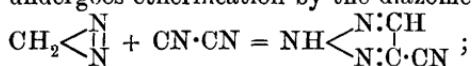
Melanoximide (*s-oxalyldiphenylguanidine*), m. p. 225°, which is obtained most conveniently by warming diphenylguanidine cyanide with dilute acetic acid, is also converted by sodium ethoxide into *as-oxalyldiphenylguanidine*.

With phenylcarbimide at 120°, diphenylparabanimide yields the *carbanilide*, $\text{NPh}\cdot\text{CO}\cdot\text{N}:\text{C}\begin{array}{c} \text{CO} \\ \swarrow \\ \text{NPh}\cdot\text{CO} \end{array}$, m. p. 233°, which is therefore the final product of the action of hydrogen cyanide on phenylcarbimide (*loc. cit.*). By prolonged heating with glacial acetic acid, the carbanilide yields diphenylparabanic acid, whereas hydrolysis by a mixture of hydrochloric and glacial acetic acids forms in addition phenylcarbamide.

Phenylcarbamide is hydrolysed by boiling acetic acid yielding diphenylcarbamide and small quantities of aniline and acetanilide; by dilute hydrochloric acid giving ammonium chloride, aniline hydrochloride, and carbon dioxide, and by boiling water forming diphenylcarbamide, ammonia, aniline, and carbon dioxide.

C. S.

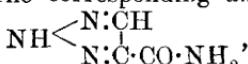
Action of Diazo-derivatives of Aliphatic Hydrocarbons on Cyanogen and its Derivatives. I and II. Cyanogen. ALBERTO PERATONE and E. AZZARELLO (*Atti R. Accad. Lincei*, 1907, [v], 16, ii, 237—243; 318—328. Compare Azzarello, *Abstr.*, 1905, i, 867).—An ethereal solution of cyanogen reacts violently with a 2—5% ethereal solution of diazomethane or diazoethane, forming a cyano-derivative of osotriazole, which, unless special precautions are taken, undergoes etherification by the diazomethane :



In order to prevent the etherification, a very small amount of the diazo-compound must be treated with a large excess of cyanogen in cold ethereal solution. The fact that only one of the CN groups in the cyanogen molecule reacts with the diazo-hydrocarbon, no com-

pound consisting of two triazole nuclei joined by their carbon atoms being formed, would indicate a structure other than $\text{N}:\text{C}\cdot\text{C}:\text{N}$ for cyanogen. The balance of evidence, which the authors review, is, however, in favour of the above formula.

3-Cyano-osotriazole, $\text{NH} < \begin{matrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{C}\cdot\text{CN} \end{matrix}$, separates from benzene in small, white crystals, m. p. $113-114^\circ$, and gives precipitates with salts of many heavy metals. The corresponding *amide*,



prepared by the action of alcoholic potassium hydroxide on the cyano-compound, is deposited from alcohol in small, white crystals, m. p. $256-257^\circ$. When treated with 40% alcoholic potassium hydroxide solution, or with concentrated hydrochloric acid, it yields the osotriazole-carboxylic acid described by Baltzer and von Pechmann (*Abstr.*, 1891, 1116), and this, when heated at $230-240^\circ$, is converted into the osotriazole prepared by these authors.

3-Cyano-1-methylosotriazole, $\text{NMe} < \begin{matrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{C}\cdot\text{CN} \end{matrix}$, is a colourless, neutral liquid, b. p. $95^\circ/30$ mm., having a fruity odour. When heated with 40% alcoholic potassium hydroxide, it is converted quantitatively into the potassium derivative of *1-methylosotriazole-3-carboxylic acid*, $\text{NMe} < \begin{matrix} \text{N}:\text{CH} \\ | \\ \text{N}:\text{C}\cdot\text{CO}_2\text{H} \end{math>, which is deposited from acetone or benzene in small, white crystals, m. p. $141-142^\circ$. The *potassium*, $\text{C}_4\text{H}_4\text{O}_2\text{N}_3\text{K}$, *barium*, $(\text{C}_4\text{H}_4\text{O}_2\text{N}_3)_2\text{Ba}, 3\frac{1}{2}\text{H}_2\text{O}$, and *calcium* salts, and the *ethyl ester*, $\text{C}_2\text{N}_3\text{HMe}\cdot\text{CO}_2\text{Et}$, b. p. $115^\circ/60$ mm., were prepared.$

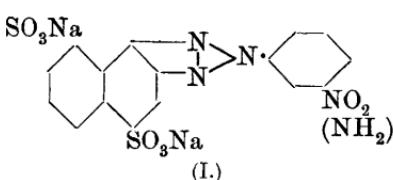
4-Cyano-3-methylosotriazole, $\text{NH} < \begin{matrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{C}\cdot\text{CN} \end{matrix}$, separates from benzene in small, white crystals, m. p. 84° , b. p. $160^\circ/30$ mm., has the normal molecular weight in freezing acetic acid, and, in aqueous solution, has an acid reaction. The *silver derivative*, $\text{C}_4\text{H}_3\text{N}_4\text{Ag}$, is a white powder stable towards light.

3-Methylosotriazole-4-carboxylic acid, $\text{NH} < \begin{matrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{C}\cdot\text{CO}_2\text{H} \end{matrix}$, separates from water in shining, acicular crystals, m. p. 214° (decomp.); the *calcium salt*, $(\text{C}_4\text{H}_4\text{O}_2\text{N}_3)_2\text{Ca}$, was prepared.

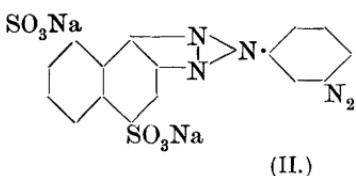
4-Cyano-3-methyl-1-ethylosotriazole, $\text{NMe} < \begin{matrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{C}\cdot\text{CN} \end{matrix}$, is an oily, neutral liquid, b. p. $105^\circ/28$ mm. *3-Methyl-1-ethylosotriazole-4-carboxylic acid*, $\text{NMe} < \begin{matrix} \text{N}:\text{CMe} \\ | \\ \text{N}:\text{C}\cdot\text{CO}_2\text{H} \end{math}, crystallises from benzene in shining, white needles, m. p. 131° ; its *calcium salt*, $(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)_2\text{Ca}$, was prepared.$

T. H. P.

[**3' - Aminophenyl - $\alpha\beta$ - naphthatriazole - 5 : 9 - sulphonic Acid.**] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.P. 174548).—*Sodium-3'-nitrophenyl - $\alpha\beta$ - naphthatriazole - 5 : 9-sulphonate*,



(I) was prepared by coupling *m*-nitrodiazobenzene chloride with α -naphthylamine-3:8-disulphonic acid in sodium carbonate solution, and then, after 20 hours, warming the liquid to 70–75° and adding aqueous sodium hypochlorite. The product was salted out and reduced with iron filings and water acidified with hydrochloric acid ; the solution was rendered alkaline with sodium carbonate and 3-aminophenyl- $\alpha\beta$ -naphthatriazole-4 : 9-disulphonic acid (I) precipitated from the filtrate by adding hydro-



G. T. M.

The Mechanism of the Indamine and Azine Synthesis. Willstätter's Paper on Aniline-Black. HANS TH. BUCHERER (*Ber.*, 1907, 40, 3412—3419). Compare this vol., i, 641).—The syntheses of indamines, azines, thiazines, and oxazines are represented by a single scheme, based on the two following facts. (1) The readiness with which *o*- and *p*-diamines, -aminophenols, dihydroxy-derivatives, and the corresponding sulphur compounds are oxidised. (2) The readiness with which monoimines, di-imines, quinols, and the corresponding sulphur compounds form additive compounds. In addition, attention is drawn to the readiness with which groups attached to nitrogen, oxygen, or sulphur wander into the nucleus. The two reactions, which occur alternately in the case of a *p*-diamine, may be represented as (a) *p*-diamine + O → *p*-di-imide and (b) *p*-di-imide + HX → *p*-diamine with the X group attached to nitrogen.

Several examples are worked out in detail, more especially the formation of safranine, methylene-blue, and Meldola's blue. Also the formation of 2 : 2'-diaminoazobenzene from *o*-quinonedi-imine and of di-aminoazodiphenyl from the oxidation product of benzidine.

Willstätter's formula for aniline-black is criticised. J. J. S.

Action of Hydroxylamine on Safranones. OTTO FISCHER and FRITZ RÖMER (*Ber.*, 1907, 40, 3406—3411). Compare Fischer and Arntz, this vol., i, 94; Kehrmann and Prager, *ibid.*, 447).—Kehrmann and Prager's view of the constitution of the aminoisorosindone, obtained by the action of hydroxylamine on *is*orosindone, is confirmed, since the ethers obtained by the action of alkyl iodides and potassium hydroxide on the corresponding hydroxyisorosindone are not identical with the ethers of naphthasafranol. The ortho-position of the methoxy-

group in the methyl ether has been established by the synthesis of the ether from nitrosoguaiacol and β -phenylnaphthylamine.

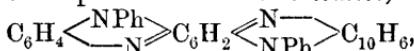
It appears that only those safranones yield amino-derivatives with hydroxylamine which are free from substituents in the two ortho-positions with respect to the quinone oxygen. Thus rosindone, *o*-methoxyisorosindone, and β -*o*-methylisorosindone (Abstr., 1901, i, 417) do not yield amino-derivatives.

Safranol does not yield an amino-derivative with hydroxylamine, but safranol ethyl ether yields *o*-aminosafranol ethyl ether, $C_{20}H_{17}O_2N_3$, which crystallises from alcohol in brilliant brown plates, m. p. about 250° . The addition of concentrated hydrochloric acid to the alcoholic or acetic acid solution produces a yellowish-green coloration. The corresponding methyl ether is less soluble in alcohol.

o-Anilinoisorosindone, $C_{28}H_{19}ON_3$, obtained by heating *o*-aminoisoroindone with aniline and aniline hydrochloride at 150° , crystallises from alcohol in bronze-coloured needles, m. p. 282—284°.

A naphthafluorindine, $C_6H_4\begin{array}{c} \text{NH} \\ \swarrow \\ \text{N} \\ \searrow \end{array} C_6H_2\begin{array}{c} \text{N}^- \\ \swarrow \\ \text{NPh} \\ \searrow \end{array} C_{10}H_6$, is obtained when *o*-aminoisoroindone, *o*-phenylenediamine, and its hydrochloride are heated with ethyl alcohol at 140 — 150° for three hours; it crystallises from pyridine in golden-bronze, glistening plates, which dissolve in glacial acetic acid yielding a pure blue solution. The same product is formed when isorosindone is used instead of its amino-derivative, and even more readily from isorosinduline salts and *o*-phenylenediamine (compare Fischer and Hepp, Abstr., 1896, i, 323).

o-Aminoisoroindone, or isorosindone, when heated with *o*-amino-diphenylamine, its hydrochloride, and absolute alcohol at 150° for four hours, yields a green naphthafluorindine derivative,



which crystallises from dimethylaniline in prisms.

Aminoisoroindone, or isorosinduline, and *o*-naphthylenediamine also yield a green dye. These naphthafluorindine dyes exhibit but little fluorescence except in concentrated sulphuric acid or pyridine solutions (compare Nietzki and Vollenbruck, Abstr., 1904, i, 1062). J. J. S.

Disulphides with Neighbouring Double Linkings. Action of Amines and Hydrazines on Thiourets. New Synthesis of Triazoles. II. EMIL FROMM & EMIL VETTER (*Annalen*, 1907, 356, 178—196). Compare Fromm, Abstr., 1906, i, 656; Fromm and Schneider, *ibid.*, 656, 714; Hantzsch and Wolvekamp, Abstr., 1904, i, 719).—Perthiocyanic acid and thiouret undergo analogous reactions with potassium hydroxide, yielding sulphur and potassium cyanoaminodithiocarbonate and phenyliminocyanatoaminothiocarbonate respectively. The present work was undertaken to determine if thiouret reacts with aniline and phenylhydrazine in a manner analogous to the reaction of perthiocyanic acid with these reagents, which leads to the formation of phenyldithiobiuret and derivatives of triazole respectively.

When heated with aniline on the water-bath in absence of a solvent, phenylthiouret hydrochloride yields thiocarbanilide, but if the reaction

is moderated by dilution of the mixture with alcohol, sulphur and *phenylguanidophenylthiocarbamide*, $\text{NHPH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NPh})\cdot\text{NH}_2$, are formed. This crystallises in white leaflets, m. p. 197°, forms a crystalline *hydrochloride*, $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}\cdot\text{HCl}$, m. p. 179°, and on treatment with benzyl chloride and alcoholic sodium hydroxide yields the *benzyl derivative*, $\text{C}_{21}\text{H}_{20}\text{N}_4\text{S}$, m. p. 157°.

The constitution of the products of the action of amines on thiouret hydrochlorides is confirmed by the formation of isomeric substances from phenylthiouret hydrochloride and *p*-phenetidine, on the one hand, and from *p*-phenetylthiouret hydrochloride and aniline, on the other, since if the products of the reaction had the constitution



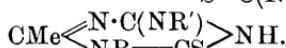
these two combinations would yield the same substance.

p-Phenetylguanidophenylthiocarbamide, $\text{C}_{16}\text{H}_{18}\text{ON}_4\text{S}$, formed from phenylthiouret hydrochloride and *p*-phenetidine, crystallises in leaflets, m. p. 168°, and forms a *benzyl derivative*, $\text{C}_{23}\text{H}_{24}\text{ON}_4\text{S}$, m. p. 230°.

The action of *p*-phenetidine on perthiocyanic acid leads to the formation of *p-phenetylthiocobiuret*, $\text{C}_{10}\text{H}_{13}\text{ON}_3\text{S}_2$, crystallising in leaflets, m. p. 178°, and *di-p-phenetylthiocarbamide*, $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2\text{S}$, crystallising in leaflets, m. p. 170°.

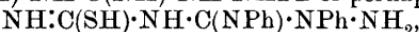
p-Phenethylthiouret hydrochloride, $\text{C}_{10}\text{H}_{11}\text{ON}_3\text{S}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$, m. p. 137°, reacts with aniline, forming *phenylguanido-p-phenetylthiocarbamide*, m. p. 170°. This yields a *benzyl derivative*, $\text{C}_{23}\text{H}_{24}\text{ON}_4\text{S}$, crystallising in leaflets, m. p. 166°.

The arylguanidoarylthiocarbamides form acetyl derivatives, $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}(\text{NR}')\cdot\text{NHAc}$, which are converted by the action of alkalis into anhydro-compounds : $\text{CMe}\begin{array}{l} \swarrow \\ \text{N}\cdot\text{C}(\text{NR}') \\ \searrow \end{array}>\text{NH}$ or

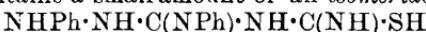


Acetylphenylguanidophenylthiocarbamide, R and R' = Ph, m. p. 240°; the *anhydro*-compound, needles, m. p. 200°; when heated with benzyl chloride and potassium hydroxide, it forms the *benzyl derivative* of *phenylguanidophenylthiocarbamide*. *Acetyl-p-phenetylguanidophenylthiocarbamide*, m. p. 183°; the *anhydro*-compound, m. p. 204°. *Acetyl-phenylguanido-p-phenetylthiocarbamide*, needles, m. p. 172°; the *anhydro*-compound, m. p. 187°.

When heated with phenylhydrazine in alcoholic solution, *phenylthiouret hydrochloride* forms sulphur and *anilguanidophenylthiocarbamide*, $\text{NPh}\cdot\text{C}(\text{SH})\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{NPh}$ or perhaps



which separates from alcohol in crystals, m. p. 167°, and if heated with alcoholic sodium hydroxide or dilute hydrochloric acid yields 3-amino-5-anilino-1-phenyltriazole or its hydrochloride (Fromm and Göncz, this vol., i, 872). The filtrate from the preparation of *anilguanidophénylthiocarbamide* contains a small amount of an *isomeride*,



or $\text{NH}_2\cdot\text{NPh}\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{C}(\text{NPh})\cdot\text{SH}$, which on successive treatment with sodium hydroxide and hydrochloric acid yields 5-amino-3-anilino-1-phenyltriazole hydrochloride (Fromm and Göncz, *loc. cit.*).

Anilguanido-p-phenetylthiocarbamide, $\text{C}_{16}\text{H}_{19}\text{ON}_5\text{S}$, m. p. 168°

(decomp.), when boiled with sodium hydroxide in alcoholic solution, yields 3-amino-5-p-phenetidino-1-phenyltriazole, $C_{16}H_{17}ON_5$, m. p. 134° ; the hydrochloride of this, $C_{16}H_{17}ON_5 \cdot HCl$, crystallises in thin leaflets, m. p. 66° . The acetyl derivative, $C_{20}H_{28}O_3N_5 \cdot H_2O$, crystallises in needles, m. p. $145-148^\circ$.

Aminophenylguanido-p-phenetylthiocarbamide, $C_{16}H_{19}ON_5S$, obtained from the mother-liquor from the preparation of its isomeride, crystallises in white leaflets, m. p. 236° , and when treated successively with sodium hydroxide and hydrochloric acid yields 5-amino-3-p-phenetidino-1-phenyltriazole hydrochloride, m. p. 175° , which is sparingly soluble. The free triazole forms a gelatinous mass and is readily soluble in alcohol.

G. Y.

isoPurone. JULIUS TAFEL and PERCY ALFRED HOUSEMAN (*Ber.*, 1907, 40, 3743—3751. Compare Tafel, *Abstr.*, 1901, i, 236).—The products obtained by the electrolytic reduction of uric acid are treated with concentrated ammonium hydroxide to separate the tetrahydro-uric acid, with sodium hydroxide to remove *isopurone*, and the residue yields purone by crystallisation from hot water. *isoPurone* is an unsaturated substance which can be estimated by iodine and thiosulphate. The molecular weights of purone and of *isopurone* determined in aqueous solution by the ebullioscopic method correspond with the formula $C_5H_8O_2N_4$.

isoTetrahydrouric acid, $C_5H_8O_3N_4$, prepared by the action of bromine on an aqueous solution of *isopurone* at 0° , crystallises in colourless needles, decomposes at 200° , has a neutral reaction, and dissolves readily in alkalis. A boiling solution of barium hydroxide converts it into the yellow *barium* salt of α -*isouracil*, $C_4H_6O_4N_2Ba$, from which careful treatment with 2*N*-hydrochloric acid at -10° liberates α -*isouracil*, $C_4H_4O_2N_2$. This substance crystallises in needles, decomposes at 350° , has an acid reaction, dissolves in dilute alkalis, decolorises bromine water, and gives a violet-brown coloration with ferric chloride.

The mother-liquor from which the barium salt of α -*isouracil* has been precipitated contains β -*isouracil*, $C_4H_4O_2N_2$, which crystallises in slender needles, has a neutral reaction, dissolves in dilute alkalis, and forms a crystalline substance with phenylhydrazine which seems to be a hydrazone.

C. S.

Reduction of Theophylline and Paraxanthine. JULIUS TAFEL and JULIUS DODT (*Ber.*, 1907, 40, 3752—3757. Compare *Abstr.*, 1900, i, 121).—The electrolytic reduction of theophylline in 30% sulphuric acid at the ordinary temperature, with prepared lead cathodes and a current density of 12 amperes per sq. dm., results in the formation of *deoxytheophylline*, $C_7H_{10}ON_4$, which separates from hot water in crystals containing $3H_2O$, darkens at 200° and has m. p. $215-225^\circ$, has a faintly alkaline reaction, and is soluble in dilute acids or alkalis; the hydrochloride and the picrate are mentioned. By the action of bromine in cold glacial acetic acid, the substance yields *bromodeoxytheophylline*, $C_7H_9ON_4Br$, which is converted by sodium hydroxide into *6-hydroxydeoxytheophylline*, $C_7H_{10}O_2N_4 \cdot 2H_2O$.

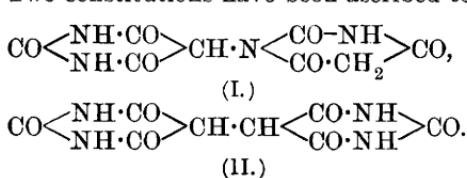
Analogous compounds are obtained from paraxanthine by similar treatment. *Deoxyparaxanthine*, $C_7H_{10}ON_4$, crystallises from water with $\cdot 1H_2O$, decomposes at 250° , has a neutral reaction, and is not more soluble in dilute alkalis than in water. *Bromodeoxyparaxanthine*, $C_7H_9ON_4Br$, dissolves in water to a strongly acid solution, and is converted by sodium hydroxide into *6-hydroxydeoxyparaxanthine*, $C_7H_{10}O_2N_4 \cdot 2H_2O$, which darkens at 230° .

C. S.

Acidity of Deoxyxanthines. JULIUS TAFEL and JULIUS DODT (*Ber.*, 1907, 40, 3757—3759. Compare preceding abstract).—It has been shown that deoxyxanthine, 3-methyldeoxyxanthine, and deoxytheophylline, unlike deoxyheteroxanthine, deoxyparaxanthine, and deoxytheobromine, are more soluble in dilute alkalis than in water. The authors have measured the strengths of these compounds by Wood's method (*Trans.*, 1906, 89, 1839) and arrive at the conclusions that the deoxyxanthines are weaker acids than the xanthines, and that in the deoxyxanthines the acid properties are conferred solely by the glyoxaline ring.

C. S.

Hydurlilic Acid. MAX CONRAD (*Annalen*, 1907, 356, 24—31).—Two constitutions have been ascribed to hydurlilic acid (I and II).

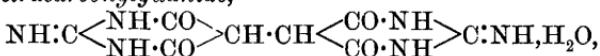


The author shows that the constitution II is the correct one. Since barbituric acid when heated with concentrated hydrochloric acid is hydrolysed forming carbon dioxide, ammonia, and acetic

acid, an acid of the constitution II must under the same conditions yield carbon dioxide, ammonia, and succinic acid. It is found that when heated with concentrated hydrochloric acid at 200 — 230° , hydurlilic acid yields succinic acid in almost quantitative amount.

The constitution II is supported also by the formation of hydurlilic acid by condensation of ethyl ethanetetracarboxylate with carbamide by means of alcoholic sodium ethoxide at 60 — 70° , and together with small amounts of succinic acid by hydrolysis of ethanetetracarbonylguanide by means of dilute hydrochloric acid at 150° .

Ethanetetracarbonylguanide,



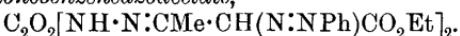
is prepared in a 63% yield by heating ethyl ethanetetracarboxylate with guanidine hydrochloride and sodium ethoxide in alcoholic solution at 70° ; it crystallises in needles, decomp. when heated, is readily soluble in alkali hydroxides or carbonates, separates in prisms on prolonged heating of its ammoniacal solution, and dissolves in cold nitric acid. The silver salt, $C_8H_6O_4N_6Ag_2 \cdot \frac{1}{2}H_2O$, was analysed; the hydrochloride crystallises in white needles. Ammonium hydurlilate gives a green coloration with ferric chloride, becoming colourless on addition of hydrochloric acid or on heating, and forms a red solution with potassium nitrite in acetic acid.

G. Y.

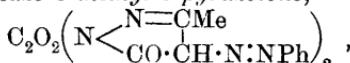
Azo-derivatives of Esters of Bis- β -ketonic Acid Oxalyldihydrazone. CARL BÜLOW [and, in part, MARTIN LOBECK] (*Ber.*, 1907, 40, 3787—3798).—The two methylene groups in ethyl oxalylbischydrazoneacetacetate (Bülow and Lobeck, this vol., i, 301) are capable of reacting, like the methylene group in compounds of the type $\text{COR}''\cdot\text{NH}\cdot\text{N}\cdot\text{CR}'\cdot\text{CH}_2\cdot\text{CO}_2\text{R}$, with diazobenzene chloride with the formation of *o*-azoacylhydrazones. These azo-derivatives are, generally speaking, far more stable than the parent substances.

Ethyl oxalylidihydrazone-benzeneazobisacetacetate,

$\text{CO}_2\text{Et}\cdot\text{CH}(\text{N}\cdot\text{NPh})\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, obtained by the action of diazobenzene chloride on ethyl oxalylbischydrazoneacetacetate in alcoholic solution in the presence of sodium acetate at low temperatures, crystallises in yellow, felted needles, m. p. 155° (unsharp); at the same time, is formed a small quantity of *ethyl oxalylbischydrazonebenzeneazoacetacetate*,



The latter compound alone is produced by using very dilute solutions, but is better prepared by the interaction of oxalylhydrazide and ethyl benzeneazoacetacetate in alcoholic or acetic acid solution. It forms colourless crystals, swells and froths up at $211-212^\circ$ or $217-218^\circ$, and decomposes slightly above this temperature into alcohol and 1 : 1-oxalylbis-4-benzeneazo-3-methyl-5-pyrazolone,



obtained as a yellowish-red, crystalline powder, m. p. $256-257^\circ$. This compound is decomposed by hot potassium hydroxide solution or pyridine into oxalic acid and 4-benzeneazo-3-methyl-5-pyrazolone (compare von Rothenburg, *Abstr.*, 1895, i, 686).

Ethyl oxalylbischydrazonebenzeneazoacetacetate is decomposed on boiling with phenylhydrazine in acetic acid solution with the formation of alcohol, oxalylhydrazide, and 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone.

The author replies to the criticisms of Curtius, Darapsky, and Müller (this vol., i, 451). W. H. G.

Action of Diazobenzene Chloride on *p*-Hydroxybenzoic Acid. EUGEN GRANDMOUGIN and H. FREIMANN (*Ber.*, 1907, 40, 3453—3454. Compare Limpricht, *Abstr.*, 1891, 1036).—Diazobenzene chloride reacts with a solution of *p*-hydroxybenzoic acid in the presence of sodium carbonate, yielding bisbenzeneazophenol together with a small amount of benzeneazo-*p*-hydroxybenzoic acid (Auwers and Röhrig, *Abstr.*, 1897, i, 341). In the presence of sodium hydroxide, the chief product is trisbenzeneazophenol (this vol., i, 664). J. J. S.

Preparation of 1-Diazo- β -naphtholdi- and tri-sulphonic Acids. KALLE & Co. (D.R.-P. 184477).—The 1-amino- β -naphthol-monosulphonic acids are diazotised normally with sodium nitrite in the presence of organic acids (*Abstr.*, 1905, i, 161); the corresponding di- and tri-sulphonic acids are readily converted into diazo-derivatives in the presence of sulphuric acid, provided that dilute solutions are

employed at 0° to 5°. The diazo-derivatives may be partially salted out from the yellowish-brown solution in the form of a brown mass.

G. T. M.

[The Diazotisation of 1-Amino- β -naphtholsulphonic Acids.]
GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 181714).—The interaction of nitrous acid and the 1-amino- β -naphtholsulphonic acids leads to the production of quinonoid substances, so that the reaction is largely one of oxidation. If, however, the sodium salts of these 1-amino- β -naphtholsulphonic acids are acetylated in the hydroxyl group with acetic anhydride, then the acetyl derivatives thus obtained furnish yellow, crystalline diazo-compounds, such as 2-acetoxy-1-diazonaphthalene-4-sulphonic acid, which, on treatment with dilute aqueous alkalis, lose their acetyl group and give rise to the corresponding 2-hydroxy-1-diazonaphthalenesulphonic acids. This elimination of acetyl may be effected similarly after combining the 2-acetoxy-1-diazonaphthalenesulphonic acid with phenol and aromatic amines, and in this way 2-hydroxyazonaphthalene colouring matters are produced which may be employed as mordant dyes. G. T. M.

Bisazo-derivatives of Salicylic Acid. EUGEN GRANDMOUGIN, J. R. GUISAN, and H. FREIMANN (*Ber.*, 1907, 40, 3450—3453. Compare Limpricht, *Abstr.*, 1891, 1036).—A mixture of bisbenzeneazosalicylic acid, benzeneazosalicylic acid, and the trisazo-derivative of phenol (this vol., i, 664) is formed when a solution of diazobenzene chloride and salicylic acid dissolved in sodium hydroxide is kept at 0° for some five days. The monoazo-compound remains dissolved in the alkaline solution, and may be precipitated by the addition of acid. The *bisbenzeneazosalicylic acid*, $\text{OH}\cdot\text{C}_6\text{H}_2(\text{N}_2\text{Ph})_2\cdot\text{CO}_2\text{H}$, may be extracted with hot dilute sodium hydroxide solution, and crystallises from chloroform in reddish-brown, felted needles, m. p. 218°. With sulphuric acid, it gives the colorations characteristic of bisazo-compounds, and when reduced with stannous chloride yields 3:5-diamino-salicylic acid.

The *acetyl* derivative of the bisazo-compound has m. p. 196°. *Bis-o-tolueneazosalicylic acid*, $\text{C}_{21}\text{H}_{18}\text{O}_3\text{N}_4$, forms dark violet crystals with a metallic lustre, m. p. 170°, and yields an *acetyl* derivative, m. p. 173°. *o-Tolueneazosalicylic acid*, $\text{C}_{14}\text{H}_{12}\text{O}_3\text{N}_2$, forms yellowish-brown needles, m. p. 191°, and yields an *acetyl* derivative, m. p. 145°.

Tris-o-tolueneazophenol, $\text{C}_{27}\text{H}_{22}\text{ON}_6$, forms bronze-coloured needles, m. p. 198°, and its *acetyl* derivative orange-coloured needles, m. p. 195°. Diazotised nitroanilines yield monoazo-derivatives together with bisazo-derivatives of phenol.

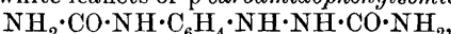
Bis-p-nitrobenzeneazophenol, $\text{C}_{18}\text{H}_{12}\text{O}_5\text{N}_6$, crystallises from nitrobenzene or tetrachloroethane in brown, felted needles, and its *acetyl* derivative has m. p. 208°. J. J. S.

Aromatic - aliphatic - *p* - aminoazo - compounds. WALTHER BORSCHE and A. RECLAIRE (*Ber.*, 1907, 40, 3806—3815).—The

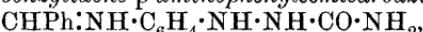
condensation products of quinoneoximes and semicarbazides (compare Borsche, Abstr., 1906, i, 319) are converted on reduction with tin and hydrochloric acid and subsequent oxidation, into aromatic-aliphatic-*p*-aminoazo-compounds of the type $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NHR}$, corresponding with the quinonemonosemicarbazones,



The reduction of either *p*-nitrophenylsemicarbazide (Hyde, Abstr., 1899, i, 688) or benzoquinone oximesemicarbazone (Thiele and Barlow, Abstr., 1899, i, 47) with tin and hydrochloric acid results in the formation of *p*-aminophenylsemicarbazide (*p*-aminobenzenehydrazoformamide) hydrochloride, colourless leaflets, decomposing at 195—196°; ammonia liberates the free base, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, as small, colourless needles, which rapidly oxidise in the air. A solution of the hydrochloride on treatment with potassium cyanate and sodium acetate deposits pearly, white leaflets of *p*-carbamidophenylsemicarbazide,



m. p. 201—202° (decomp.). Benzaldehyde reacts with the base with the formation of benzylidene-*p*-aminophenylsemicarbazide,



yellowish-white leaflets, m. p. 204° (decomp.).

p-Aminobenzeneazoformamide, obtained only in the form of a hydrate, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, is prepared by the oxidation of the hydrazo-compound; it crystallises in dark red needles with a blue reflex, m. p. 125—126° (decomp.). The molecule of water is not removed by keeping the compound some days in a vacuum desiccator. It is converted by strong hydrochloric acid into a greenish-yellow hydrochloride, and is decomposed on heating with potassium hydroxide solution according to the equation : $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2 + 2\text{KOH} = \text{NH}_2\text{Ph} + \text{N}_2 + \text{NH}_3 + \text{K}_2\text{CO}_3$; at the same time, a small quantity of a substance is formed, which crystallises in brown needles. *p*-Carbamidobenzene-azoformamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, prepared by acting on a solution of the hydrazo-compound with ammonia and hydrogen peroxide, crystallises in small, brick-red needles, m. p. 178° (decomp.).

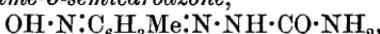
Phenylcarbamido-p-aminobenzeneazoformamide,



which results from the interaction of phenylcarbamide and the azo-compound, crystallises in yellowish-red needles, decomposing at 202°.

Benzoyl-p-aminobenzeneazoformamide, $\text{NHBz}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2$, forms small, orange needles, m. p. 218° (decomp.). Bromine acts on the parent azo-compound yielding 3:5(?)-dibromo-4-aminobenzeneazoformamide, $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{N}_2\cdot\text{CO}\cdot\text{NH}_2$, small, yellow needles, m. p. 183°.

2-Toluquinoneoxime-5-semicarbazone,

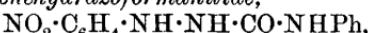


prepared by the interaction of 2-toluquinoneoxime and semicarbazide hydrochloride, is a brown, crystalline powder, decomposing at 220°. It yields, on reduction with tin and hydrochloric acid and subsequent oxidation of the hydrazo-compound, 2-aminotoluene-5-azoformamide, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}_2\cdot\text{H}_2\text{O}$, small, reddish-brown needles, m. p. 85—86° (decomp.). In the same way, are obtained 3-toluquinone-

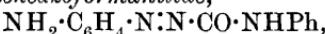
oxime-6-semicarbazone, small, brown needles, decomposing at 243°, and *2-thy whole quinone oxime-5-semicarbazone*,

$\text{OH}\cdot\text{N}:\text{C}_6\text{H}_3\text{MePr}^2\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$,
small, yellow needles, m. p. 221—222°, which also give rise to amino-azo-compounds.

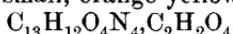
Phenylcarbamide combines with the three nitrophenylhydrazines, forming *o-nitrobenzenehydrazoformanilide*,



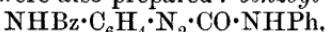
small, slender, yellow needles, m. p. 220°; *m-nitrobenzenehydrazoformanilide*, yellow leaflets, m. p. 220°, and *p-nitrobenzenehydrazoformanilide*, small, yellowish-white needles, m. p. 220°. Both the latter compound and benzoquinoneoximephenylsemicarbazone (Borsche and Kühl, Abstr., 1906, i, 320) yield on reduction with tin and hydrochloric acid *p-aminobenzenehydrazoformanilide hydrochloride*, small, colourless, slender needles, which decompose and turn violet above 190°; sodium carbonate liberates the free base, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPH}$, long, colourless needles, m. p. 187° (decomp.), which is converted on oxidation into *p-aminobenzeneazoformanilide*,



large, blood-red leaflets, m. p. 160—161° (decomp.). The salts of the latter compound with acids are stable only in the presence of the free acid; *hydrochloride*, small, orange-yellow needles; *oxalate*,



dark brown, crystalline powder, decomposing at 186—187°. The following compounds were also prepared: *benzoyl derivative*,



small, yellow needles, m. p. 219—220°; *phenylcarbamido-derivative*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CO}\cdot\text{NHPH}$, reddish-yellow needles, decomposing at 210°; *dibromo-derivative*, $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{N}_2\cdot\text{CO}\cdot\text{NHPH}$, small, yellow needles, m. p. 155—156°.

By the same methods as described above are obtained: *2-amino-toluene-5-azoformanilide*, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}:\text{N}\cdot\text{CO}\cdot\text{NHPH}$, reddish-brown, leafy crystals, decomposing at 150—151°, and *3-aminotoluene-6-azoformanilide*, dark red needles with green reflex, m. p. 137°.

W. H. G.

Action of Dilute Sulphuric Acid on Proteins. LEO LANGSTEIN (*Biochem. Zeitsch.*, 1907, 5, 410—412).—Recent authors have stated that the digestion of protein with 0·5% hydrochloric acid leads to the formation of the same end products as are found in gastric digestion, but more slowly. The present experiments confirm earlier views of the author that protein is very resistant to dilute sulphuric acid. After eight months' digestion in 1% acid at 37°, only 18% of dried egg-albumin goes into solution; rather more of the other proteins investigated (serum-albumin, &c.) were dissolved. The dissolved nitrogenous substances were completely precipitable by phosphotungstic acid.

W. D. H.

Influence of Solutions of Pigments on the Heat Coagulation of Proteins. HANS ARON (*Biochem. Zeitsch.*, 1907, 5, 413—418).—Acid pigments (eosin and aurantia) or their free acids,

when added to protein solutions (dilute serum), destroy the heat-coagulability of the latter. The explanation advanced is that complex colloid is formed, in which the pigment acts towards the protein as a "protective colloid."

W. D. H.

Dissociation of Serum-Globulin at Varying Hydrogen Ion Concentrations. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1907, 11, 437—460. Compare *Abstr.*, 1906, ii, 828; Hardy, *Abstr.*, 1906, i, 121).—Equations are deduced by means of which an expression containing the ratio of the acid and basic constants, k_a and k_b , of such an amphoteric electrolyte as serum-globulin can be calculated from two experimental observations. The hydrogen ion concentrations of globulin solutions containing varying proportions of acid were measured by means of concentration cells and the conductivities of globulin solutions to which varying proportions of acid had been added were also measured; from these data, by an indirect method, the value $68 \cdot 3 \times 10^{-8}$ was obtained for the expression Kk_a/k_b , where K is the dissociation constant for water. By another and probably less accurate method, the value 265×10^{-8} was obtained for the same expression. For the velocity of the serum-globulin ion, the value 7×10^{-5} cm./sec. under a potential gradient of 1 volt/cm. was deduced, whilst Hardy (*loc. cit.*) by a direct method obtained 10×10^{-5} cm./sec.

Serum-globulin is a fairly strong acid, but its basic properties are so slight that it behaves to alkalis as a non-amphoteric acid.

Some evidence has been obtained that solutions of proteins contain more or less complex polymerides of the type HXOH , and that the equilibrium is displaced by the addition of acids, salts, &c. In the case of serum-globulin, therefore, there is no definite molecular concentration in acid solution, but in alkaline solution, owing to its slightly basic character, the degree of polymerisation and therefore the molecular weight is constant. The molecular weight of serum-globulin in alkaline solution is given as 1967, and the average molecular weight in acid solution as 1684, but the latter value is very uncertain.

G. S.

Formation of Polypeptides by the Hydrolysis of Proteins. EMIL FISCHER and EMIL ABDERHALDEN (*Ber.*, 1907, 40, 3544—2562). In part already published (this vol., i, 737. Compare also 1906, i, 718).—When treated with 70% sulphuric acid at 36° , gliadin gives rise to *l*-leucyl-*d*-glutamic acid, $[\alpha]_D^{20} + 10 \cdot 2$, m. p. 232° (corr.), identical with the synthetical product. Levene's claim to have first isolated a dipeptide from the decomposition products of proteins is shown to be inaccurate.

E. F. A.

Hydrolysis of Glycinin, the Globulin of the Soy Bean, and of the Crystalline Globulin of the Squash Seed (*Cucurbita maxima*). THOMAS B. OSBORNE and SAMUEL H. CLAPP (*Amer. J. Physiol.*, 1907, 19, 468—474, 475—481).—Acid hydrolysis led to the following percentage results calculated on a moisture and ash-free basis for the two proteins mentioned:

	Soy bean.	Squash seed.		Soy bean.	Squash seed.
Glycine.....	0·97	0·57	Serine.....	not isolated	not isolated
Alanine.....	not isolated	1·92	Tyrosine ...	1·86	3·07
Valine	0·68	0·26	Arginine....	5·12	14·44
Proline	3·78	2·82	Histidine ...	1·39	2·63
Phenylalanine	3·86	3·32	Lysine.....	2·71	1·99
Aspartic acid	3·89	3·30	Ammonia ...	2·56	1·55
Glutamic acid	19·46	12·35	Tryptophan	present	present
Leucine	8·45	7·32	Cystine	—	0·23

W. D. H.

The Formation of Acetone from Acetoacetates by means of Organ-extracts and Proteins. LEO POLLAK (*Beitr. chem. Physiol. Path.*, 1907, 10, 232—250).—By digestion of sodium acetoacetate with blood-serum or organ-extracts, there is a rapid decomposition of the salt, with the formation of carbon dioxide and acetone. The agent in the serum responsible for this is protein. Serum-globulin, crystalline serum-albumin, caseinogen, Witte's peptone, amino-acids (leucine, alanine, &c.) all have the same action. All these substances contain the amino-group.

W. D. H.

Combining Power of Casein with Certain Acids. JOHN H. LONG (*J. Amer. Chem. Soc.*, 1907, 29, 1334—1342).—In previous papers (Abstr., 1905, i, 498; 1906, i, 391), it has been shown that casein unites with alkalis to form salts. It has now been found that casein also combines with acids, and the behaviour of various acids has been investigated. At the ordinary temperature, 1 gram of dry casein unites with nearly 7 c.c. of *N*/10 hydrochloric, hydrobromic, hydriodic, sulphuric, and acetic acids. It also combines with tartaric, phosphoric, and oxalic acids, but not with boric acid. If the casein solution is evaporated in presence of dilute acid, a larger quantity of the latter, in the case of hydrochloric acid, four times as much, enters into combination. This is due, to some extent at least, to the partial hydrolysis of the casein and the union of the acid with the products of such hydrolysis.

E. G.

Action of Dilute Acids on Casein when Soluble Compounds are not Formed. LUCIUS L. VAN SLYKE and DONALD D. VAN SLYKE (*Amer. Chem. J.*, 1907, 38, 383—456).—In a previous paper (Abstr., 1905, i, 499), it has been shown that casein unites with acids to form insoluble products. A study has now been made of the behaviour of casein with hydrochloric, sulphuric, lactic, and acetic acids of concentrations from *N*/125 to *N*/2000, at temperatures of 0°, 25°, and 45°, and during periods varying from five minutes to forty-eight hours. The results indicate that the insoluble substances formed are not salts, but are produced by adsorption of the acid by the casein. The precipitate produced when milk turns sour is casein containing adsorbed lactic acid.

In carrying out the investigation, casein was shaken with dilute

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acids of known strength, and, after filtration, the quantity of acid removed from the solution was calculated from the decrease in conductivity. Experiments were made to ascertain the conditions in which casein is soluble in dilute acids in order that such conditions might be avoided. It was found that the protein does not dissolve to an appreciable extent when left for several hours at 0° in contact with acids of concentration of $N/1000$ or less, but that the solubility increases with the concentration, the temperature, and the time of contact. The rate at which casein dissolves in different acids of equivalent strength is not proportional to the concentration of the hydrogen ions or to the degree of dissociation, but is disproportionately great for the weak organic acids. From dilute acids of equal concentration, the dissolved protein takes up a larger proportion of acid than the undissolved. The solubility of casein in dilute acids is probably due to decomposition of the protein. Casein neither dissolves in $N/125$ magnesium sulphate or $N/50$ potassium chloride nor adsorbs either of these salts.

The amount of acid withdrawn by casein from dilute solutions in which it does not dissolve varies with the concentration of the acid, the duration of contact until equilibrium is reached, the degree of agitation until equilibrium is reached, the temperature, and the particular acid employed. The acid is never entirely removed from the solution.

Determinations have been made of the amount of each of the acids adsorbed by 1 gram of casein at the equilibrium point and of the rate at which equilibrium is produced under different conditions. The acid can be removed from the casein by shaking it with water.

E. G.

Sulphohæmoglobin. T. WOOD CLARKE and W. H. HARTLEY (*J. Physiol.*, 1907, 36, 62—67).—Sulphohæmoglobin is regarded as a definite compound in aqueous solution. It could not be obtained in crystalline form. The action of carbon monoxide on sulphohæmoglobin, or of hydrogen sulphide on carboxyhaemoglobin, is to form a new compound, carboxysulphohæmoglobin. Reduction of oxyhaemoglobin is a necessary preliminary for the formation of sulphohæmoglobin. Selenohaemoglobin closely resembles sulphohæmoglobin.

W. D. H.

Hair Pigment, Choroid Pigment, and other Melanins. EDUARD SPIEGLER (*Beitr. chem. Physiol. Path.*, 1907, 10, 253—264).—The pigment of melanotic livers is different from that of the hair, but both resemble the choroid pigment (from pigs' eyes) in not yielding haemopyrrole, and so their origin from the blood is impossible. On decomposition of the pigments, acetone derivatives or condensation products of acetone residues are found; the differences between these products in the various pigments, accounts for the differences of the pigments. The parent substances of the pigments are tryptophan and acetone; possibly other aromatic groups of the protein molecule, such as phenylalanine and tyrosine, participate in their formation.

W. D. H.

The Chemical Nature of the Fundamental Colouring Matter of Urine. S. DOMBROWSKI (*Compt. rend.*, 1907, 145, 575—577).—The yellow urinary colouring matter, *urochrome*, has been prepared and examined. It may be separated from fresh urine which has been freed from most of its salts by the addition of cupric acetate in a cold faintly acid medium. The analytical data are: C, 43·09; H, 5·14; N, 11·15; S, 5·09; O, 35·53%. The free acid and its *calcium* and *silver* salts are soluble in water. It is readily decomposed by alkalis and reduces ferric salts or iodic acid. The acid contains a pyrrole group which reacts with diazo-salts in much the same manner as pyrrole itself, but quite differently from hemipyrrrole.

The pyrrole group, when exposed to the air, in an acidified alcoholic solution, polymerises, and the product gives an absorption band identical with that observed in the spectrum of polymerised pyrrole. When heated with hydrochloric acid, urochrome is decomposed, yielding a *black pigment*: C, 59·16; H, 4·91; N, 9·69; S, 3·55; O, 22·69%.

The normal amount of urochrome eliminated by the human organism in twenty-four hours varies between 0·4 and 0·7 gram, but in cases of infectious diseases, such as typhoid fever, increases considerably.

J. J. S.

Nucleic Acid from the Pancreas (Guanylic Acid). OTTO VON FÜRTH and ERNST JERUSALEM (*Beitr. chem. Physiol. Path.*, 1907, 10, 174—187).—Bang states that guanylic acid, the nucleic acid obtained from the pancreas, differs from other nucleic acids, inasmuch as it yields a derivative of glycero-phosphoric acid, yields one-third of its weight on hydrolysis in the form of a reducing sugar, and contains only one basic substance, guanine. All these assertions are now alleged to be incorrect, and there is no necessity to distinguish between guanylic and other nucleic acids of animal origin. W. D. H.

Gelatin Forms Produced by Precipitates of Salts and Crystals. RAPHAEL E. LIESEGANG (*Chem. Zentr.*, 1907, ii, 415; from *Zeitsch. Chem. Ind. Kolloide*, 1, 364—367. Compare this vol., ii, 337).—The formation of a precipitate, or of crystals of salt or water, may induce gelatin to take certain forms or shapes which are retained after the cause has been removed. Experiments on the crystallisation of potassium dichromate have shown that, contrary to Molisch's theory (*Unters. über das Erfrieren der Pflanzen*, Jena, 1897), the gelatin accumulates at the places where the crystals form. Experiments on freezing gelatin films which had been dyed with methylene-blue proved, however, that both accumulation and dispersion of the gelatin may be caused by the formation of crystals even in the same preparation. E. W. W.

The Amounts of Cystin in Various Horny Materials. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1907, 52, 474—481. Compare Mörner, *Abstr.*, 1900, i, 128; 1902, i, 331).—The following percentages of cystine have been obtained from the materials mentioned: human hair, 13—14·5; human nails, 5·15; horse hair, 7·98; horses' hoofs, 3·20; ox hair, 7·27; hoofs of oxen, 5·37; pigs' bristles, 7·22; pigs' hoofs, 2·17. J. J. S.

Nitrochitins. OTTO VON FÜRTH and EMIL SCHOLL (*Beitr. chem. Physiol. Path.*, 1907, 10, 188--198).—Chitin is attacked by warm or cold fuming nitric acid alone, or in the presence of sulphuric acid, yielding a mixture of nitrates corresponding in properties with the nitro-celluloses. The chitin dissolves in the acid, and the nitro-products are precipitated by pouring the solution into water. Two products are formed, one of which is insoluble in all the ordinary organic solvents, whereas the other dissolves readily in alcohol, acetone, ethyl acetate, and glacial acetic acid. They are true nitrates, as when hydrolysed with acids or alkalis they yield nitric acid.

Chitosan reacts with nitrous acid, yielding a product with reducing properties soluble in water, acids, and alkalis, but precipitated by alcohol.

J. J. S.

Diamino-acids from Koilin. ERICH VON KNAFFL-LENZ (*Zeitsch. physiol. Chem.*, 1907, 52, 472—473).—The following diamino-acids have been obtained by hydrolysing koilin (compare this vol., i, 884) with sulphuric acid: histidine 0·034, arginine 3·596, lysine 1·640. The numbers are parts per 100 of air-dried and ash-free koilin.

J. J. S.

A New Solvent for Some Proteins. IWAN OSTROMYSSLENSKY (*J. pr. Chem.*, 1907, [ii], 76, 267—268).—As Fischer has shown that proteins are complicated amides, it was to be expected (this vol., ii, 847) that they would prove to be soluble in simple amides. It is found that the albumoses and peptones dissolve in formamide and fused acetamide. The latter dissolves over 30% of the peptone of egg-albumin, whereas the albumins, such as egg- and serum-albumins, do not dissolve in this solvent. The concentrated solutions in formamide are viscid at the ordinary temperature, gradually become reddish-brown, and can be filtered. The solubility in formamide may be used in the separation of proteins from each other and from inorganic material. The solutions in acetamide are suitable for use in cryoscopic investigations.

G. Y.

Hydrolysis of the Albumoses Occurring in Meat Extract. KARL MICKO (*Zeitsch. Nahr. Genussm.*, 1907, 14, 253—298).—The experiments described were undertaken for the purpose of ascertaining the origin of the amino-acids obtained in the hydrolysis of meat extract (Abstr., 1906, i, 778). The portion of meat extract precipitated by zinc or ammonium sulphate is not identical with either gelatin or gelatoses, and unaltered gelatin cannot be detected in true meat extract itself. During the manufacture of meat extract, gelatin may pass into solution, but it is converted by the lactic acid present into gelatoses or acid glutin. The greater part of the portion precipitated by ammonium sulphate consists of a mixture of proteins having the general properties of albumoses and showing no indications of having been derived from gelatin. A small proportion of these albumoses, however, gives reactions very similar to those obtained with gelatoses, &c. Hydrolysis of the constituents of meat extract which are soluble in saturated ammonium sulphate solution yields monoamino-acids.

W. P. S.

Coaguloses. D. LAWROFF (*Zeitsch. physiol. Chem.*, 1907, **53**, 1—7).—In the peptic digestion of proteins, as well as in their digestion by dilute mineral acids, at least two types of coagulose-yielding substances are recognisable. The first are of the type of proteoses, and the coaguloses which arise from them yield on hydrolysis monoamino-acids and basic nitrogenous cleavage products. The second type of coagulose-yielding substances are of the type of polypeptides, and the coaguloses which arise from them yield on hydrolysis only mono-amino-acids.

W. D. H.

Racemic Tryptophan. RUDOLF A. ALLERS (*Biochem. Zeitsch.*, 1907, **6**, 272—275).—Racemic tryptophan, prepared according to Neuberg's method, and the synthetic preparation of Ellinger and Flamand (this vol., i, 737) both begin to melt at 256°. Optically active tryptophan is stated to melt at 273° by Hopkins and Cole and by Neuberg and Popowsky; at 289° by Abderhalden and Kempe. Racemisation is probably due to the ammonia added at 60° in the process of preparation (compare following abstract).

G. B.

Tryptophan. CARL NEUBERG (*Biochem. Zeitsch.*, 1907, **6**, 276—282).—An iodine solution, when added to tryptophan dissolved in alkali hydroxide, produces a pale brown, amorphous precipitate having the composition of a mixture of mono- and di-iodotryptophan (compare Neuberg and Popowsky, this vol., i, 253; Nürnberg, this vol., i, 805).

Silver nitrate added to tryptophan dissolved in slightly less than 1 mol. of sodium hydroxide produces a silver salt, $C_{11}H_{11}O_2N_2Ag$.

Tryptophan is racemised by concentrated hydrochloric acid at 170°, and then melts at 254—255°. An optically inactive specimen was also obtained by Neuberg's method of preparation, which involves boiling with lead carbonate and ammonia (compare preceding abstract).

G. B.

The Non-existence of Protagon as a Definite Chemical Compound. OTTO ROSENHEIM and M. CHRISTINE TEBB (*J. Physiol.*, 1907, **36**, 1—16).—Liebreich's, Gamgee and Blankenhorn's, and Cramer's protagons represent the same substance as cérébrote prepared by Couerbe in 1834. A similar substance is obtained by extracting brain with boiling acetone after the cholesterol has been removed by cold acetone. All these substances may be split into substances of widely varying phosphorus and nitrogen percentage by simple fractional crystallisation at different temperatures, or with different solvents. They also show great difference in optical activity and in the amount of galactose split off by acid hydrolysis. The base sphingosine as well as choline is found amongst the products of protagon hydrolysis. Protagon is not a definite chemical compound, but a mixture of substances, some of which (such as phrenosin) are phosphorus-free and others (such as sphingomyelin) rich in phosphorus.

W. D. H.

Protagon. WILLIAM J. GIES (*J. Biol. Chem.*, 1907, **3**, 339—358).—The non-identity of protagon as a chemical individual is maintained,

and Cramer's attempt to rehabilitate it (see preceding abstract) is shown to rest on obviously fallacious reasoning. W. D. H.

Effect of Colouring Matters on some of the Digestive Enzymes. H. W. HOUGHTON (*J. Amer. Chem. Soc.*, 1907, 29, 1351—1357).—A study of the effect of various colouring matters on the activity of pepsin has led to the following conclusions. Annatto does not affect the activity of the enzyme towards fibrin, but when present in certain proportions diminishes the activity towards egg-albumin and casein. Saffron lessens the activity towards fibrin, casein, and egg-albumin when it is used in the proportion of 1 : 400, but smaller quantities have no effect. Turmeric reduces the activity towards casein and egg-albumin, but, when present in as small a proportion as 1 : 800, does not affect the digestion of fibrin. Cochineal and Bismarck-brown, when used in a smaller proportion than 1 : 400, do not decrease the activity of the enzyme towards fibrin, but a proportion of 1 : 1600 lessens the activity towards egg-albumin. Crocein-scarlet 1B (1 : 1600) inhibits entirely the action of the enzyme on fibrin, and, when present in the proportion of 1 : 200, it diminishes the activity towards casein and egg-albumin.

Annatto and oil-yellow are found to assist the hydrolysis of butter-fat by lipase, and it is therefore assumed that these colouring matters contain some lipolytically active substance. E. G.

Behaviour of Hippuric Acid to Erepsin. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1907, 52, 526. Compare Abstr., 1906, ii, 294).—Hippuric acid dissolved in sodium hydrogen carbonate solution is not hydrolysed by erepsin. J. J. S.

Action of the Proteolytic Ferment of *Bacillus pyocyaneus*. EMIL ZAK (*Beitr. chem. Physiol. Path.*, 1907, 10, 287—298).—The ferment not only cleaves proteoses into simpler products, but evidence is adduced that it also has a synthetic action both in bouillon cultures and in the filtrate freed from organisms. Taylor (this vol., i, 665) has described previously a reversible action in the case of trypsin.

W. D. H.