

Organic Chemistry.

Action of Chlorine on Trimethylene. By G. GUSTAVSON (*J. pr. Chem.* [2], **42**, 495—500).—Chlorine has hardly any action on trimethylene in the dark, but explodes with it in direct sunlight. Chlorine was passed into a globe ($7\frac{1}{4}$ litres) containing the trimethylene (7 litres) and water; the globe was kept cool, and the oil allowed to collect in a separating funnel ground into the neck. The oil consisted almost entirely of dichlorotrimethylene.

Dichlorotrimethylene, $C_3H_4Cl_2$, is a colourless liquid of peculiar odour; it boils at 75° (746 mm.), and is nearly insoluble in water. Its chemical stability is great; nitric acid decomposes it with difficulty; water at 180 — 190° has scarcely any action on it, and it

can be distilled over sodium, which only acts on it at 160—165°, producing substances still under investigation. When dichlorotrimethylene and bromine (equal mols.) are sealed in a tube and exposed to sunlight for 4—5 summer days, or heated at 140—150° for 3—4 hours, the dibromide, $C_3H_4Cl_2Br_2$, is produced; it is a heavy, colourless liquid which boils almost without any decomposition at 203—207° (770 mm.).

Allylene dichloride is the only compound of the formula $C_3H_4Cl_2$ which boils at 75°; that dichlorotrimethylene is not identical with this is shown by the fact that the dibromo-compound obtained from allylene dichloride boils at 190° (Friedel and Silva; 188°, Pinner).

Of the three possible formulæ for this dichlorotrimethylene, the author favours $CCl_2<\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}$; for the dibromide approximates in boiling point to α -epidichlorhydrin dibromide, $CH_2Cl\cdot CClBr\cdot CH_2Br$, and therefore, probably, has a similar structure.

A. G. B.

Hexylene Dibromide obtained from Diallyl. By N. DEMYANOFF (*J. Russ. Chem. Soc.*, **22**, 117—118).—In order to prepare hexylene dibromide, well cooled diallyl (b. p. 59—60°) was saturated with hydrogen bromide, when a mixture of a solid with a liquid was obtained. After washing with water, the two compounds were separated by filtration and suction. The liquid product was a hexylene dibromide boiling at 212—220° with decomposition. The solid product, after recrystallisation from ether, was obtained in large, rhombic scales melting at 38—39°, and boiling almost without decomposition at 210°. The author considers the liquid compound to be $CH_2Br[CH_2]_4CH_2Br$, and the solid as $CHMeBr\cdot CH_2\cdot CH_2\cdot CHMeBr$, and that diallyl is a mixture of two (geometrical) isomerides.

B. B.

Oxidation of Potassium Cyanide with Potassium Permanganate. By J. VOLHARD (*Annalen*, **259**, 377—380).—Carbamide can be very conveniently prepared in moderately large quantities in the following manner:—A solution of potassium permanganate (33 grams) in water (1 litre) is gradually added to a solution of potassium cyanide (39 grams) and potassium hydroxide (10 grams) in water (100 c.c.), the temperature being kept below 17°; but it is unnecessary to wait until the pink colour has disappeared before continuing the addition of the permanganate. The solution is then placed in cold water for seven to eight hours until it becomes colourless, mixed with a concentrated solution of ammonium sulphate (70 grams), heated to boiling, and filtered; the precipitate is washed with boiling water, the filtrate and washings evaporated to dryness, and the carbamide extracted with 95 per cent. alcohol. The yield is 68 per cent. of the theoretical, but the product still contains a little ammonium chloride and traces of the sulphate, from which it can most easily be freed by treating its aqueous solution with a little precipitated barium carbonate, evaporating to dryness, and then extracting with absolute alcohol.

F. S. K.

Combination of Mercuric Cyanide with Cadmium Salts. By R. VARET (*Compt. rend.*, **111**, 679—681).—Powdered mercuric cyanide, 25 parts, is gradually added to a boiling concentrated solution of cadmium iodide, 30 parts, and the liquid is filtered and allowed to evaporate over sulphuric acid. The compound $\text{HgCy}_2\text{CdCy}_2\text{HgI}_2 + 7\text{H}_2\text{O}$ separates in transparent lamellæ, which alter rapidly when exposed to air, and dissolve in water and ammonia. It becomes anhydrous at 110° , and at the same time decomposes with liberation of mercuric iodide. Dilute acids decompose it with liberation of mercuric iodide and hydrocyanic acid, while mercuric cyanide and the cadmium salt of the particular acid used remain in solution. When heated with a solution of cupric sulphate, cyanogen is evolved, and a precipitate of the composition $\text{Cu}_2\text{Cy}_2\text{HgI}_2$ is formed. These facts show that all the cyanogen is not combined with the mercury, and that the salt is not simply a compound of cadmium iodide with mercuric cyanide.

Cadmium bromide (18 parts), added gradually to a boiling solution of mercuric cyanide (25 parts), yields slender needles of the compound $2\text{HgCy}_2\text{CdBr}_2 + 4\frac{1}{2}\text{H}_2\text{O}$, which alters but little when exposed to air, dissolves in water and in ammonia, and becomes anhydrous at 100° . Dilute acids liberate hydrocyanic acid, but no mercuric bromide sublimes when the salt is gently heated; but when more strongly heated, cyanogen and mercury are evolved and some mercuric cyanide sublimes. It follows that the salt is a compound of mercuric cyanide and cadmium bromide.

If a solution containing 25 parts of mercuric cyanide and 30 parts of cadmium bromide is gently evaporated on a water-bath, the salt $\text{HgCy}_2\text{CdBr}_2\text{H}_2\text{O}$ separates in small, very hard, granular crystals which alter but little when exposed to air, become anhydrous at 100° , and are less soluble in water and in ammonia than the preceding compound.

If a concentrated solution of 20 parts of cadmium chloride is added drop by drop to a saturated solution of 25 parts of mercuric cyanide, heated at 80° , and the liquid is slowly concentrated after addition of sufficient warm water to dissolve the white precipitate which forms, the compound $\text{HgCy}_2\text{CdCl}_2 + 2\text{H}_2\text{O}$ separates in small, granular crystals. It is soluble in water and in ammonia, is decomposed by dilute acids, and becomes anhydrous at 110° .

C. H. B.

Action of Alcoholic Potassium Cyanide on Halogen Derivatives of Amylene. By C. HELL and M. WILDERMANN (*Ber.*, **23**, 3210—3215).—It is well known that whereas the primary dibromides of normal olefines are readily converted into the corresponding dinitriles, the derivatives of the iso-compounds only give very small yields on treatment with alcoholic potassium cyanide. Thus isoamylene bromide forms, besides the dinitriles, large quantities of bromamylene and of humous substances. The authors find that the reaction takes place more readily if isoamylene chloride is employed in place of the bromide, and the mixture is heated in a sealed tube at 180° . The nitrile formed gave on hydrolysis a crystalline acid seemingly identical with the trimethylsuccinic acid obtained by

Schad (*Inaug. Diss., Berne, 1886*), and an oily acid which could not be obtained crystalline. The yield of both these acids was better than that given by the bromide.

It was also found that addition of hydrochloric acid to the mixture of isoamylene chloride and alcoholic potassium cyanide causes a great increase in the quantity of humous substance formed, whence it would appear that the formation of the latter is due to the action of hydrochloric acid on the hydrocyanic acid; this was confirmed by adding hydrochloric acid to an alcoholic solution of potassium cyanide which had previously been boiled for some time without undergoing alteration, when, after a few minutes, a copious separation of humus took place. Hence all those substances which readily lose hydrogen chloride or bromide by the action of potassium cyanide will give large quantities of humus, owing to the action of the acid thus set free on the hydrocyanic acid, azulmic and hydrazulmic acids being formed.

When isoamylene bromide is heated with bromine, it is converted into a *tribromopentane*, the most probable formula of which is $\text{CMe}_2\text{Br}\cdot\text{CMeBr}_2$. This is readily acted on by alcoholic potassium cyanide without formation of humus or of bromamylene in any quantity. The nitrile formed is almost insoluble in water and ether, but dissolves readily in alcohol. The hydrolysis is best performed by heating it in a sealed tube at 130—150° with concentrated hydrochloric acid, and extracting the product with ether. After removing the latter by evaporation, a yellowish, syrupy acid remains which gradually deposits a small quantity of needles; these after repeated crystallisation from water, melted at 96—97°, and evolved carbonic anhydride at 130—140°; the quantity of the substance was too small, however, to allow of its being obtained in a pure condition. The syrupy acid, after purification by successive conversion into the calcium, barium, and silver salts, was obtained as a pale-yellow syrup which did not crystallise, even when kept for some time; it has the composition of a trimethylsuccinic or dimethylglutaric acid, but its exact constitution has not yet been determined. It only evolves minimal quantities of carbonic anhydride on heating, due to the presence of traces of the above crystalline acid.

H. G. C.

Derivatives of Melidoacetic Acid. By R. KRÜGER (*J. pr. Chem. [2], 42, 473—494*; compare this Journal, 1875, 1184).—Melidoacetic acid is best obtained as follows:—10 grams of sodium is dissolved in alcohol, the solution cooled and mixed with a solution of cyanamide (20 grams) in alcohol (40 c.c.); an equal volume of ether is then added, and the resulting precipitate is heated with a mixture of cyanamide (10 grams) dissolved in alcohol (20 c.c.) and ethyl chloracetate (30 grams) for 6 to 8 hours in a reflux apparatus. The whole is then dissolved in dilute soda, filtered, and the melidoacetic acid precipitated by acetic acid; it is purified by dissolving it in dilute hydrochloric acid and passing hydrogen chloride into the cooled solution, when its hydrochloride separates in large needles which are recrystallised and decomposed by adding ammonia to the aqueous solution. The *potassium*, *sodium*, *calcium*, and *barium* salts were obtained.

Ammelidoacetic acid, $C_3N_3(OH)_2 \cdot NH \cdot CH_2 \cdot COOH$, is obtained by heating melidoacetic acid with excess of barium oxide and water in a reflux apparatus until no more ammonia is evolved, and crystallising the portion which remains undissolved from hot hydrochloric acid. It crystallises in rhombic or monoclinic tables, and dissolves freely in hot water, but not in alcohol. The *copper salt*, $(C_5H_5N_4O_4)_2Cu + 6H_2O$, crystallises in dark-blue, rhombic tables; the *silver salt* is a white precipitate of uncertain composition: the *basic lead salt*, $C_5H_4N_4O_4Pb$, crystallises in transparent crystals which are insoluble in water: the *barium salt*, $C_{20}H_{34}N_{16}O_{24}Ba_3 + 8H_2O$, crystallises in long, rhombic tables, soluble in much hot water; the *strontium salt*, $C_{10}H_{10}N_8O_8Sr + 4H_2O$, forms rhombic or monoclinic tables; the *calcium salt*, which was obtained like the last two salts, namely, by adding calcium hydroxide to a solution of the acid, precipitating the excess of calcium with carbonic anhydride, filtering, and crystallising, forms crystals which are similar to the strontium salt, but have an uncertain composition; the *calcium salt*, $C_{10}H_{10}N_8O_8Ca + 4H_2O$, obtained by mixing the calculated quantities of calcium oxide and ammelidoacetic acid and crystallising, forms glistening, quadratic prisms; the *sodium, potassium, and ammonium salts* (each with 2 mols. H_2O) are of normal composition, and easily soluble in water.

Cyanuracetic acid, $C_3N_3(OH)_2 \cdot O \cdot CH_2 \cdot COOH$, is obtained when melidoacetic acid is heated in a sealed tube with strong hydrochloric acid at 180° for several hours until it has all dissolved; when the tube is opened the liquid froths up from the escape of gas, and after a time the new acid crystallises out, together with ammonium chloride, from which it is separated by its solubility in absolute alcohol. It crystallises (with 1 mol. H_2O) in prisms and needles, and dissolves very freely in water. There are three series of salts: the *copper salt*, $C_{10}H_8N_6O_6Cu + 2H_2O$; the *silver salt*, $C_6H_2N_3O_6Ag_3 + H_2O$; the *barium salt*, $C_5H_3N_3O_6Ba + 2H_2O$, and the *potassium salt*, $C_5H_4N_3O_6K + H_2O$, are here described; the *ethyl salt*, $C_5H_4N_3O_6Et$, crystallises in silky needles which melt at 208° and solidify at 195° .

Cyanuracetic acid is synthetically obtained by heating disodium cyanurate with sodium chloracetate in aqueous solution.

A. G. B.

Two New Butyl Nitrates. By G. BERTONI (*Gazzetta*, **20**, 372—376).—Of the four theoretically possible butyl nitrates, only one, the isoprimary salt, has hitherto been prepared (Wurtz, *Compt. rend.*, 1854).

The *normal primary nitrate*, $CH_2Pr^{\alpha}NO_3$, is prepared by adding quantities of 10 c.c. of pure normal butyl alcohol, drop by drop, to a strongly cooled mixture of 2 vols. of sulphuric acid (sp. gr. = 1.85) and 1 vol. of nitric acid (sp. gr. = 1.4), and proceeding as in the manufacture of nitroglycerol. It is a colourless liquid, with a pleasant ethereal odour and a sweet taste, which becomes pungent after a time. It boils at 136° , and its sp. gr. at 0° is 1.048. It dissolves in alcohol, ether, acetic acid, carbon bisulphide, &c., but not in water. With acids, it behaves like other ethereal nitrates. It burns with an olive-green flame, and explodes with violence when heated in a sealed tube to a higher temperature than its boiling point.

Secondary butyl nitrate, $\text{CHEtMe}\cdot\text{NO}_3$, is prepared like the preceding compound, the temperature being carefully kept below 0° during the whole of the reaction. It is a colourless, mobile liquid, with a pleasant, penetrating odour, boils at 124° , and has a sp. gr. of 1.0382. It dissolves in most organic solvents, but not in water. It is more readily decomposed than its isomerides by sulphuric or hydrosulphuric acid. Its vapour explodes when superheated. S. B. A. A.

Action of Hydrogen Chloride and Bromide on Ethyl Allyl Ether. By S. N. KIJNER (*J. Russ. Chem. Soc.*, 22, 27—32).—The author has made attempts to convert ethyl allyl ether into ethyl propyl ether by acting on it with hydrogen bromide, but the result was quite different when ethyl allyl ether, saturated with hydrogen bromide at -15° , was heated in a sealed tube at $30-40^\circ$ for 10 hours; it was found to be decomposed with formation of allyl bromide and ethyl bromide, this reaction taking place to some extent even at -15° . Hydrogen chloride and allyl ethyl ether in like manner yield allyl and ethyl chlorides, but the reaction requires more time and a higher temperature. This result accords with the fact that the reaction takes place with development of heat. This is evident from the thermochemical data, and the reaction will be more energetic with the gaseous acids than with the aqueous solution, as more heat is developed by the action in the first case than in the second.

B. B.

Tetramethylene Glycol. By P. J. DEKKERS (*Rec. Trav. Chim.*, 9, 92—102; see also *Abstr.*, 1889, 950).—Tetramethylene glycol is the only dihydroxy-derivative of normal butane which has not been prepared up to the present time. The author endeavoured to obtain its dibenzoate by the action of sodium on chlorethyl benzoate, $\text{C}_2\text{H}_4\cdot\text{Cl}\cdot\text{OBz}$, but only obtained a mixture of sodium chloride, sodium benzoate, and ethylene benzoate. The action of sodium and silver nitrite on a solution of tetramethylenediamine sulphate or oxalate also gave negative results, although with the former salt a liquid was obtained which was possibly tetramethylene oxide.

The following method was then adopted with more satisfactory results. Tetramethylenediamine, when mixed with methyl carbonate in the cold, gradually deposits white crystals of *methyl tetramethylene-diamidoformate*, $\text{C}_4\text{H}_8(\text{NH}\cdot\text{COOMe})_2$, which, after recrystallisation from water, melt at 128° . When the latter is treated with five times its weight of cold absolute nitric acid, it yields *methyl tetramethylenedinitramidoformate*, $\text{C}_4\text{H}_8[\text{N}(\text{NO}_2)\cdot\text{COOMe}]_2$, which separates from alcohol in crystals melting at $61-62^\circ$. To convert this into the nitrainine, it is warmed with ammonia, the solution precipitated with acetic acid, the precipitate washed with cold water, and recrystallised from the hot liquid. The *tetramethylenedinitramine*, $\text{C}_4\text{H}_8(\text{NH}\cdot\text{NO}_2)_2$, thus obtained forms hard crystals melting at 163° , which are fairly soluble in hot water. When it is warmed on the water-bath with very dilute sulphuric acid, a volatile liquid distils over, and a gas is formed which is partially absorbed by hydrobromic acid with formation of tetramethylene bromide, and by bromine with formation of butine tetrabromide. The unabsorbed gas consists of nitrous oxide. When

the residual liquid in the flask is distilled under reduced pressure it yields *tetramethylene glycol*, $C_4H_8(OH)_2$, as a thick, colourless liquid which boils at 203—205° under 752 mm., and at 152—153° under 120 mm. pressure, and yields succinic acid on oxidation. When shaken with benzoic chloride and soda solution, it yields the *dibenzoate*, $C_4H_8(OBz)_2$, melting at 81—82°.

As mentioned above, a volatile liquid distils over when tetramethylenenitramine is warmed with dilute sulphuric acid. This separates into two layers, the upper one consisting of a liquid boiling at 67°, and the lower of an aqueous solution of a liquid boiling at 83—88°. These have not been closely examined, but the former probably is tetramethylene oxide.

H. G. C.

Starch. By K. ZULKOWSKI (*Ber.*, **23**, 3295—3297).—Starch dissolves in hot glycerol, and is converted into the soluble modification; by further heating and treatment with alcohol, erythrodextrin and achroodextrin are obtained free from sugar; from the alcoholic filtrate, two soluble carbohydrates may be separated by treatment with barium hydroxide, absolute alcohol, and anhydrous ether; the second of these remains dissolved in the ether-alcohol, and may be precipitated by means of barium hydroxide.

From the extreme difficulty experienced in removing the glycerol, the author suggests that it may take part in the reaction.

J. B. T.

α - and β -Amyrin. By A. VESTERBERG (*Ber.*, **23**, 3186—3190; see also *Abstr.*, 1887, 733). The elemi resin employed in these researches, after trituration with alcohol, showed, under the microscope, numerous crystals of amyrin, together with a few isodiametric crystals of elemic acid. The total amount of α - and β -amyrin is 20—25 per cent., a large portion of the residue being of an alcoholic nature, as it is acted on by acetic anhydride. The empirical formula of both α - and β -amyrin was found, from analysis and determination of the hydrolysis equivalent of their acetates, to be $C_{30}H_{50}O$. The compounds are extremely similar, and form slender, elastic, silky needles which are readily soluble in benzene, ether, acetic acid, and hot alcohol, sparingly in cold alcohol and light petroleum. The ratio of their solubility in alcohol at 19—19.5° is 3 : 5.12. α -Amyrin melts at 181—181.5, and rotates the plane of polarisation to the right, $[\alpha]_D = +91.59^\circ$, whilst β -amyrin melts at 193—194°, and rotates the plane of polarised light more strongly to the right, $[\alpha]_D = 99.81^\circ$.

Both compounds, unlike cholesterin and lactucerol, crystallise from aqueous alcohol without water of crystallisation. They are probably secondary alcohols, as they give acetyl and benzoyl derivatives, and on oxidation yield α - and β -amyron, which are probably ketones. Phosphorus pentachloride converts them into dextrorotatory hydrocarbons, $C_{30}H_{48}$, which may be termed amyrilenes. Phosphorus pentoxide, on the other hand, yields with α -amyrin a laevorotatory amyrilene.

α - and β -*Amyrin acetates*, $C_{30}H_{49}OAc$, are formed in the separation of the amyrins (*loc. cit.*), but are only obtained pure by repeated

crystallisation from light petroleum or benzene. Both are sparingly soluble in alcohol and ether, readily in light petroleum, and more easily in benzene and chloroform. The α -compound crystallises in large plates, melts at 221° , and has a sp. rot. power $[\alpha]_D = +77^\circ$. The β -compound forms long, prismatic crystals melting at 236° , and having a sp. rot. power $[\alpha]_D = 78.6^\circ$. Both are oxidised by chromic acid to oxyamyrin acetates, $C_{36}H_{47}O_2Ac$.

The α - and β -amyrin benzoates are obtained by heating α - and β -amyrin with benzoic chloride at 130° . The α -compound is crystallised from alcoholic ether, and is sparingly soluble in alcohol, more readily in ether, and very easily in light petroleum and benzene. The β -compound, after recrystallisation from light petroleum, is almost insoluble in cold alcohol, sparingly soluble in ether and cold light petroleum, readily in the hot liquid and in benzene.

When α - and β -amyrin acetates are dissolved in chloroform or carbon bisulphide, and bromine added, either alone or diluted with acetic acid, the solutions are coloured brownish-yellow, and hydrogen bromide is evolved. The crystalline masses which remain after spontaneous evaporation are recrystallised from benzene (α) or light petroleum (β), and the finely-powdered bromacetates treated with alcoholic potash.

Brom- α -amyrin, $C_{30}H_{48}Br\cdot OH$, melts at $177-178^\circ$, is sparingly soluble in cold acetic acid and alcohol, readily in benzene, and almost insoluble in light petroleum; it is dextrorotatory, and has a sp. rot. power $[\alpha]_D = +72.8^\circ$. Its *acetate*, $C_{30}H_{48}Br\cdot OAc$, crystallises from benzene in six-sided plates or flat prisms, containing benzene of crystallisation, which is evolved when the crystals are allowed to remain in the air. It has not, however, been obtained quite pure, but appears to melt at about 268° ; the bromine is not removed by alcoholic potash, ammonia, or aniline.

Brom- β -amyrin could not be obtained crystalline, the warm solutions in alcohol, benzene, and light petroleum solidifying to jellies. It is very soluble in hot acetic acid and benzene, less readily in alcohol and light petroleum. After drying at 98° , it melts at $182-186^\circ$. The *acetate* forms prismatic crystals, readily soluble in chloroform and benzene, sparingly in light petroleum, which, after recrystallisation from the latter, melt at 238° . As it is fairly soluble in hot light petroleum, it may be thus easily separated from the brom- α -acetate, and can, therefore, be prepared directly from the mixture of amyrins.

H. G. C.

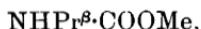
Isopropylamines. By H. MALBOT and A. MALBOT (*Compt. rend.*, **111**, 650-652).—The action of isopropyl iodide on an equivalent quantity of highly concentrated aqueous ammonia, at the ordinary temperature, is very slow, but is complete, the product consisting entirely of isopropylamine hydriodide. At 100° , the action is still slow, and requires about four days before it is complete. The chief product is isopropylamine hydriodide, but a small quantity of the diamine is also formed. Ammonium iodide is formed in quantity larger than that corresponding with the quantity of diamine, a result due to the liberation of some propylene. At $120-130^\circ$, and at

140—155°, the chief product is still the monamine, mixed with a small quantity of diamine, the proportion of the latter being practically the same in both cases. The quantity of propylene liberated is, however, considerably greater at the higher temperature. The quantity of diisopropylamine hydriodide does not exceed a certain value, because it reacts with the monamine, with elimination of propylene.

Isopropyl chloride reacts with aqueous ammonia at 140°, and the monamine is mixed with some diamine, but the change is far from complete, because the amines are present partly in the free state. In this respect isopropyl chloride differs from isopropyl iodide, and more nearly resembles orthopropyl, isobutyl, and isoamyl chlorides, which yield the free amines. There is, however, this difference, that whilst it is easy to obtain tripropyl-, triisobutyl-, and triiso-amylamines, diisopropylamine is the final term in the action of ammonia on the haloid salts of isopropyl.

C. H. B.

Propylnitramine and Isopropylnitramine and their Derivatives. By J. C. A. SIMON THOMAS (*Rec. Trav. Chim.*, 9, 69—91).—Propylnitramine and isopropylnitramine are readily obtained in a similar manner to methylnitramine (Franchimont and Klobbie, *Abstr.*, 1888, 492). The propylamine and isopropylamine required for their preparation were obtained by Hoogewerff and van Dorp's method (*Abstr.*, 1887, 245; 1888, 1194), and converted into the corresponding amidoformates by the action of methyl chloroformate in 25 per cent. aqueous solution, extraction with ether, and fractionation. *Methyl propylamidoformate*, $\text{NHPr}^\beta\text{-COOMe}$, is a colourless liquid, which has a faint penetrating odour, and boils at 180° under 755 mm. pressure. Its sp. gr. is 0·992 at 15°. *Methyl isopropylamidoformate*,



is likewise a colourless liquid, having a faint penetrating odour, which boils at 165·5° under 760 mm. pressure, and has a sp. gr. of 0·981 at 15°. Both compounds are readily converted into the nitro-derivatives by gradually adding them to cooled absolute nitric acid, with continuous shaking. In the case of the isopropyl compound, cooling with ice and very gradual addition of the amidoformate, is necessary, as otherwise oxidation readily takes place. The acid solution is then, in both cases, poured on to soda crystals covered with a little water, the yellowish liquid which separates taken up with ether, the ether distilled off, and the residual liquid dried over sulphuric acid. *Methyl propylnitramidoformate*, $\text{NO}_2\text{-NPr}^\alpha\text{-COOMe}$, is thus obtained as an almost colourless liquid, which has a sweetish odour, and does not solidify at —20°. It has a sp. gr. of 1·187 at 15°, and evolves gas when heated at 139°. *Methyl isopropylnitramidoformate*, $\text{NO}_2\text{-NPr}^\beta\text{-COOMe}$, has a sp. gr. of 1·1585 at 15°, and commences to decompose at 120°.

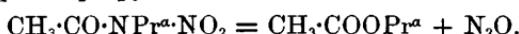
To convert these compounds into the nitramines, dry ammonia gas is passed into their ethereal solutions. The ammonium salt of propylnitramine is precipitated as a crystalline mass, which is collected, washed with ether, decomposed by sulphuric acid, and the propyl-

nitramine extracted with ether. After evaporating off the ether and drying the residue over sulphuric acid, *propylnitramine*, $\text{NPr}^{\alpha}\cdot\text{NO}_2$, is obtained as a colourless, inodorous liquid, which cannot be distilled without decomposition at the ordinary pressure, but boils at $128-129^{\circ}$ under 40 mm. pressure. It has a sp. gr. of 1.102 at 15° , decomposes at 142° , and solidifies between -21° and -23° , and is not coloured on exposure to light. Its aqueous solution has an alkaline reaction, and gives a precipitate with many salts of the heavy metals. The *potassium salt*, $\text{NPr}^{\alpha}\text{K}\cdot\text{NO}_2$, obtained by acting on the nitramine with the theoretical quantity of alcoholic potash, forms small, nacreous, hygroscopic plates, and the *silver salt*, $\text{NPr}^{\alpha}\text{Ag}\cdot\text{NO}_2$, crystallises in small, slender needles, which blacken in the light.

Isopropynitramine, $\text{NHPr}^{\beta}\cdot\text{NO}_2$, is obtained in the same manner as the normal compound, but must be further purified by dissolving it in potassium carbonate solution, extracting the latter with ether, and acidifying the residual solution with sulphuric acid. It is a colourless compound which melts at -4° , distils at $90-91^{\circ}$ under 10 mm. pressure, commences to decompose at 150° , and has a sp. gr. of 1.098 at 15° . It is scarcely soluble in water, but mixes with alcohol and ether in every proportion. The *potassium salt*, $\text{NPr}^{\beta}\text{K}\cdot\text{NO}_2$, forms long, slender, very hygroscopic needles, and the *silver salt*, $\text{NPr}^{\beta}\text{Ag}\cdot\text{NO}_2$, crystallises in thin plates.

When the potassium salts of these nitramines are treated with an alkyl bromide, or the silver salts with an alkyl iodide in alcoholic solution, dialkylnitramines are obtained. The following have been prepared in this manner:—*Dipropylnitramine*, $\text{NPr}^{\alpha_2}\cdot\text{NO}_2$, a colourless liquid boiling at $76-79^{\circ}$ under 10 mm. pressure; *di-isopropylnitramine*, $\text{NPr}^{\beta_2}\cdot\text{NO}_2$, boiling at $55-57^{\circ}$ under 10 mm. pressure; *propylisopropylnitramine*, $\text{NPr}^{\alpha}\text{Pr}^{\beta}\cdot\text{NO}_2$, boiling at $65-68^{\circ}$ under the same pressure; and *benzylpropylnitramine*, $\text{NO}_2\cdot\text{NPr}^{\alpha}\cdot\text{CH}_2\text{Ph}$, melting at $8-10^{\circ}$, and boiling at $200-205^{\circ}$ under 40 mm. pressure. The first three compounds do not solidify in a mixture of solid carbonic anhydride and ether. The silver and potassium salts of propylnitramine, unlike the corresponding methyl derivatives, do not yield a picryl compound on treatment with picric chloride, the latter being simply converted into silver or potassium picrate. Ethyl and isopropylnitramine behave in a similar manner.

When the silver salts of the nitramines are warmed with acetic or benzoic chloride, a simple reaction does not take place. Some silver chloride is precipitated, and nitrous oxide is evolved. It appears probable that the acetyl or benzoyl compound is first formed, and then splits up into propyl acetate or benzoate and nitrous oxide:—



The author has succeeded in isolating propyl benzoate from the product of the reaction with benzoic chloride.

The molecular weights of picrylmethylnitramine (Abstr., 1886, 455) and of isopropylnitramine have been determined by Raoult's method, the results agreeing with the formulæ above ascribed to them.

H. G. C.

Amylamines. By A. BERG (*Compt. rend.*, **111**, 606—608).—Amyl chloride and saturated aqueous ammonia are mixed in equivalent proportions, and sufficient alcohol of 92° is added to completely dissolve the mixture. The liquid is heated at 110—120° for eight or nine hours, poured off from the crystals of ammonium chloride (mixed with a small quantity of diamylamine hydrochloride), acidified with hydrochloric acid, and distilled, to remove alcohol and unaltered amyl chloride. The residual liquid, when allowed to cool, deposits nacreous plates of diamylamine hydrochloride, which can be almost completely separated by successive concentrations. If recrystallised from boiling water after treatment with animal charcoal, it is obtained in perfectly pure, large plates, with a micaceous lustre.

The mother liquor from the diamylamine hydrochloride is evaporated to dryness and made alkaline with potash or soda; the liberated base consists of almost pure amyłamine mixed with a very small quantity of the di- and tri-amine, the proportions in which the three bases are obtained from the original product being monamine 6 parts, diamine 9 parts, triamine $\frac{1}{2}$ to 1 part. The same result is obtained with only half the quantity of alcohol. Alcoholic ammonia yields similar results, but the diamine is formed in still larger proportions.

Pure amyłamine is obtained by the method of Duvillier and Buisine. A dilute aqueous solution is mixed with a suitable quantity of ethyl oxalate, a rise of temperature being avoided; diamyloxamide is precipitated, and is almost completely insoluble in water. The mother liquor, when concentrated, yields amyłamine amyloxamate, $C_6H_{11}\cdot NH\cdot CO\cdot COOH, NH_2\cdot C_5H_{11}$, very soluble in hot water, but much less soluble in cold water, and easily decomposed by aqueous potash, which has very little action on diamyloxamide. With calcium chloride, amyłamine amyloxamate yields a precipitate of calcium amyloxamate, which crystallises readily from hot water in small, brilliant, hydrated lamellæ.

C. H. B.

Diethylenediamine. By A. W. v. HOFMANN (*Ber.*, **23**, 3297—3303).—Diethylenediamine purified by treatment with sodium melts at 104°, boils at 145—146°, and solidifies on cooling, forming a hard, white, crystalline mass, which is extremely soluble in water, and is deposited from absolute alcohol in large, transparent crystals. The benzoyl derivative is deposited from alcohol in rhombic crystals which melt at 191°. A technical product termed "spermin," "piperazin," or "piperazin" is found to be identical with diethylenediamine (compare Sieber, *Abstr.*, 1890, 476).

J. B. T.

Action of Zinc and Ethyl Chloracetate on Ketones and Aldehydes. By S. REFORMATSKY (*J. Russ. Chem. Soc.*, **22**, 44—64).—Acetone, when treated with ethyl chloracetate and zinc, gives a product which, on decomposition with water yields the β -dimethyl- α -enelactic acid (hydroxyvaleric acid), $OH\cdot CMe_2\cdot CH_2\cdot COOH$, of M. and A. Saytzeff. Methyl propyl ketone, under similar conditions, yields β -methylpropylethylene-lactic acid, $OH\cdot CMePr\cdot CH_2\cdot COOH$. This, on distillation with dilute sulphuric acid, yields methylpropylacrylic acid, $CMePr\cdot CH\cdot COOH$. Diethyl ketone, when similarly treated, yields

Shinokoff's β -diethylethylenelactic acid, $\text{OH}\cdot\text{CET}_2\cdot\text{CH}_2\cdot\text{COOH}$. By distillation with dilute sulphuric acid, this acid loses the elements of water, and β -diethylacrylic acid, $\text{CET}_2\cdot\text{CH}\cdot\text{COOH}$, is obtained. The above reaction when applied to butyrone gives rise to Shinokoff's β -dipropylethylenelactic acid, $\text{OH}\cdot\text{CPr}_2\cdot\text{CH}_2\cdot\text{COOH}$, which, on losing the elements of water, is converted into Albitzky's dipropylacrylic acid. This acid yields a dibromide melting at $102-104^\circ$, whereas the dibromide prepared by the author from Albitzky's original acid melts at $80-82^\circ$. This difference is probably due to geometrical isomerism, as the compounds contain an asymmetrical carbon atom. The above reaction may be represented by the general scheme, $\text{RR}_1\text{CO} + \text{CH}_2\text{Cl}\cdot\text{COOEt} + \text{Zn} = \text{CRR}_1(\text{OZnCl})\cdot\text{CH}_2\cdot\text{COOEt}$, and this with $3\text{H}_2\text{O}$ gives $\text{RR}_1\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$. Analogous results obtained with aldehydes will be communicated in a future paper. B. B.

Action of Phosphorus Trichloride on Organic Acids and Water. By C. H. BOTHAMLEY and G. R. THOMPSON (*Chem. News*, **62**, 191).—Thorpe showed (*Trans.*, 1880, 186) that the equation $3\text{CH}_3\cdot\text{COOH} + 2\text{PCl}_3 = 3\text{CH}_3\cdot\text{COCl} + \text{P}_2\text{O}_3 + 3\text{HCl}$ represented the action of phosphorus trichloride on acetic acid. The authors agree that this does represent the fundamental change (which is similar for other monobasic organic acids), and therefore true within certain narrow limits, but with excess of either reagent various secondary reactions take place, which increase with other acids of the series, as the molecular weights become greater and the volatility of the products less. With benzoic acid and phosphorus trichloride, secondary changes take place to a very considerable extent. In fact, this reaction cannot be regarded, as it hitherto has been, as a good method for preparing acid chlorides. Even the action of phosphorus as trichloride on water, which is as follows, $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$, as long as the water is in considerable excess, is disturbed by various secondary reactions as soon as the phosphorus chloride is in excess, giving rise to the formation of yellow phosphorus oxide and other oxides, including the soluble form of the oxide P_4O_6 , which becomes insoluble at 70° ; the yellow oxide was also produced in the other cases given above. Various conditions affect these changes, especially temperature. D. A. L.

Paracrylic and Hydracrylic Acids. By E. KLIMENKO (*J. Russ. Chem. Soc.*, **22**, 100—102).—The author's method of preparing paracrylic acid by the action of silver oxide on β -iodopropionic acid yields larger quantities of the pure acid with difficulty only. The author's improved method consists in evaporating hydracrylic acid with hydrochloric acid on the water-bath. On treating paracrylic acid with an excess of bromine, it yields bromopropionic acid. When paracrylic acid is heated with water at 100° for six hours, it is converted into an acid $\text{C}_3\text{H}_6\text{O}_3$, having the composition of hydracrylic acid. By the action of phosphorus pentachloride on hydracrylic acid, a chloride is produced, which with alcohol yields ethyl β -chloropropionate. B. B.

β -Chlorocrotonic Acids. By W. AUTENRIETH (*Annalen*, **259**, 358—362).—The sodium salt of β -chlorocrotonic acid, unlike the free

acid, does not undergo intramolecular change when it is heated at 170—180° for 12 hours, but is almost completely decomposed into allylene, sodium chloride, and carbonic anhydride; the sodium salt of β -chloroisocrotonic acid is completely decomposed under the same conditions yielding the same products as the isomeride. F. S. K.

Preparation and Properties of Ethyl Sodaacetacetate and Ethyl Sodethylacetacetate. By H. ELION (*Ber.*, 23, 3123—3124).

—It has been previously shown (*Rec. Trav. Chim.*, 3, 231) that anhydrous ethyl sodaacetacetate and anhydrous ethyl sodethylacetacetate are readily soluble in ether, but that both compounds form a hydrate which is insoluble in ether. In preparing the anhydrous compounds by the author's method (*loc. cit.*), they are obtained in ethereal solution; this solution can be most suitably employed for carrying out reactions in which the presence of water or alcohol is to be avoided, and the anhydrous compounds can be readily obtained in a solid state by evaporating the ether at a low temperature. Otto and Rössing's statement (*Abstr.*, 1890, 1137) that anhydrous ethyl sodaacetacetate can be obtained by keeping the hydrate over sulphuric acid is contrary to the author's experience, and Michael's assumption (*Abstr.*, 1888, 1054) that pure anhydrous ethyl sodaacetacetate exists in two forms, one of which is soluble, the other insoluble in ether, is quite unwarranted.

F. S. K.

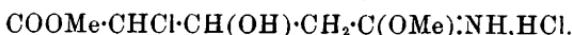
γ -Cyanacetacetates and their Chlorimido-derivatives. By A. HALLER and A. HELD (*Compt. rend.*, 111, 647—650).—Ethyl γ -cyanacetacetate, boiling at 135—138° under a pressure of 40—45 mm., is mixed with its own volume of absolute alcohol, and the mixture is added to about double the quantity of absolute alcohol saturated with hydrogen chloride and cooled to 0°. Heat is developed, ammonium chloride separates, and the liquid contains a chlorine derivative and ethyl acetodicarboxylate. If ammonium chloride does not separate, the liquid is evaporated in a vacuum, mixed with fine sand, and extracted with ether. The ethereal solution yields slender, white needles of the hydrochloride of the imido-ether of ethyl acetodicarboxylate $\text{COOEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{HCl}$, which is decomposed by water with formation of ethyl acetodicarboxylate, $\text{CO}\cdot(\text{CH}_2\cdot\text{COOEt})_2$.

If ethyl γ -cyanacetacetate is dissolved in two or three times its weight of methyl alcohol, and hydrogen chloride is passed into the cooled liquid, crystals are obtained which melt with decomposition at 122°, and consist of the methyl-imido-ether of ethyl acetodicarboxylate plus one molecule of hydrogen chloride. When treated with silver nitrate, half the chlorine is precipitated, but the remainder can only be removed by boiling with potash. When boiled with dilute and slightly acidified alcohol, the compound yields ammonium chloride and an oily chlorinated product.

Methyl γ -cyanacetacetate, obtained in the same way as the ethyl compound, is a somewhat thick, colourless liquid, which rapidly becomes yellow. It boils at 217—218° under normal pressure, and at 127—128° under a pressure of 20—30 mm.; it does not solidify even at a very low temperature. When treated with hydrogen chloride in presence of methyl alcohol, it yields confused white prisms which

melt with decomposition at 144° , and consist of the hydrochloride of the imido-ether of methyl acetodicarboxylate plus one molecule of hydrogen chloride. It dissolves in water and in alcohol, and with potash, acidified alcohol, and silver nitrate it behaves like the corresponding ethyl compound.

It is necessary to assume that under the conditions of experiment the alkyl cyanacetooacetate undergoes molecular change, and behaves as an unsaturated compound, the chloro-derivatives having the constitution $\text{COOMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CHCl}\cdot\text{C}(\text{OMe})\text{:NH}, \text{HCl}$ or



C. H. B.

Mesitene Lactone and Isodehydracetic Acid. By R. ANSCHÜTZ, P. BENDIX, and W. KERP (*Annalen*, **259**, 148—186).—The authors have repeated a number of experiments made by Hantzsch (*Annalen*, **222**, 1) in his investigation of the condensation products of ethyl acetoacetate; they have proved that the formulæ assigned by Hantzsch to mesitene lactone and isodehydracetic acid are correct, and that the original condensation product (m. p. $61-62^{\circ}$) is a mixture of two substances and not a compound of the composition $\text{C}_{18}\text{H}_{22}\text{O}_9$, as was supposed by Hantzsch; they also obtained results at variance with those of Hantzsch in studying the action of ammonia and alkalies on ethyl isodehydracetate, as will be described below.

When the crude condensation product of ethyl acetoacetate is repeatedly extracted with cold chloroform or benzene and the extract mixed with light petroleum, isodehydracetic acid (m. p. 155°) is precipitated in a pure condition, and its ethyl salt and mesitene lactone remain in solution. The acid can be more easily isolated by dissolving the condensation product in a mixture of ether and chloroform and shaking the solution, with concentrated potassium carbonate; on acidifying the alkaline solution, the acid is precipitated in a pure condition, and the ethereal chloroform solution, on evaporation, yields the ethyl salt and mesitene lactone, the last-named compound being invariably produced when ethyl acetoacetate is treated with concentrated sulphuric acid.

Ethyl isodehydracetate and mesitene lactone can be separated from one another by fractional distillation under a pressure of about 12 to 14 mm.; the mesitene lactone passes over at $128-130^{\circ}$, the ethyl salt at 166° .

Methyl isodehydracetate, $\text{C}_9\text{H}_{16}\text{O}_4$, prepared by treating the potassium salt with methyl iodide, crystallises from ether in long, colourless needles, melts at $67-67.5^{\circ}$, and boils at 167° under a pressure of 14 mm.; it can also be obtained, together with isodehydracetic acid and small quantities of mesitene lactone, by treating methyl acetoacetate with concentrated sulphuric acid.

When a mixture of pure ethyl isodehydracetate and the free acid is crystallised from dilute alcohol, a substance is obtained which is identical in appearance with, and has the same melting point ($59-60^{\circ}$) as, the original condensation product.

Attempts to prepare the homomesaconic acid described by Hantzsch were unsuccessful; when ethyl isodehydracetate is hydrolysed with

potash, it gives varying quantities of two new acids, melting at 221° and 149° respectively, together with oily by-products. These two acids were prepared by warming the pure ethyl salt (5 grams) on the water-bath, quickly adding a solution of potash (13 grams) in boiling water (4·5 grams), and then warming the mixture for 10 minutes; 50 grams of the ethyl salt yield 13 grams of the higher melting and 2·5 grams of the lower melting compound.

The acid melting at 221° has the composition $C_5H_6O_2$, but its molecular formula is probably $C_{10}H_{12}O_4$; it is almost insoluble in ether, benzene, chloroform, and cold water, and only moderately easily soluble in boiling water, from which it crystallises in transparent, prismatic needles melting at 221° with decomposition. The potassium salt, $C_{10}H_{10}O_4K_2$, is a vitreous, very hygroscopic compound. The barium salt, $C_{10}H_{10}O_4Ba + 4H_2O$, crystallises from cold water in spherical aggregates and is moderately easily soluble (19·1 parts of anhydrous salt in 100 parts at 20°) in water. The copper salt, $C_{10}H_{10}O_4Cu + 3\frac{1}{2}H_2O$, is apple-green and almost insoluble in water. The silver salt was not obtained in a pure condition. The methyl salt, $C_{10}H_{10}O_4Me_2$, prepared by treating the silver salt with methyl iodide, crystallises from ether in colourless, transparent prisms, melts at 71°, and is readily soluble in ether, alcohol, benzene, and chloroform, but is precipitated from the solutions on the addition of light petroleum.

The acid melting at 149° has the composition $C_8H_{10}O_3$; it crystallises from boiling water, in which it is more sparingly soluble than the acid melting at 221°, in colourless needles, and is readily soluble in alcohol, ether, and chloroform; it decomposes about 160°. The barium salt, $(C_8H_9O_3)_2Ba + 2H_2O$, crystallises in microscopic needles, and is very sparingly soluble in water. The silver salt, $C_8H_9O_3Ag$, is moderately stable in the light.

Mesitene lactam (pseudolutidostyryl,) is formed in small quantities when mesitene lactone is treated with aqueous or anhydrous ammonia under various conditions. It is best prepared by passing anhydrous ammonia for 14 or 15 hours into mesitene lactone (15 grams) heated at 150 to 160°; the lactam (8·5 grams) thus produced is separated from the unchanged lactone (4·5 grams) by fractional distillation. The compound obtained in this way is identical with Hantzsch's pseudolutidostyryl (Abstr., 1884, 1045, and 1885, 397). The *platinum-chloride*, $C_{14}H_{18}N_2O_2H_2PtCl_6$, separates from alcohol in dark-orange, transparent crystals.

When mesitene lactone is treated with alcoholic ammonia, a small quantity of the lactam is obtained, together with ammonium carbamate and a liquid, unstable compound, the nature of which was not determined.

Anhydrous ammonia converts ethyl isodehydracetate into the corresponding lactam, which is identical with the substance (m. p. 137°) obtained by Collie (Abstr., 1887, 501) by the condensation of ethyl β -amidocrotonate.

A compound of the composition $C_{10}H_{18}O_4N_2$ is precipitated as a colourless powder when anhydrous ammonia is passed into an alcoholic ethereal solution of ethyl isodehydracetate, moisture being carefully excluded. It melts at 104° with evolution of ammonia, being recon-

verted into ethyl isodehydracetate, and its constitution is probably represented by the formula $\text{COOEt}\cdot\text{C} \begin{array}{c} \text{CMe:CH} \\ \swarrow \quad \searrow \\ \text{CMe-O} \end{array} \text{C}(\text{NH}_2)\cdot\text{ONH}_4$; when its concentrated aqueous solution is treated with copper chloride, a dark-green, crystalline, copper compound of the composition $(\text{C}_{10}\text{H}_{14}\text{O}_4\text{N})_2\text{Cu} + \text{H}_2\text{O}$ is precipitated.

Ethyl isodehydracetate can be prepared by boiling ethyl sodacetacetate with a benzene solution of ethyl chlorisocrotonate; methyl isodehydracetate can be obtained in like manner.

The synthesis of ethyl isodehydracetate in this way shows that the acid has the constitution assigned to it by Hantzsch; it is probable, therefore, that the acid obtained by Collie (*loc. cit.*) from the lactam, $\text{C}_{10}\text{H}_{13}\text{NO}_3$ (m. p. 137°), referred to above, has an analogous constitution, $\text{COOH}\cdot\text{C} \begin{array}{c} \text{CMe:CH} \\ \swarrow \quad \searrow \\ \text{CMe-NH} \end{array} \text{CO}$, that of the acid obtained by Collie from the isomeric lactam (m. p. 165°) being probably represented by the formula $\text{COOH}\cdot\text{CH}_2\cdot\text{C} \begin{array}{c} \text{CH-CMe} \\ \swarrow \quad \searrow \\ \text{NH-CO} \end{array} \text{CH}$.

F. S. K.

Action of Methylene Iodide and Chloride on Ethyl Malonate in the Presence of Sodium Ethoxide. By S. TANATAR (*J. Russ. Chem. Soc.*, **22**, 32–39).—The experiments were undertaken with the view of obtaining an acid, $\text{C}_4\text{H}_4\text{O}_4$, isomeric or identical with fumaric or maleic acid. The proportion of the substances taken was calculated from the equation $\text{C}_3\text{H}_2\text{Et}_2\text{O}_4 + 2\text{Na} + \text{CH}_2\text{I}_2 + 15\text{C}_2\text{H}_6\text{O}$. Sodium was dissolved in absolute alcohol and ethyl malonate was added to the solution. As on the addition of methylene diiodide, so much heat is developed that the solution will boil if care be not taken, it is advisable, to add the iodide in small portions at a time; to complete the reaction, the mixture was heated for 12 hours in a reflux apparatus. The alcohol was then removed by distillation, water added, and the oily product, which is partly soluble in water, extracted with ether. After distilling off the ether, the residue, containing some unchanged ethyl malonate and methylene iodide, was saponified with a 15 per cent. solution of potash, but part of it remained unchanged. From a solution of the potassium salt thus obtained, the acid was liberated by acidifying with hydrochloric acid and extracting with ether; the iodine was then removed from it by treatment with molecular silver. The free acid forms a honey-like syrup, which does not crystallise, but, on being kept in a desiccator for several months, becomes converted into a hard, gum-like substance. It can be further purified by converting it into the lead or silver salt and decomposing the latter with hydrogen sulphide. The calcium salt, $\text{C}_6\text{H}_8\text{CaO}_5$, is less soluble in hot than in cold water. The free acid, $\text{C}_6\text{H}_{10}\text{O}_5$, is called, by the author, *adipomalic acid*. The silver salt is $\text{C}_6\text{H}_8\text{Ag}_2\text{O}_5$; the barium salt, $\text{C}_6\text{H}_8\text{BaO}_5 + 2\text{H}_2\text{O}$.

That portion of the original product of the reaction which remained unchanged on boiling with 15 per cent. potash was saponified by boiling with strong potash, the potassium salt converted into the lead salt, and this, on decomposition and saturation with lime, into a salt $\text{C}_6\text{H}_6\text{Ca}_2\text{O}_9$. From the filtrate, alcohol precipitates a calcium salt

containing a little less calcium than the salt $C_6H_8Ca_2O_9$, which shows that a mixture of acids was obtained. From a second portion, iodine was removed with silver nitrate, and the silver salt, $C_6H_8Ag_4O_{10}$, was obtained, so that probably the original acids were $C_6H_{10}O_5$ and $C_8H_{12}O_5$. Methylene dichloride and ethyl sodiomalonate, in like manner, yielded the compound $C_4H_2Et_2O_4$, which, on hydrolysis and conversion of the potassium salt, gave the silver salt $C_8H_8Ag_4O_9$. The free acid $C_6H_{10}O_5$ crystallises in prisms which melt at 108—109°.

B. B.

Reaction between Methylene Iodide and Ethyl Malonate. By S. TANATAR (*J. Russ. Chem. Soc.*, **22**, 39—44).—The acid $C_6H_{10}O_5$ (see preceding paper), when heated with water at 150°, undergoes no change, but if heated with hydriodic acid at 150° it yields ethyl iodide and an acid, $C_4H_6O_5$, thus: $C_6H_{10}O_5 + HI = C_2H_5I + C_4H_6O_5$. This acid, $OH \cdot CH_2 \cdot CH(COOH)_2$, the author calls (?) "hydroxymethylmalonic acid," whereas the original adipomalic acid, $C_6H_{10}O_5$, is regarded as ethoxyisosuccinic acid, $EtO \cdot CH_2 \cdot CH(COOH)_2$. On heating the acid at 250°, decomposition takes place, carbonic anhydride being liberated, and a yellow oil distilling over. This is a neutral ethereal salt, which on hydrolysis yields a potassium salt, which is converted into the lead salt, $C_6H_8PbO_5$. The free acid is a thick syrup: the calcium salt is not thrown down on boiling its aqueous solution, so that the acid $C_6H_{10}O_5$ is not identical but isomeric with ethoxyisosuccinic acid, being probably dilactylic acid, as shown by the properties of the calcium and lead salts.

B. B.

Succinamic Acid. By R. SERDA and J. WIEDEMANN (*Ber.*, **23**, 3284—3287).—Succinamic acid, $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COOH$, prepared by treating succinimide with barium hydroxide, as described by Teuchert (*Annalen*, **134**, 139), is identical with the acid prepared by heating nitrosoglutaric acid (Wolff, *Annalen*, **260**, 114). It crystallises from hot acetone in long needles, melts at 156—157°, and is moderately easily soluble in water, but very sparingly soluble or insoluble in alcohol, benzene, and light petroleum; it is converted into ammonium succinate on prolonged boiling with water, and when heated alone at 200°, it is transformed into succinimide.

F. S. K.

Synthesis of Asparagine. By A. PIUTTI (*Gazetta*, **20**, 402—406).—When silver γ -oximidosuccinate, $OH \cdot N < \begin{matrix} CH \cdot COOEt \\ | \\ CH \cdot COOAg \end{matrix}$ (Abstr., 1889, 381), is heated on the water-bath with an excess of an ethereal solution of ethyl iodide, the silver iodide removed, and the solution evaporated at 60—70°, *diethyl nitrilosuccinate*, $N < \begin{matrix} C \cdot COOEt \\ | \\ CH \cdot COOEt \end{matrix}$ remains as a neutral, yellowish oil, which may be distilled in a vacuum with partial decomposition. When this substance is shaken with strong aqueous ammonia, *ethyl nitrilosuccinamate*, $N < \begin{matrix} C \cdot CONH_2 \\ | \\ CH \cdot COOEt \end{matrix}$ or $N < \begin{matrix} C \cdot CONH_2 \\ | \\ CH \cdot O \cdot COEt \end{matrix}$, is formed; this compound crystallises from alcohol

or acetic acid in brilliant, rhombic plates, melts at 166—167°, and yields a bromide, $C_6H_7N_2O_3Br$, which melts with decomposition at about 140°.

On reducing an acetic acid solution of this amide with sodium amalgam (5 per cent. Na), care being taken to maintain the liquid acid, separating the bulk of the sodium acetate by crystallisation, and allowing the mother liquor to remain in prolonged contact with copper acetate, a crystalline deposit of insoluble copper salts is formed, which, on decomposition with hydrogen sulphide, yields a solution containing three asparagines. These may be obtained perfectly pure by precipitating their concentrated solution with alcohol and recrystallising from water. On leaving the mixture in a vacuum, the inactive α -compound loses its water of crystallisation and falls to powder; the β -asparagines may then be separated by their microscopic characters.

The author regards ethyl nitrilosuccinamate as a derivative of the nucleus $N\begin{array}{c} CH \\ \swarrow \\ CH_2 \end{array}$, which he terms "etazole," and has prepared a long series of derivatives of nitrilosuccinic acid in support of this view.

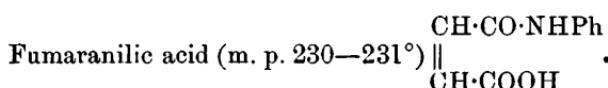
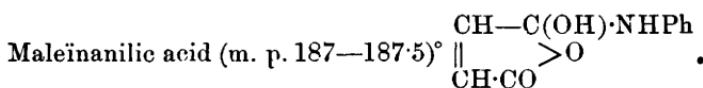
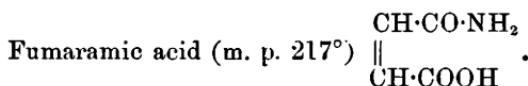
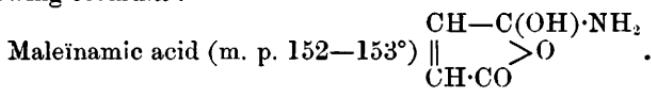
S. B. A. A.

Amic and Anilic Acids of Fumaric Acid and Maleic Acid.
By R. ANSCHÜTZ (*Annalen*, 259, 137—148).—*Maleïnamic acid*, $C_4H_5NO_3$, is obtained when anhydrous ammonia is passed into a chloroform or benzene solution of maleic anhydride, and the gum-like ammonium salt which is gradually precipitated warmed with water until the evolution of ammonia is at an end; on acidifying with hydrochloric acid, the maleïnamic acid is precipitated in crystals, the yield being about 70 per cent. of the theoretical. It crystallises from water in large, transparent, anhydrous plates, melts at 152—153°, and is readily soluble in hot alcohol and water, but only sparingly in hydrochloric acid, and almost insoluble in benzene, ether, and chloroform; when treated with alcoholic potash, it is converted into fumaric acid, but with aqueous alkalis and barium hydroxide in the cold, it yields salts of maleic acid.

Fumaranilic chloride, $C_{10}H_8ClNO_2$, is obtained when fumaric chloride is treated with aniline in ethereal solution, the quantity of base employed being less than is theoretically necessary to convert the chloride into fumaric acid dianilide; the diauilde and aniline hydrochloride produced are separated by filtration, the ethereal filtrate evaporated, and the residue recrystallised from ether. Fumaranilic chloride forms transparent, yellow, prismatic needles, and melts at 119—120°; with alcohols, it yields crystalline ethereal salts, and with amines, it gives amides. When treated with cold water or dilute alkalis, it is converted into an acid of the composition $C_{10}H_9NO_3$, which melts at 230—231°, and is quite different from the fumaranilic acid (m. p. 187—187.5°) previously obtained by the author and Wirtz (*Abstr.*, 1887, 934) from maleïnanil in like manner; the acid melting at 187—187.5° is, therefore, in future to be termed *maleïnanilic acid*, to distinguish it from the acid melting at 230—231°, which is named fumaranilic acid.

Fumaranilic acid is only sparingly soluble in boiling water, but more readily than maleïnanilic acid, and when warmed with alcoholic or aqueous potash, it is, like the latter, converted into fumaric acid.

Judging from their behaviour, the amido- and anilido-derivatives of maleïc and fumaric acids have the constitution expressed by the following formulæ:—



The article concludes with a short criticism of Bischoff's paper on dynamical isomerism (compare Abstr., 1890, 723). F. S. K.

Diglycollic Anhydride. By R. ANSCHÜTZ (*Annalen*, **259**, 187—193).

—*Diglycollic anhydride*, $\text{O} < \begin{array}{c} \text{CH}_2\text{CO} \\ | \\ \text{CH}_2\text{CO} \end{array} > \text{O}$, is obtained when finely divided diglycollic acid is boiled with acetic chloride, or when the acid is distilled under a pressure of 11 to 12 mm. It separates from warm chloroform in long, spear-shaped crystals, melts at 97° , and boils at 120° (12 mm.); it is only sparingly soluble in ether, and is readily reconverted into the acid by cold water.

Diglycollanilic acid, $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}$, is gradually deposited in crystals when an ethereal solution of the anhydride is treated with aniline; it melts at 118° . F. S. K.

Dilactylic Acid. By S. TANATAR and CH. TCHELEVIEFF (*J. Russ. Chem. Soc.*, **22**, 107—110).—It was shown by Friedel and Wurtz that calcium lactate, when heated at $270\text{--}280^{\circ}$, loses 1 mol. H_2O , and becomes calcium dilactate, but neither the salt nor the acid was investigated by them. The experiment was repeated by the authors, and from the calcium dilactate obtained, the free acid, $\text{C}_6\text{H}_{10}\text{O}_5$, was separated by decomposing it with oxalic acid. The syrupy liquid obtained was purified by distillation at 170° , under a pressure of 80—90 mm. The distillate, after remaining for some time in the desiccator, was converted into monoclinic, prismatic crystals melting at $105\text{--}107^{\circ}$, easily soluble in water, ether, chloroform, and acetic acid, but only slightly in benzene. It gives an acid potassium salt, $\text{C}_6\text{H}_8\text{O}_5\text{K}$, and a silver salt, $\text{C}_6\text{H}_8\text{O}_5\text{Ag}_2$, which, on treatment with methyl iodide, gave the methyl salt, $\text{C}_6\text{H}_8\text{O}_5\text{Me}_2$, boiling at 260° . The

zinc salt, $C_6N_8O_3Zn + 3H_2O$, is amorphous. Hydriodic acid at 150° is without action on dilactylic acid.

B. B.

Synthesis of Citric Acid. By A. HALLER and A. HELD (*Compt. rend.*, **111**, 682—685).—Ethyl acetodicarboxylate is prepared from ethyl γ -cyanacetoacetate in the manner previously described (this vol., p. 171), and the ethereal solution of the crude product from 10 grams of the cyanacetacetate is converted into a cyanhydrin by cooling it in a mixture of ice and salt, adding 5 to 6 grams of finely-powdered potassium cyanide, and then, drop by drop, concentrated hydrochloric acid in quantity exactly equivalent to the cyanide. The mixture is allowed to remain in a closed vessel in a cool place for 24 hours, and is then filtered, and the ether distilled off. The cyanhydrin is boiled for two or three hours with concentrated hydrochloric acid in an apparatus with a reflux condenser, the ammonium chloride is removed and the liquid, after being concentrated to expel excess of acid, is boiled with excess of potash. The liquid now contains potassium citrate and chloride with other products formed in the course of the reactions. The citric acid is best separated by means of lead acetate, the precipitate being decomposed by hydrogen sulphide, and the citric acid extracted by means of ether.

50 grams of ethyl γ -cyanacetoacetate yield about 6·2 grams of pure citric acid, and a further quantity of about 4 to 5 grams remains in the syrupy mother liquor.

C. H. B.

Action of Phosphorus Pentachloride on Citric and Aconitic Acids. By E. KLIMENKO and BUCHSTAB (*J. Russ. Chem. Soc.*, **22**, 96—99).—Pebal, by acting with phosphorus pentachloride on citric acid, obtained the solid hydroxychlorocitric acid and two liquid chlor-anhydrides. The authors have treated citric acid (1 part) with phosphorus pentachloride (3 parts) without heating; after some time, the solid contents of the vessel became converted into a liquid, which after the addition of some more citric acid became partly solid. It was then extracted with dry carbon bisulphide and Pebal's hydroxy-chlorocitric was left together with some citric acid; this when treated with alcohol, yielded a liquid boiling between 283° and 285° , identical with Malagutti's triethyl citrate, so that the solid chloride obtained at the beginning of the reaction is $C_6H_5Cl_3O_4$. The same chloride is contained in the liquid product of the reaction. On heating citric acid with phosphorus pentachloride, the liquid product is found to prevail, and this contains some aconitic chloride. Aconitic acid with phosphorus pentachloride gives the chloride $C_6H_5O_3Cl_3$ identical with the above bye-product, and this, on being treated with ethyl alcohol, yields Mercadante's triethyl aconitate. The formula $C_6H_6O_5Cl_2$ given to the solid chloride by Skinner and Ruhemann (*Trans.*, 1889, 235) is contradicted by the authors, who find that the solid product is not homogeneous, but always contains citric acid and probably some aconitic acid.

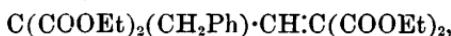
B. B.

Alkyl Substitution Products of Ethyl Dicarboxyglutaconate, and a New Synthesis of $\alpha\alpha$ -Dialkylglutaric Acids. By M.

GUTHZEIT and O. DRESSEL (*Ber.*, **23**, 3179—3186).—The authors have already described a method by which dialkylglutaric acids containing two similar alkyl groups may be prepared (*Abstr.*, 1889, 860). To prepare disubstituted glutaric acids containing two different alkyl groups, it is necessary to start with ethyl dicarboxyglutaconate, $\text{CH}(\text{COOEt})_2\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2$. When the sodium compound of this ethereal salt is heated with an excess of ethyl iodide in a sealed tube at 170 — 180° , it yields the *ethyl* derivative, $\text{CEt}(\text{COOEt})\cdot\text{CH}\cdot\text{C}(\text{COOEt})_2$, as a colourless oil boiling without decomposition at 195 — 202° under 11 mm. pressure. It could not be obtained crystalline, and gives no coloration with ferric chloride. Alcohol must not be employed in the preparation of this substance, as it decomposes the sodium compound at a high temperature. The fact that the ethyl compound is volatile without decomposition, whilst the unalkylated compound decomposes on heating with formation of an α -pyrone derivative, is in full accordance with the explanation already given by the authors of the latter reaction (*loc. cit.*).

On hydrolysis, ethyl ethyldicarboxyglutaconate is converted into *ethylglutaconic acid*, $\text{COOH}\cdot\text{CHEt}\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$, which is a white, crystalline compound melting at 118 — 120° . Its silver salt is a white precipitate, and fairly stable towards light.

Ethyl benzylidicarboxyglutaconate,



is prepared in the manner described by Conrad and Guthzeit (*Annalen*, **222**, 258), and is also volatile without decomposition, boiling at 240° (uncorr.) under 11—12 mm. pressure; it crystallises from alcohol in glassy, rectangular crystals melting at 78° . It is very slowly reduced by zinc-dust and acetic acid.

The ethyl compound, on the other hand, is readily reduced by these reagents with formation of *ethyl ethyldicarboxyglutarate*, $\text{CEt}(\text{COOEt})\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})_2$, which is also an oil boiling at 195 — 197° (uncorr.) under 10—11 mm. pressure. On treatment with sodium ethoxide and benzyl chloride, it is converted into *ethyl ethyl-benzylidicarboxyglutarate*, $(\text{COOEt})_2\text{CEt}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Ph})(\text{COOEt})_2$, which is an extremely thick oil boiling at 210 — 230° under 12 mm. pressure. On hydrolysis, it yields a syrupy tetracarboxylic acid which slowly becomes crystalline, and loses carbonic anhydride on heating at 100 — 210° ; a syrup then remains which on analysis gave numbers approximately agreeing with those required by *ethylbenzyl glutaric acid*, $\text{COOH}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{COOH}$. It has not yet been obtained pure or crystalline, but the neutral solution of its ammonium salt yields more or less insoluble precipitates with salts of most of the heavy metals.

H. G. C.

Thiocarbimidoacetic Acid and Thiohydantoïn. By P. KLASON (*Chem. Centr.*, 1890, ii, 344; from *Ofv. Königl. Vet. Akad.*, 1890, 87).—The author considers that Claus and Neuhöffer's reaction of ethyl bromide on thiohydantoïn is explained thus:—The ethyl bromide reacts with the alcohol with formation of hydrogen bromide, which then reacts with the thiohydantoïn with formation of ammonia

ard thiocarbimidoacetic acid, the latter becoming further converted into thioglycollic acid, carbonic anhydride, and ammonia. *Ethyl thiocarbimidoacetate*, $\text{CSN}\cdot\text{CH}_2\cdot\text{COOEt}$, is formed by the action of carbon thiochloride on ethyl amidoacetate. The carbon thiochloride is diluted with ether, and the ethyl amidoacetate added drop by drop, the mixture being kept cool; ether is then added, filtered from the ethyl amidoacetate hydrochloride, the filtrate distilled, the impure ethyl thiocarbimidoacetate distilled with steam, extracted from the water with ether, and finally distilled in a vacuum. It is thus obtained as a colourless, somewhat thick liquid, having a feeble odour of oil of mustard, boiling at 110° under a pressure of 12 mm. Sp. gr. = 1·1649 at $18^\circ/4^\circ$.

Thiohydantoïn is obtained by heating a mixture of ethyl amidoacetate hydrochloride and dry potassium thiocyanate in molecular proportion at $140-150^\circ$. The mass is dissolved in water, hydrochloric acid added, and the solution evaporated. The compound has the formula $\text{CS} < \begin{matrix} \text{NH}\cdot\text{CH}_2 \\ \text{NH}\cdot\text{CO} \end{matrix}$. When heated with barium hydroxide, *thiohydantoic acid*, $\text{C}_3\text{H}_6\text{N}_2\text{SO}_2$, is formed, which crystallises in beautiful, colourless prisms, very slightly soluble in cold water. Mercuric oxide converts it into hydantoic acid. Ethyl hydantoate is formed in like manner to thiohydantoïn if potassium cyanate is substituted for the thiocyanate, and forms beautiful prisms somewhat readily soluble in hot water, and melting at 138.5° . J. W. L.

Hydrolysis of Sulphones. By E. STUFFER (*Ber.*, **23**, 3226-3241; compare *Abstr.*, 1890, 987).—*Diisopropylsulphonediethylmethane*, $\text{CEt}_2(\text{SO}_2\text{Pr}^{\beta})_2$, is formed in small quantities, the principal product being potassium isopropylsulphonate, when the condensation product of diethyl ketone and isopropyl mercaptan is oxidised with potassium permanganate and dilute sulphuric acid. It crystallises from hot water in small plates, melts at 97° , and is insoluble in cold water and alcohol, but readily soluble in ether, chloroform, benzene, and hot alcohol. Like diethylsulphonediethylmethane (sulphonal), it is not hydrolysed by boiling 30 per cent. aqueous or alcoholic potash.

Potassium isopropylsulphonate, $\text{C}_3\text{H}_6\text{SO}_3\text{K}$, crystallises from hot alcohol in plates, and is readily soluble in water.

Diisobutylsulphonediethylmethane, $\text{CMe}_2(\text{SO}_2\text{CH}_2\text{Pr}^{\beta})_2$, prepared by oxidising the condensation product of acetone and isobutyl mercaptan, forms colourless crystals, melts at 64° , and is only sparingly soluble in hot water, but moderately easily in alcohol, and readily in chloroform, carbon bisulphide, benzene, and ether; it is not hydrolysed by boiling aqueous or alcoholic potash. The yield of the sulphone is only small, as the principal product of the reaction is the potassium salt of the sulphonic acid.

Diisoamylsulphonediethylmethane, $\text{CMe}_2(\text{SO}_2\text{CH}_2\text{CH}_2\text{Pr}^{\beta})_2$, obtained in like manner from isoamyl mercaptan, forms crystalline scales, melts at 72° , and resembles the preceding compound in its behaviour with solvents and alkalis.

Diethylsulphonemethane (compare Fromm, *Abstr.*, 1890, 55) is not

acted on by boiling alcoholic or aqueous potash or by sodium ethoxide in boiling alcoholic solution, but when heated with sodium ethoxide at a temperature above 100°, it is completely decomposed.

Diisobutylsulphonemethane, $\text{CH}_2(\text{SO}_2\text{CH}_2\text{Pr}^8)_2$, prepared by oxidising the condensation product of formaldehyde and isobutyl mercaptan, forms colourless crystals, melts at 85°, and is soluble in alcohol, ether, chloroform, benzene, and hot water, but insoluble in cold water; it resembles diethylsulphonemethane in its behaviour with alkalis. The dibromo-derivative, $\text{CBr}_2(\text{SO}_2\text{CH}_2\text{Pr}^8)_2$, is a crystalline compound melting at 77—78°.

Propylene diethyl sulphide is obtained when propylene bromide is treated with ethyl mercaptan and sodium ethoxide; it is a mobile oil, cannot be distilled, and is decomposed by oxidising agents, but without yielding propylenediyethylsulphone.

Propylene diphenyl sulphide can be prepared by boiling phenyl mercaptan with propylene bromide and 10 per cent. soda for a few hours; it is a heavy oil and cannot be distilled.

Propylenediphenylsulphone, $\text{C}_3\text{H}_6(\text{SO}_2\text{Ph})_2$, is formed by oxidising the sulphide with potassium permanganate; it forms colourless, lustrous plates, melts at 113°, and is soluble in hot alcohol, benzene, chloroform, and hot water, but only sparingly soluble or insoluble in ether and carbon bisulphide, and insoluble in cold water. When boiled with dilute potash, it is decomposed into benzenesulphinic acid and a colourless oil which is probably phenylsulphonepropyl or phenylsulphoneisopropyl alcohol.

Trimethylenediethylsulphone, $\text{C}_3\text{H}_6(\text{SO}_2\text{Et})_2$, can be easily prepared by oxidising trimethylene diethyl sulphide, the condensation product of trimethylene bromide and ethyl mercaptan, with potassium permanganate and dilute sulphuric acid. It crystallises in colourless plates or needles, melts at 183°, and is readily soluble in hot water, but only sparingly in ether, chloroform, benzene, cold alcohol, and cold water; it is not decomposed by hot soda, in which it is soluble, and it is very stable towards bromine and oxidising agents.

Trimethylenediphenylsulphone, $\text{C}_3\text{H}_6(\text{SO}_2\text{Ph})_2$, obtained by heating trimethylene bromide with sodium benzenesulphinate in alcoholic solution, separates from dilute alcohol in crystals, melts at 125—126°, and is almost insoluble in water and cold alcohol, but moderately easily soluble in hot alcohol, benzene, and ether, and very readily in chloroform. It is not acted on by boiling soda or by oxidising agents.

A *trisulphone* of the constitution $\text{SO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CMe}(\text{SO}_2\text{Et})_2$ is obtained when chloracetone is heated with ethyl mercaptan and concentrated hydrochloric acid, and the light-yellow oily product oxidised with potassium permanganate and sulphuric acid. It crystallises from hot water in needles, melts at 137°, and is readily soluble in hot alcohol; it is completely decomposed by warm soda, yielding ethylsulphinic acid.

F. S. K.

Action of Acid Chlorides on Bases in presence of Alkali.
By W. MARCKWALD (*Ber.*, 23, 3207—3218).—It has already been

pointed out by Hinsberg (this vol., p. 49) that the reaction employed by Schatten and Baumann for the preparation of benzoyl derivatives is of very general application. The author has found that a benzene solution of carbonyl chloride also acts in a similar manner on organic bases in presence of an excess of alkali, thus forming a ready method of preparing symmetrically substituted carbamides; the urethanes may also be prepared in a similar manner from the alkyl chloroformates.

In addition to the substituted carbamides which are known, the following derivatives of furylamine, $\text{CH} \cdot \text{O} \geqslant \text{C} \cdot \text{CH}_2 \cdot \text{NH}_2$, have been prepared.

Symmetrical Difurylcarbamide, $\text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{C}_4\text{H}_3\text{O})_2$.—To obtain this compound, a mixture of furylamine with aqueous caustic potash is shaken with a slight excess of a benzene solution of carbonyl chloride until the odour of the latter has disappeared, part of the carbamide separating out. The benzene is evaporated, the separated difurylcarbamide collected, and recrystallised from benzene. It forms small, nacreous plates which are sparingly soluble in all the ordinary solvents, melts at 128° , and has an intense odour resembling that of the dwarf plume-thistle (*Carlina acaulis*).

Ethyl furylcarbamate, $\text{C}_4\text{H}_3\text{O} \cdot \text{CH}_2 \cdot \text{NHCOOEt}$, is obtained in a corresponding manner from furylamine and ethyl chloroformate. It is extracted from the aqueous solution with ether, and remains, after distilling off the latter, as a yellowish oil which has a pleasant odour. On heating, it distils at 240° , forming a colourless liquid, which has, however, then an unpleasant odour, probably owing to the formation of traces of furylcarbamine.

H. G. C.

Rationale of Reactions in the presence of Aluminium Chloride and Bromide. By G. GUSTAVSON (*J. pr. Chem.* [2], **42**, 501—507).—Friedel and Crafts (Abstr., 1889, 241) attributed the action of aluminium chloride and bromide in facilitating the displacement of the hydrogen in benzene, &c., to the formation of such compounds as $\text{C}_6\text{H}_5 \cdot \text{Al}_2\text{Cl}_5$, which, however, could only be isolated in the absence of hydrochloric acid, for this decomposes them. If such be the case, the author asserts that such a compound as $\text{C}_6\text{H}_5\text{SO}_2 \cdot \text{Al}_2\text{Cl}_5$ should also exist, for aluminium chloride brings about a reaction between sulphurous anhydride and benzene (*loc. cit.*) ; but there is no evidence that such a compound is formed when sulphurous anhydride is passed into a mixture of benzene and aluminium chloride; indeed, according to Adrianowsky (Abstr., 1879, 915), quite a different reaction takes place.

Friedel and Crafts fail to see how the compounds $\text{AlCl}_3(\text{C}_6\text{H}_5)_3$, &c., which are formed according to the author's theory (Abstr., 1885, 363), and are exothermic, can facilitate substitution ; the author replies that it is equally difficult to explain how hydrogen which has combined with nitrogen in the exothermic compound ammonia should be more ready to react with methyl chloride, &c., than when in the free state. The author has obtained and analysed the compound $\text{AlCl}_3 \cdot 3\text{C}_6\text{H}_5$; such compounds as this are decomposed by heat, and

will not explain those reactions which only take place at high temperatures.

A. G. B.

Meta- and Para-ethylisopropylbenzene. By P. v. d. BECKE (*Ber.*, **23**, 3191—3196).—The preparation of these hydrocarbons may be readily carried out by means of Friedel and Crafts' reaction. It has been shown by Gustavson (*Ber.*, **11**, 1251), Silva (Abstr., 1885, 1054), and Kekulé and Schrötter, that in the presence of aluminium chloride the propyl group is converted into isopropyl, and in preparing the above hydrocarbon it is immaterial whether propyl or isopropyl bromide is employed. 300 grams of ethylbenzene were therefore mixed with 50 grams of aluminium chloride, and 450 grams of propyl bromide gradually added. After remaining for eight days, the product is washed, dried, and fractionated; the fractions 189—195° and 195—201° contain the meta- and para-ethylisopropylbenzene respectively. The fraction 150—155° is isopropylbenzene, the properties of which agree with the statements of Ciaus and Tonn (Abstr., 1885, 903), except that the author finds the melting point of the sulphonamide to be 93—94° instead of 127°. The fraction 179—185° contains diethylbenzenes, and that boiling at 204—208° consists probably of di-isopropylbenzenes.

To obtain the pure hydrocarbons from the fractions boiling at 189—195° and at 195—201° respectively, both are sulphonated with a mixture of 1 vol. of concentrated sulphuric acid and $\frac{1}{2}$ vol. of fuming acid, the first sulphonic acid being isolated as the barium salt, and the second as the magnesium salt. These are then converted into the potassium salts, and the latter heated with hydrochloric acid under pressure.

Metethylisopropylbenzene is a colourless, pleasant-smelling liquid, which boils at 190—192°, does not solidify at —20°, and on oxidation yields isophthalic acid. *Barium metethylisopropylbenzenesulphonate* crystallises in anhydrous, fascicular aggregates of needles, sparingly soluble in water, whilst the *copper* salt crystallises with 4 mols. H₂O in blue plates which have a satin-like lustre. The *sulphochloride* and *sulphonamide* are oils.

Parethylisopropylbenzene is a liquid which is more strongly refractive than water, boils at 197—198°, and does not become solid at —20°. On oxidation, it is converted into terephthalic acid. *Magnesium parethylisopropylbenzenesulphonate* crystallises with 4 mols. H₂O in tablets which are sparingly soluble in water. The *copper* salt also crystallises with 4 mols. H₂O, and forms blue, satiny plates; whilst the *potassium* salt could only be obtained as an amorphous, readily soluble mass. The *sulphochloride* is an oil, and the *sulphonamide* only becomes partially solid in the exsiccator. The *sulphonanilide*, on the other hand, crystallises in nodular aggregates of prisms melting at 92—93°.

Nitroparethylisopropylbenzene is obtained by the nitration of the hydrocarbon in acetic acid solution, and forms a yellowish-brown oil which boils at 265° with partial decomposition. On treatment with zinc and acetic acid, it is slowly reduced to *amidoparethylisopropylbenzene*, the hydrochloride of which forms fascicular aggregates of

needles, becoming brown in the air. *Parethylisopropylphenol* is obtained by fusing the potassium sulphonate with caustic potash, and is a yellow oil boiling at 228—230°, almost insoluble in water, but readily soluble in alcohol and ether.

The author has also prepared *parethylpropylbenzene* according to Sempotowski's method (Abstr., 1890, 54). It boils at 199—200°, and yields, on sulphonation, only one *sulphonic acid*, the magnesium salt of which crystallises in small prisms containing 4 mols. H₂O, and is readily soluble in water. The *sulphonamide* crystallises from dilute alcohol in small plates which melt at 84°, and the *sulphonanilide* in fascicular aggregates of slender needles melting at 97—98°.

H. G. C.

Diisopropylbenzene. By E. UHLHORN (*Ber.*, **23**, 3142—3144).—A mixture of two hydrocarbons, boiling at 200—210°, is obtained in the preparation of isopropylbenzene (b. p. 153°) by Friedel and Craft's method; the two compounds can be separated from one another by shaking the mixture with concentrated sulphuric acid, converting the sulphonic acids thus produced into their copper or barium salts, and separating the salts by fractional crystallisation.

Barium metadiisopropylbenzenesulphonate crystallises in long needles with 2 mols. H₂O, and is only sparingly soluble in water. The *copper* salt, with 4½ mols. H₂O, forms long, bluish needles, and is readily soluble. The *magnesium* salt, with 4 mols. H₂O, crystallises in well-defined, prismatic plates, and is rather sparingly soluble in water. The sodium and the calcium salts crystallise in needles, and are very readily soluble in water.

Metadiisopropylbenzenesulphonamide crystallises in colourless plates, and melts at 145°.

Trinitrometadiisopropylbenzene forms yellowish needles, and melts at 110—111°. *Metadiisopropylbenzene*, prepared by heating the sulphonamide with hydrochloric acid at 180°, boils at 204°, and, on oxidation with dilute nitric acid, is converted into isophthalic acid.

Copper orthodiisopropylbenzenesulphonate crystallises in plates with 6½ mols. H₂O, and is sparingly soluble in water. The magnesium, calcium, and sodium salts are very readily soluble. The *sulphonamide* melts at 102°, and yields *orthodii-isopropylbenzene* boiling at 209°, which, on oxidation, is converted into phthalic acid.

F. S. K.

Nononaphthene and its Derivatives. By I. KONOVALOFF (*J. Russ. Chem. Soc.*, **22**, 4—23 and 118—148).—Several years ago, Markovnikoff and Ogloblin obtained from Caucasian petroleum a series of hydrocarbons, "naphthenes," of the general formula C_nH_{2n}, having the properties of saturated compounds of the aromatic series. Nononaphthene was obtained from Balachana and Bibi-Eibat petroleum by treating the fraction boiling between 125—140° with fuming sulphuric acid at 40°, washing with aqueous soda and water, drying, and rectifying over sodium, and, after repeated fractional distillation, again purifying it in the same manner. The fraction boiling at 135—136° consists of the hydrocarbon *nononaphthene*, C₉H₁₆; its sp. gr., when prepared from the first-named source, is 0·7664 (20/20°), from the second 0·7647. As sulphuric acid acts on nononaphthene, it is not without reason that

Mendeléeff recommended that the use of this reagent for its purification should be avoided. With excess of sulphuric acid, nononaphthene gives pseudocumenesulphonic acids. Sulphur or antimony pentachloride at high temperatures gives indefinite mixtures of thio- or chloro-derivatives. By the action of bromine and aluminium bromide, part of the hydrocarbon is converted into tribromopseudocumene. Nitric acid of sp. gr. 1·4 is without action in the cold, but if the hydrocarbon is heated at 120—130°, with the same acid diluted with two volumes of water, nitro-derivatives are obtained such as $C_8H_{15}NO_2$; this boils at 218—220°, and on treatment with hydrochloric acid and tin, an amine, $C_8H_{15}NH_2$, isomeric with coniïne is obtained. It smells like that alkaloid, boils between 172° and 177°, and gives only in a feeble degree Hofmann's reaction for primary amines. Its sp. gr. is 0·8727 at 0°, and it is a strong base, combining with acids, and absorbing carbonic anhydride from the atmosphere.

Nononaphthene was heated with hydriodic acid with the object of hydrogenating it, but nonane was not formed. By the action of chlorine, chlorides were obtained, containing principally $C_9H_{17}Cl$, boiling at 185—187°. The chloride was converted into the iodide $C_9H_{17}I$ by heating it with strong hydriodic acid at 150—160°; this boils at 108—111° under a pressure of 200 mm. On heating the chloride or the iodide with silver acetate and acetic acid, the acetate, $CH_3COOC_9H_{17}$, was obtained; it boils at 208·5°. This, on hydrolysis, yields *nononaphthyl alcohol*, $C_9H_{17}OH$, boiling at 189—192°; sp. gr. = 0·8972 at 20°/20°; and the alcohol, on treatment with phosphorus pentachloride, yields the chloride $C_9H_{17}Cl$, mentioned above and having the same properties. A solution of the iodide in ether, when heated with silver oxide, yields the ether ($C_9H_{17})_2O$, boiling at 300·5°; sp. gr. 0·8662 at 20°/20°. The elements of hydrogen chloride are easily removed from the chloride, $C_9H_{17}Cl$, with formation of *nononaphthylene*, C_9H_{16} ; this boils at 135—137°, and has sp. gr. 0·8068 at 0°. With bromine, nononaphthylene yields a dibromide, $C_9H_{16}Br_2$, which is easily split up into hydrogen bromide and the bromo-derivative $C_9H_{15}Br$, but it is impossible to saturate the compound with bromine up to the limit. Oxidation of nononaphthene and its alcohol with chromic mixture yields a complicated mixture of acids. Nononaphthene is proved to be *hexahydropseudocumene* [b. p. 135—138°; sp. gr. 0·7667 (20/0°)]. It has hitherto been found to be impossible to convert it by hydrogenation into nonane, the corresponding saturated hydrocarbon of the fatty series.

B. B.

Caucasian Petroleum. By V. MARKOVNIKOFF (*J. Russ. Chem. Soc.*, 22, 23—26).—By fractional distillation of the lower boiling portions of Caucasian petroleum, previously purified by fuming sulphuric acid, the author has obtained a series of fractions boiling between 32° and 72°, and not further separable by fractional distillation. The relation between the boiling points and the densities shows that the higher fractions contain a comparably larger proportion of naphthenes having a higher density than the corresponding paraffins, whereas the latter are more abundant in the fractions of lower boiling point. It is shown that the portion boiling between 57° and 60° contains neither

hexanaphthalene nor benzene, and that it consists principally of di-pseudopropyl C_6H_{14} . The fraction 45—48° contains hexane (dimethylethylmethane) and pentane; the fraction 32—36° consists chiefly of dimethylethylmethane, whilst the fraction boiling above 60° contains normal hexane.

B. B.

Action of Thionyl Chloride on the Phenols. By G. TASSINARI (*Gazzetta*, **20**, 362—366).—The action of thionyl chloride on the phenols results in the formation of a mixture of variable quantities of three substances, namely (1), a compound of high melting point not examined further; (2) a dihydroxythiobenzene identical with that obtained by the action of sulphur dichloride on phenol (Abstr., 1889, 245); (3) chlorinated and sulphuretted resins. Hydrogen chloride and sulphurous anhydride are also evolved during the reaction. Thionyl chloride has a similar action on orthocresol and thymol, the only difference being that with orthocresol a good deal of the compound of high melting point is formed, and but little of the dihydroxythiobenzene, the reverse occurring with thymol; paracresol is scarcely affected in the cold, only a trifling quantity of liquid chloroparacresol being formed.

The dihydroxythiobenzene previously described (*loc. cit.*) has the following crystallographic characters. The crystals belong to the monoclinic system:— $a : b : c = 0\cdot41564 : 1 : 0\cdot26415$; $\beta = 86^\circ 48'$. The derived hydroxysulphonebenzide crystallises in the rhombic system:— $a : b : c = 0\cdot78133 : 1 : 0\cdot415568$; $\beta = 90^\circ$. S. B. A. A.

Condensation Products of Glyoxal and some Mercaptans. By E. STUFFER (*Ber.*, **23**, 3241—3245).—Glyoxal combines with ethyl mercaptan in presence of hydrochloric acid, but the product cannot be obtained in a pure condition, nor can it be converted into a tetrasulphone by oxidation with potassium permanganate.

Tetrathiophenylglyoxal, $CH(SPh)_2CH(SPh)_2$, is formed when glyoxal sodium hydrogen sulphite is warmed with phenyl mercaptan in alcoholic hydrochloric acid solution. It separates from alcoholic chloroform as a colourless powder, melts at 115°, and is very readily soluble in chloroform, but only sparingly in boiling alcohol, and insoluble in water and alkalis. It dissolves in warm concentrated sulphuric acid with a cherry-red coloration, is readily oxidised and decomposed by concentrated nitric acid, and combines with bromine, yielding a yellow, oily compound; when treated with potassium permanganate under various conditions, it is either unchanged or completely decomposed, so that the corresponding sulphone cannot be obtained.

F. S. K.

Nitrometacresols. By W. STAEDEL and A. KOLB (*Annalen*, **259**, 208—227; compare Abstr., 1889, 497).—The two metanitrocresols which are obtained by nitrating pure cresol, prepared from thymol, can be easily separated by distillation with steam. The non-volatile compound (m. p. 129°) crystallises from water and alcohol in needles, is very readily soluble in benzene, ether, chloroform, alcohol, and hot water, and dissolves in alkaline carbonates with evolution of carb-

onic anhydride. The ammonium derivative forms long, yellow needles, and the silver derivative is a yellowish-red compound almost insoluble in water. The potassium derivative, $C_7H_9NO_3K + 2H_2O$, and the sodium derivative, with $2H_2O$, crystallise in yellow plates, and the barium derivative in silky needles. The ethyl derivative melts at $53-54^\circ$, and is identical with the compound obtained by nitrating metacresol ethyl ether.

Orthonitrometatoluidine [$Me : NH_2 : NO_2 = 1 : 3 : 6$], prepared by heating nitrometacresol ethyl ether with concentrated ammonia at $140-150^\circ$, crystallises from water in slender, yellow needles, melts at 134° , and is readily soluble in alcohol, ether, and hot water; when treated with sulphuric acid and sodium nitrite in alcoholic solution, it is converted into nitrotoluene (b. p. 220-221°).

Amidometacresol [$Me : OH : NH_2 = 1 : 3 : 6$], obtained by reducing the nitro-compound with tin and hydrochloric acid, is a grey powder melting at 174° with decomposition. The *hydrochloride*, $C_7H_9ON.HCl$, crystallises in colourless plates. The *acetyl derivative*, $C_9H_{11}NO_2$, crystallises from water, in which it is readily soluble, in colourless plates containing 1 mol. H_2O ; these melt at 80° and lose their water at $110-120^\circ$; the anhydrous compound melts at 125° , and is sparingly soluble in benzene.

Methylquinonechlorimide, C_7H_6NOCl , is precipitated when a concentrated solution of calcium hypochlorite is added to a dilute aqueous solution of amidometacresol hydrochloride. It crystallises from alcohol in golden prisms, melts at 75° , and explodes at a higher temperature.

Dinitrometacresol ethyl ether [$Me : OEt : (NO_2)_2 = 1 : 3 : 4 : 6$] is formed when the corresponding mononitro-compound is treated with fuming nitric acid. It crystallises from dilute alcohol in colourless needles, and melts at 97° .

Dinitrometatoluidine, prepared by heating the preceding compound with ammonia at 100° , separates from xylene in yellow crystals, melts at 195° , and is only sparingly soluble in alcohol and benzene; when treated with nitrous acid under suitable conditions, it is converted into α -dinitrotoluene [$Me : (NO_2)_2 = 1 : 4 : 6$].

Trinitrometacresol ethyl ether [$Me : (NO_2)_3 : OEt = 1 : 2 : 4 : 6 : 3$] crystallises from alcohol in slender needles or in thick prisms melting at 75° ; it is probably identical with the compound (m. p. 72°) obtained by Nöltig and von Salis from the silver derivative of trinitro-cresol; when treated with alcoholic ammonia, it is converted into trinitrotoluidine (m. p. 136°).

The volatile nitrometacresol (m. p. 56°) crystallises from ether in yellow plates, and is only very sparingly soluble in water, but very readily in alcohol, ether, benzene, and chloroform. The potassium derivative crystallises in red needles, and is very readily soluble in water. The ethyl derivative, $C_8H_{11}NO_3$, crystallises from alcohol in colourless needles, melts at $50-51^\circ$, and is very readily soluble in most of the ordinary solvents.

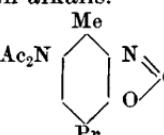
Nitrometatoluidine [$Me : NH_2 : NO_2 = 1 : 3 : 4$], prepared by heating the ethyl derivative with ammonia at $140-150^\circ$, crystallises from water in golden plates, melts at 109° , and is moderately easily

soluble in alcohol, ether, benzene, chloroform, and hot water; ethyl nitrite at 100° converts it into paranitrotoluene.

When nitrometacresol ethyl ether (m. p. 50—51°) is treated with nitric acid, it is converted into a dinitro-compound identical with that (m. p. 97°) obtained from the isomeride described above.

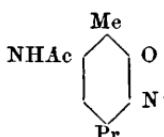
F. S. K.

Constitution of Thymol and Carvacrol Derivatives. By G. MAZZARA (*Gazzetta*, **20**, 417—427).—*Tetracyldiamidothymol acetate* [$\text{Me} : \text{N}(\text{Ac}_2)_2 : \text{OAc} : \text{Pr} : \text{N}(\text{Ac}_2)_2 = 1 : 2 : 3 : 4 : 6$], prepared by heating diamidothymol hydrochloride with acetic anhydride, crystallises from dilute alcohol in shining, white scales, softens at 179°, and melts at 184—186°. It is insoluble in alkalis.

Diacetylamidoethenylamidothymol, , is obtained as

a bye-product in the preparation of the preceding compound. It is prepared by heating that compound or its constituents at a temperature of 200° to 260°. It crystallises from light petroleum in large, colourless, transparent, rhombohedral tables, melts at 92—94°, and dissolves in the ordinary solvents. It is decomposed by prolonged digestion with alkalis yielding products which impart a violet coloration to the liquid. The action of dilute hydrochloric acid removes one acetyl group from this compound, leaving *monacetyl-amidoethenylamidothymol*, a substance which crystallises from alcohol in yellowish or violet needles melting at 132—134°. It dissolves readily in alcohol and benzene. It is reconverted into the diacetyl derivative by heating with acetic anhydride at 200°. It is decomposed by digestion with alkalis or acids.

The action of acetic anhydride on diamidothymol hydrochloride at 160° results in the formation of a mixture of *di*-, *tri*-, and *tetracyldiamidothymol*. These compounds are all soluble in potash, forming pink solutions, from which acids precipitate the diacetyl derivative. They also dissolve in boiling water and in dilute alcohol, crystallising out in white or pale-violet scales. The tetracyl compound melts at 216—222°, the triacetyl compound at 238—240°, and the diacetyl derivative at 260—262°.

Acetylamidoethenylamidocarvaerol, , prepared by

heating diamidocarvacrol hydrochloride with excess of acetic anhydride at 210°, crystallises from alcohol in yellowish needles and melts at 190—192°. The formation of this ethenyl derivative and of the benzenyl derivative previously described (this vol. p. 48) support the author's view, that in dinitrocarvacrol the two nitroxyl groups are in the meta-position relatively to each other. S. B. A. A.

Constitution of Rhodizonic Acid. By R. NIETZKI (*Ber.*, **23**, 3136—3141).—The author agrees with Nef (*Abstr.*, 1890, 1270) that rhodizonic acid has the constitution $C_6O_4(OH)_2$ [$O_4 : (OH)_2 = 1 : 2 : 3 : 4 : 5 : 6$], and not the symmetrical constitution [$O_4 : (OH)_2 = 1 : 2 : 4 : 5 : 3 : 6$]. One of the principal facts which points to this conclusion is that croconic acid hydride, $C_5H_4O_5$, a compound which is formed from rhodizonic acid under the influence of concentrated alkalis, does not combine with orthodiamines, whereas croconic acid, $C_5H_2O_5$, is readily converted into azines. This difference in behaviour is best accounted for by assuming that the hydride has the constitution $O\cdot H < \begin{matrix} CO\cdot C\cdot OH \\ || \\ CO\cdot C\cdot OH \end{matrix}$, and the formation of a compound of this nature from rhodizonic acid can only be explained by assuming that the latter has the asymmetrical structure. The existence of dinitroso-resorcinoltetroxime, $C_6H_2(N\cdot OH)_4$ [$(NOH)_4 = 1 : 2 : 3 : 4$], seems to show that the quinone of the constitution $C_6H_2O_4$ [$O_4 = 1 : 2 : 3 : 4$] is also capable of formation, whereas no symmetrical paradiquinone has yet been obtained; this argument, as well as the behaviour of rhodizonic acid with orthodiamines, bears out the author's views regarding the constitution of rhodizonic acid.

F. S. K.

Replacement of the Hydrogen Atoms in the Methylene Group. By O. WALLACH (*Annalen*, **259**, 300—309).—The hydrogen atoms of a methylene group which is in direct combination with basic radicles are readily displaced by negative elements, more especially by sulphur; and in most cases, the reaction proceeds so well that it can be conveniently employed for the preparation of various sulphur compounds.

When benzylaniline (1 mol.) is heated with sulphur (2 atoms) at 220° until the evolution of hydrogen sulphide ceases, thiobenzanilide is formed; if, however, the temperature is raised to 250 — 260° , and the heating is continued, benzenylamidothiophenol (m. p. 115°) is obtained. Benzyltoluidine and other benzyl bases behave like benzylaniline.

Tetramethyldiamidothiobenzophenone can be easily obtained by heating tetramethyldiamidophenylmethane (50 grams) with sulphur (15 grams) at 230° until the evolution of hydrogen sulphide is at an end; thiobenzamide can be prepared by heating benzylamine with sulphur at 180° .

Tribenzylamine combines with bromine in glacial acetic acid solution, yielding a compound of the composition $(C_7H_7)_3NBr_2$; this substance crystallises in golden needles, melts at 157 — 159° , is reconverted into tribenzylamine by sulphurous acid, and when boiled with water, is decomposed into benzaldehyde, dibenzylamine, and tribenzylamine.

When benzylamine is treated with bromine in glacial acetic acid solution, it yields a crystalline substance melting at 103° , which seems to have the composition $CH_2Pb\cdot NH_2Br_2$; this bromo-compound is decomposed by warm water and alcohol, and also on exposure to the air, into benzonitrile and benzylamine hydrobromide. F. S. K.

Action of Paratoluidine and Aniline on Phloroglucinol. By G. MINUNNI (*Gazzetta*, 20, 319—355).—Phloroglucinol reacts very energetically with paratoluidine or aniline forming compounds analogous to those obtained by the action of the aromatic amines on monhydric and dihydric phenols. Both symmetrical triparatolytriamidobenzene, $C_6H_3(NHC_6H_4)_3$, the product of the action of paratoluidine on phloroglucinol, and triphenyltriamidobenzene, obtained from aniline and phloroglucinol, together with a number of their derivatives, have already been described (*Abstr.*, 1888, 1081). The following are additional products:—The *nitrosyl* derivative of triparatolytriamidobenzene, $C_6H_3[N(C_6H_4)NO]_3$, crystallises from boiling alcohol in slender, deep-brown needles, melts at 233—234°, and dissolves sparingly in hot benzene and in alcohol after prolonged boiling; it is readily soluble in concentrated sulphuric acid forming a dirty-green solution.

Diparatolyldiamidoxybenzene, $OH \cdot C_6H_3(NHC_6H_4)_2$, prepared by heating a mixture of phloroglucinol (1 mol.) and paratoluidine (2 mols.) for six hours at 140—150°, crystallises when pure from a mixture of ether and light petroleum in colourless needles, melts at 120—121°, and, on exposure to the air, turns grey at first, but becomes intensely brown after a time. It dissolves readily in cold benzene, alcohol, and ether, and in hot alkalis, but only very sparingly in boiling water and in concentrated hydrochloric acid. It is also soluble in concentrated sulphuric acid forming a colourless solution which turns brown on heating, and reddish on addition of a little potassium nitrite. The *hydrochloride* may be obtained as a yellow, flocculent, amorphous precipitate which decomposes as soon as it is removed from the acid solution. The *platinum salt*,



crystallises in brilliant, bronze-coloured scales, insoluble in ether, and only very sparingly soluble in boiling alcohol; it is decomposed by hot water; on heating to 260°, it is converted into a brown, amorphous powder.

The *acetyl* derivative, $OH \cdot C_6H_3(NAcC_6H_4)_2$, crystallises in colourless, microscopic prisms, melts at 128—129°, and dissolves in cold alcohol and benzene, and very sparingly in ether. It is also sparingly soluble in alkalis, and more readily in concentrated acids. Ammonia precipitates it unchanged from its hydrochloric acid solution.

The *benzoyl* derivative, $OBz \cdot C_6H_3(NBzC_6H_4)_2$ (?), forms a colourless, crystalline powder consisting of microscopic plates, and melts at 262—264°. It is almost insoluble in ether, and only very sparingly soluble in alcohol and benzene. It is insoluble in alkalis, but dissolves in concentrated sulphuric acid, and is reprecipitated unchanged on diluting the solution. Its composition is doubtful.

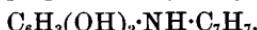
The *nitrosyl* derivative, $OH \cdot C_6H_3(NC_6H_4NO)_2$, crystallises in brownish-red, microscopic needles which darken on heating to 230°, but do not fuse even at 260°. It is very sparingly soluble in alcohol and benzene, and almost insoluble in ether.

The *nitrosyl* derivative of triphenyltriamidobenzene, $C_6H_3(NPh \cdot NO)_3$, crystallises from alcohol in brilliant, brown needles, melts at 264—265°,

and is almost insoluble in alcohol and benzene. It dissolves in cold concentrated sulphuric acid forming a solution which appears dark-green by reflected light, and copper-coloured in the magnesium light.

Diphenyldiamidoxybenzene, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NHPH})_2$, is prepared by heating phloroglucinol with aniline in the theoretical proportions for six hours at 140—150°. It crystallises from a mixture of ether and petroleum in slender, white needles which acquire a grey tinge after some time, melts at 94—95°, and dissolves readily in cold alcohol, benzene, and ether, but only sparingly in water, alkalis, and hydrochloric acid. On cooling its solution in potash, a substance separates out, readily soluble in water. It dissolves in cold concentrated sulphuric acid, and the solution turns blue on the addition of a little sodium nitrite, and brownish-red when a larger quantity is added. The *hydrochloride*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NHPH})_2\cdot 2\text{HCl}$, is an amorphous, brownish-yellow powder which is decomposed by hot water; it melts at 85—90°, and is soluble in alcohol, but not in ether. The *platinum salt*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NHPH})_2\cdot \text{PtCl}_4$, crystallises in large, yellowish-brown plates which darken at 230°; it dissolves readily in boiling alcohol, but is insoluble in ether. It is decomposed by boiling water.

The *acetyl derivative*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NPhAc})_2$, forms a white, crystalline powder which melts at 149—150°, and dissolves readily in boiling alcohol and benzene. It is moderately soluble in hot alkalis and in cold concentrated acids. Ammonia precipitates from its hydrochloric solution a white powder soluble in excess. The *benzoyl derivative*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NPhBz})_2$, is obtained by treating the base with benzoic anhydride. It crystallises from alcohol in large, bright-yellow needles, melts at 184—185°, and dissolves readily in the ordinary solvents, and also in boiling alkaline solutions and in cold concentrated sulphuric acid. The *nitrosyl derivative*, $\text{OH}\cdot\text{C}_6\text{H}_3(\text{NPh}\cdot\text{NO})_2$, crystallises from boiling glacial acetic acid in bright-red needles, and blackens without melting at 250°; it is almost insoluble in the ordinary solvents, but dissolves in cold concentrated sulphuric acid. Attempts were made to prepare a dihydroxy-derivative,



by moderating the reaction between phloroglucinol and paratoluidine, but without success, the monhydroxy-derivative being formed in every instance; a similar failure attended an attempt to prepare mixed derivatives of the type $\text{C}_6\text{H}_3(\text{NH}\cdot\text{C}_7\text{H}_7)_2\cdot\text{NHPH}$. From the foregoing results, it appears that phloroglucinol, a trihydric phenol, reacts more energetically with aromatic amines than the dihydric phenols, which in turn are more active than the monhydric compounds. The energy of reaction must, therefore, depend directly on the number of OH-groups present. Moreover, in view of the complete analogy between the action of ammonia and that of the substituted amines, it seems probable that phloramine, the product of the action of ammonia on phloroglucinol, is also a derivative of trihydroxybenzene, and not of the secondary phloroglucinol, $\text{CO}\cdot\text{CH}_2\cdot\overset{\text{CO}}{\underset{\text{CH}_2}{\text{O}}}$, as indicated by Baeyer (Abstr., 1886, 350).

S. B. A. A.

Consecutive Tetramidotoluene. By R. NIETZKI and R. RÖSEL (*Ber.*, 23, 3216—3219).—A mixture of the mono- and di-nitro-derivatives of diacetylmetatoluylenediamine is obtained when diacetylmetatoluylenediamine is mixed with carbamide nitrate, and then gradually introduced into nitric acid (6 parts), which has been previously distilled with sulphuric acid, the temperature being kept at from 5 to 10°. The two compounds are precipitated with ice and hydrolysed with dilute sulphuric acid or dilute alkalis; the mono- and di-nitrometatoluylenediamine obtained in this way can be easily separated from one another, as the latter alone is soluble in alkalies, being reprecipitated on the addition of an acid.

Dinitrometatoluylenediamine, $C_6HMe(NO_2)_2(NH_2)_2$, forms slender, golden needles and melts above 300°.

Tetramidotoluene sulphate, $C_6HMe(NH_2)_4H_2SO_4$, is obtained when the dinitro-compound just described, or tetraisonitrosoresorcinol [$Me : (NOH)_4 = 1 : 3 : 4 : 5 : 6$], is reduced with stannous chloride and hydrochloric acid; the filtered solution is treated with sulphuric acid, then mixed with a considerable quantity of alcohol, the precipitated sulphate dissolved in moderately dilute hydrochloric acid and reprecipitated with alcohol; it crystallises in small, almost colourless plates. When excess of sulphuric acid is added to a hydrochloric acid solution of this salt, a compound of the composition



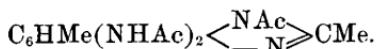
is precipitated in small plates.

Tetramidotoluene cannot be obtained by decomposing one of its salts, as it rapidly oxidises on exposure to the air; solutions of its salts are coloured brown by ferric chloride and other oxidising agents, but a definite oxidation product could not be obtained.

A *quinoxaline* of the composition $C_{35}H_{24}N_4$ is gradually deposited in yellowish-red needles when tetramidotoluene sulphate is heated with benzil and sodium acetate in alcoholic solution; it melts at 222—225°, and dissolves in concentrated sulphuric acid yielding a red solution, the colour of which changes to yellow on the addition of water.

Croconic acid also combines with tetramidotoluene, yielding a dark-brown azine, which crystallises in needles, but is so insoluble in all ordinary solvents that it cannot be purified by recrystallisation.

When tetramidotoluene sulphate is heated with sodium acetate and acetic anhydride, a compound of the composition $C_{15}H_{20}N_4O_4$ is obtained; this substance crystallises in colourless needles, melts at 305°, is moderately easily soluble in hot water, and is probably a triacetylethenyltetramidotoluene of the constitution



It dissolves in dilute hydrochloric acid, and on adding ammonia to the solution, a colourless, very readily soluble base melting at 282° is precipitated; judging from the analysis of the picrate, this base is probably diacetylethenyltetramidotoluene.

F. S. K.

Diazo-compounds. By H. GOLDSCHMIDT (*Ber.*, **23**, 3220—3222).—The author has determined the molecular weight of meta- and para-nitrodiazobenzene nitrate and of diazobenzene chloride, in aqueous solution by Raoult's method; the experiments have shown that in very dilute aqueous solutions these salts are completely dissociated, but that in more concentrated solutions the observed molecular weight increases rather rapidly, more quickly, in fact, than is the case with most metallic salts; the electrical conductivity of solutions of diazo-salts is also being investigated. F. S. K.

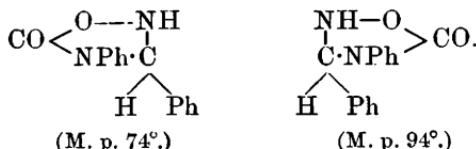
Aldoximes. By E. BECKMANN (*Ber.*, **23**, 3319—3331, and 3331—3341).—Salicylaldoxime (m. p. 57°) may be converted into an isomeric modification by the action of hydrochloric acid, either at the ordinary temperature or on heating. The α -benzyl ether of this compound is prepared by the action of sodium ethoxide and benzyl chloride, and crystallises from warm alcohol in slender, colourless, interlaced needles which melt at 62—63°.

The same compound is also obtained by heating an alcoholic solution of salicylaldehyde with α -benzylhydroxylamine hydrochloride and hydrogen sodium carbonate. The corresponding β -benzyl ether is formed in a similar manner from β -benzylhydroxylamine, and crystallises from dilute alcohol in pale-yellow, lustrous, rectangular plates which melt at 99—100°.

ACTION OF PHENYLCARBIMIDE ON THE BENZALDOXIMES.—The phenyl isocyanate employed in the following experiments boiled at 161—162°, and was absolutely free from hydrogen chloride. β -Benzaldoxime is dissolved in 12—14 parts of absolute ether, and treated at 5° with rather less than the calculated quantity of phenylcarbimide; a copious white precipitate is immediately formed, consisting of microscopic, quadratic plates which melt at 74—75° with evolution of gas; on boiling with dilute potash, carbonic anhydride, aniline, and diphenylcarbamide are formed. On warming equivalent quantities of β -benzaldoxime and phenylcarbimide dissolved in benzene, and evaporating the solution, crystals are deposited which melt at 94° with evolution of gas; the substance is isomeric with the previous compound, and has already been prepared by Goldschmidt (*Abstr.*, 1890, 251). Carbonic anhydride and a trace of diphenylcarbamide are formed by the action of dilute potash. The first of these isomerides is very sparingly soluble, and is converted into the higher melting derivative on warming with benzene, but this latter cannot be transformed into the lower melting compound. Neither of the substances reacts with phenylcarbimide; with hydrogen chloride, both yield the compound (m. p. 134°) described by Goldschmidt (*loc. cit.*). By the action of dilute soda in the cold, the lower melting compound yields chiefly β -benzaldoxime, whilst benzonitrile is the principal product from the higher melting modification.

By the action of phenylcarbimide on α -benzaldoxime in ethereal solution, a compound separates which melts at 75° and is identical with the above derivative from β -benzaldoxime; if this substance is removed and the solution allowed to remain for a short time, a second compound crystallises out in needles which melt at 135°; this has

previously been described by Goldschmidt. α -Benzaldoxime is, therefore, less stable than has hitherto been supposed; it is also found that by warming, or by keeping the β -aldoxime for some time, the yield of the β -derivative is increased. The author suggests that the two compounds obtained from β -benzaldoxime and phenylcarbimide are represented by the following formulæ:—



Benzalbenzamide, $\text{NHBz} \cdot \text{C}_6\text{H}_7$, is obtained by the action of benzoic chloride on β -benzaldoxime benzyl ether, and crystallises from benzene in colourless plates which melt at 105° . Acetic chloride and phosphorus oxychloride act in a similar manner, but hydrogen chloride in benzene solution causes no change. The compound may be prepared synthetically from benzylamine and benzoic chloride. On heating the amide with hydriodic acid, benzyl iodide, benzoic acid, and ammonia are formed, whilst in similar circumstances β -benzaldoxime benzyl ether yields a small quantity of benzoic acid and benzylamine. Goldschmidt prepared a compound (m. p. 121°) by the action of phenylcarbimide on β -benzaldoxime benzyl ether; this result is confirmed. On heating with concentrated hydriodic acid, benzyl iodide is formed; boiling hydrochloric acid is without action, but on heating at 140° , complete decomposition takes place; the compound is unchanged by sulphuric acid at ordinary temperatures.

By the action of sodium ethoxide on the carbanilido-product dissolved in alcohol, carbonic anhydride is eliminated, and a basic compound of the formula $\text{C}_{20}\text{H}_{18}\text{N}_2$ is obtained, which crystallises from dilute alcohol in large, flat, rectangular plates melting at 99 — 100° . The hydrochloride crystallises with difficulty. The same compound is formed by the action of benzanilidiimidochloride on benzylamine, and it must therefore be regarded either as symmetrical benzylphenylbenzylamidine, or as a quinazoline derivative (see below). The compound is not acted on by hydrochloric acid and alcoholic ammonia; on heating with hydriodic acid, it yields benzoic acid, ammonia, and aniline.

On heating the carbanilido-derivative with alcoholic ammonia at 100° for an hour, benzylideneaniline is formed, together with a viscous, oily liquid which yields benzylidenephenylhydrazone on treatment with phenylhydrazine; its molecular weight is 111, as determined by Raoult's method; the compound contains two CHPh groups, together with the complex NPh , but its exact constitution is not yet determined.

Of the three formulæ for β -benzaldoxime, namely, $\text{PhC.N(OH)C}_6\text{H}_7$, $\text{OH.CPh:N.C}_6\text{H}_7$, and $\text{PhCH.N.C}_6\text{H}_7$, the author has previously ad-

$\begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array}$

vanced the first two; the above results point, however, to the absence

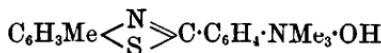
of a hydroxyl group, and consequently the third one would appear to be the most probable. The compound formed by the action of phenylcarbamide would be represented by the formula $\begin{array}{c} \text{NH}-\text{CHPh} \\ | \\ \text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO} \end{array} > \text{NPh}$, which would account for its great stability; by the elimination of carbonic anhydride, an amidine or quinazoline derivative would be formed, with the formula $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CPh}\cdot\text{NPh}$ or



respectively.

J. B. T.

Dyes of the Primuline Group. By E. TRAUTMANN (*Chem. Centr.*, 1890, ii, 440—441; from *Mon. Sci.* [4], 4, 811—820).—If dehydrothiotoluidine, prepared by heating paratoluidine with sulphur (Green, *Trans.*, 1889, 227; Gattermann and Pfitzinger, *Abstr.*, 1889, 867), be heated with methyl alcohol and hydrogen chloride or iodide at 150—200°, the salts of the ammonium base



are formed; the chloride has been introduced into the market under the name *thioflavin*, and is a similar dye to auramine. The primuline base is prepared by heating thiotoluidine or dehydrothiotoluidine, or even paratoluidine, with sulphur; its constitution has not yet been established. Treatment with fuming sulphuric acid converts it into the sulphonic acid, the sodium salt of which is primuline. (For the similar dyes obtained from metaxylyidine and pseudocumidine, see *Abstr.*, 1889, 602.) Dehydrothioxylidine unites with α -naphthol- α -sulphonic acid, forming the dye named "*Erika*." *Thiazole-yellow* is sodium amidoazodehydrothiotoluidinesulphonate; it dyes unbleached fibre greenish-yellow and cannot be deazotised on the fibre.

J. W. L.

Parachloracetotoluidide and Metaparanitrochloracetotoluide. By H. ECKENROTH and A. DONNER (*Ber.*, 23, 3287—3289).—Parachloracetotoluidide has previously been obtained by the action of chloracetic chloride on paratoluidine, and may be prepared by heating paratoluidine (1 mol.) with chloracetic acid (2 mols.) at 80—90° for two hours; the product is treated with water and recrystallised from alcohol. If the temperature is allowed to rise somewhat, a second compound is formed, which is being further investigated; it is sparingly soluble in water, but dissolves in dilute potash, and is precipitated by hydrochloric acid; from alcohol, it crystallises in white needles melting above 230° with decomposition.



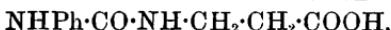
is prepared by the action of nitric acid at ordinary temperatures on the chloracetic derivative, and crystallises from alcohol in yellow needles which melt at 122° and yield metaparanitrotoluidine on treatment with potash.

J. B. T.

Action of Potassium Hypobromite on Phenylsuccinamide. By S. HOOGEWERFF and W. A. VAN DORP (*Rec. Trav. Chim.*, 9, 33—68).—In a previous communication (Abstr., 1889, 981), the authors have shown that chlorine, bromine, hydroxyl, and nitrosyl are extremely mobile when combined with nitrogen, compounds containing such a combination readily undergoing an intramolecular change, in which the negative element or group is displaced by a more positive radicle. In continuation of these researches, they have investigated the action of potassium hypobromite on phenylsuccinamide, and the properties of the bromamido-compound thus obtained.

The phenylsuccinamide required for these experiments was prepared by the method given by Menschutkin (this Journal, 1872, 497). 15 grams of this substance is dissolved in a solution of 18 grams of potash and 12 grams of bromine in 300 c.c. of water, then diluted with 600 c.c. of water, acidified with acetic acid, and the precipitate thus obtained washed with water. The product could not be obtained pure, but was found to contain bromine, and from its reactions is undoubtedly a *bromamidophenylsuccinamide*, $\text{NHBr}\cdot\text{C}_6\text{H}_4\text{O}_2\cdot\text{NHPH}$. On warming its solution in alcohol or acetone, an intramolecular change takes place, *parabromophenylsuccinamide*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\text{O}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$, being formed. The latter is sparingly soluble in cold water and ether, more readily in hot water, and very easily in boiling alcohol and acetone. It crystallises in needles or plates which melt at 213—215° with decomposition. On boiling with aqueous potash, it yields first *parabromophenylsuccinic acid* and ammonia, the former decomposing on further heating with potash into *parabromaniline* and *succinic acid*. *Parabromophenylsuccinic acid* crystallises in needles, melts at 186—187°, and is readily soluble in alcohol and acetone, sparingly in ether and water. It may also be prepared by the action of alkaline potassium hypobromite on phenylsuccinic acid. Its *barium salt* forms needles or plates, and its *copper salt* is a pale-blue precipitate.

By the action of warm dilute potash on *bromamidophenylsuccinamide*, the bromine is displaced by hydroxyl, and an intramolecular change takes place at the same time. To carry out the reaction, 10 grams of phenylsuccinamide are converted into the bromamide, and the latter is dissolved in a solution of 6 grams of potash in 34 c.c. of water, 50 c.c. of concentrated potash solution is then added, and the whole warmed for 2½ hours at 55—60°. On the addition of hydrochloric acid, a precipitate is obtained, which is purified by dissolving it in potash, reprecipitating with hydrochloric acid, reducing its alkaline solution with sodium amalgam, and recrystallising from hot water. Its composition was found on analysis to be $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$. On passing hydrogen chloride into its alcoholic solution and adding sulphuric acid, it very readily yields an ethyl salt, and therefore contains a carboxyl group. It loses the elements of water on boiling with acetic chloride, forming a substance which is reconverted by alkalis into the original compound, and on fusion with potash decomposes into carbonic anhydride, aniline, and β -amidopropionic acid. From these facts, it follows that the acid has the constitution



and it may be termed *phenyl-β-ureidopropionic acid* or *phenyl-β-lacturamic acid*. It crystallises in needles or plates melting when quite pure at 171—172°, and is readily soluble in alcohol, acetone, warm water, and warm acetic acid, sparingly in ether, and almost insoluble in benzene and light petroleum. The calcium salt, $(C_{10}H_{11}N_2O_3)_2Ca$, forms concentrically grouped needles, and the silver salt, $C_{10}H_{11}N_2O_3Ag$, an amorphous, white precipitate, which is fairly stable towards light. The ethyl salt, $C_{10}H_{11}N_2O_3Et$, crystallises from water containing a little sodium carbonate, in needles, melts at 84—85°, and is readily soluble in alcohol, ether, and benzene, sparingly in light petroleum.

As already stated, the acid is split up on fusion with potash into carbonic anhydride, aniline, and β -amidopropionic acid. The latter is best isolated as the platinochloride of its ethyl salt, which is obtained by passing hydrogen chloride into the alcoholic solution of the acid, evaporating, and treating the alcoholic solution of the residue with platinic chloride solution. It separates in yellow needles, containing water of crystallisation which is given off at 90—100°, the salt then having the composition $(C_6H_{11}NO_2)_2H_2PtCl_6$. It is readily soluble in water, melts at 193° with evolution of gas, and is identical with the compound prepared synthetically from β -iodopropionic acid. The hydrochloride, $C_5H_{11}NO_2 \cdot HCl$, forms hygroscopic crystals.

The compound obtained by the action of acetic chloride on phenylureidopropionic acid has the composition $C_{10}H_{10}N_2O_2$, and crystallises in needles which melt at 231—234°, and do not volatilise without decomposition. It stands in the same relation to phenylureidopropionic acid as hydantoin to hydantoic acid, and has, therefore, the constitution $CO<\begin{matrix} NPh \cdot CO \\ NH \cdot CH_2 \end{matrix}>CH_2$, and may be termed *phenylhydrouracil*. By the further action of acetic chloride at 100°, or by acting with an excess of the latter on the acid, *phenylacetylhydrouracil*, $C_{12}H_{12}N_2O_3$, is obtained, and crystallises in needles melting at 135—138°.

That phenylureidopropionic acid has really the constitution above assigned to it has been further shown by its synthetical formation from phenylcarbamide and β -amidopropionic acid. On heating these two compounds together at 135°, the following reaction takes place :—



The compound thus obtained is identical in all respects with the acid above described, but the yield is not good.

The formation of phenyl- β -ureidopropionic acid from phenylsuccinamide is very difficult, and perhaps impossible, to explain, if the latter has the symmetrical constitution usually assigned to it, namely, $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHPh$. It has, however, been shown by Auger (Abstr., 1888, 952) that a symmetrical succinamide can exist, and the authors believe that phenylsuccinamide has also the asymmetrical con-

stitution $\begin{matrix} CH_2 \cdot CH_2 \\ | \end{matrix} > C < \begin{matrix} NPh \\ NH_2 \end{matrix}$, the bromamido-compound then be-

coming $\text{CH}_2\cdot\text{CH}_2\begin{matrix} \text{NHPh} \\ >\text{C} \\ \text{CO}-\text{O}-\text{NBr} \end{matrix}$. The potassium salt of the latter undergoes an intramolecular change, forming the compound $\text{CH}_2\cdot\text{CH}_2\cdot\text{NK}$
 $\text{CO}-\text{O}-\text{CBr-NHPh}$, which by the further action of potash yields $\text{COOK}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}(\text{OH})(\text{OK})\cdot\text{NHPh}$; this then loses the elements of KOH , forming phenyl- β -ureidopropionic acid,
 $\text{COOK}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$.

When parabromophenylsuccinamide is treated with potassium hypobromite, it yields an unstable bromamide, which is readily converted into the corresponding *bromophenylureidopropionic acid*, $\text{C}_{10}\text{H}_{11}\text{BrN}_2\text{O}_3$, by the action of potash. This acid is readily soluble in warm alcohol, sparingly in ether, benzene, and hot water, and crystallises in flat needles which decompose at 229° . On fusion with potash, it yields parromaniline, and its alkaline solution is reduced by sodium amalgam to *phenylureidopropionic acid*. Its calcium salt is a very voluminous precipitate, and its silver salt forms white flocks.

By the action of potassium hypobromite (1 mol.) on *phenylureidopropionic acid*, no monobromo-compound could be obtained, but with 2 mols. of hypobromite, a small quantity of *dibromophenylureidopropionic acid*, $\text{C}_{10}\text{H}_{10}\text{Br}_2\text{N}_2\text{O}_3$, was formed, crystallising in needles which melt at $201-202^\circ$ and yielding dibromaniline (m. p. $78-81^\circ$) on fusion with potash. If 3 mols. of hypobromite are employed, *tribromophenylureidopropionic acid*, $\text{C}_{10}\text{H}_9\text{Br}_3\text{N}_2\text{O}_3$, is obtained, and is also formed in smaller quantity with the dibromo-compound when only 2 mols. of hypobromite are used. It separates from acetic acid in crystals which melt at $219-220^\circ$ with decomposition, and yields symmetrical tribromaniline on fusion with potash.

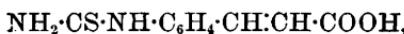
H. G. C.

Carbamide Derivatives of Amidocinnamic Acid. By F. W. ROTHSCHILD (*Ber.*, **23**, 3341—3346).—*Orthouramidocinnamic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$, is prepared by the action of potassium cyanate on orthamidocinnamic acid hydrochloride, and crystallises from water in small, pale-yellow needles which dissolve in ammonia and also in hydrochloric acid; the aqueous solution has an acid reaction.

Orthamidocinnamic acid thiocyanate,



is obtained in a similar manner to the previous compound, and is deposited from water in tufts of prismatic crystals which melt at 152° with evolution of gas. On heating the compound at $110-120^\circ$ for 18 hours, *ortho thiouramidocinnamic acid*,



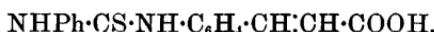
is formed, which melts at $236-239^\circ$, and is insoluble in alcohol, but dissolves in hot glacial acetic acid or ammonia.

Orthoallylthiouramidocinnamic acid,



crystallises from a small quantity of acetic acid on the addition of water in white needles which melt at 204—208° with decomposition.

Orthophenylthiouramidocinnamic acid,



crystallises from glacial acetic acid, and melts at 235—237°.

By the action of carbon bisulphide on orthamidocinnamic acid at 100°, a compound is obtained which is probably *orthocarbocinnamylidithiocarbamic acid*, $\text{CSSH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COOH}$; it crystallises from water in white, microscopic prisms, melts at 185—187°, and is soluble in ammonia but insoluble in hydrochloric acid.

Metathiocyanamidocinnamic acid is prepared by the action of thiocyanic acid on metamidocinnamic acid; it crystallises from alcohol, melts at 148—149°, and is very readily soluble in water and alcohol in the cold. The corresponding *para-derivative* crystallises from water in pale, yellowish-brown needles, which remain unmelted at 272°, but decompose on suddenly heating. It yields a white silver salt. On evaporating an aqueous solution, and heating the residue for some time at 100°, *parathiouramidocinnamic acid* is obtained as a yellow substance insoluble in alcohol; it remains solid at 273°, but melts with gas evolution when heated on platinum foil.

J. B. T.

Aromatic Alkyl Ketones; their Oxidation by Potassium Permanganate. By A. CLAUS (*J. pr. Chem.* [2], **42**, 508—516; compare *Abstr.*, 1890, 769, 979).—*Paracymyl methyl ketone* [$\text{Me : Ac : Pr} = 1 : 2 : 4$] is a nearly colourless oil which boils at 249—250° (uncorr.), and does not solidify at —10°. The *oxime* was obtained. The *phenylhydrazide* forms lustrous, colourless needles which melt at 134° (uncorr.). By reduction with zinc-dust in alcoholic potash, the ketone yields *paracymylmethylcarbinol* [$\text{Me : Pr : CHMe}\cdot\text{OH} = 1 : 4 : 2$], an uncry stallisable oil which boils above 300°. The constitution of this ketone is settled by the fact that it yields methylisophthalic acid [$\text{Me : (COOH)}_2 = 1 : 2 : 4$] (m. p. 332°), identical with Jacobsen's β -xylidene acid (*Abstr.*, 1882, 188); the *potassium* (with 2 mols. H_2O), *barium* (with 2 mols. H_2O), and *silver* (with 1 mol. H_2O) salts of this acid, and the *chloride*, and the *amide* are described; further oxidation converts this acid into trimellitic acid [$1 : 2 : 4$] (m. p. 210°, uncorr.).

Paracymylglyoxylic acid [$\text{Me : CO}\cdot\text{COOH : Pr} = 1 : 2 : 4$], obtained by oxidising the ketone in the cold with potassium permanganate, is a thick, yellow oil; it decomposes at 220°, and dissolves in the usual solvents except water; the *calcium* (with 2 mols. H_2O), *barium* (with 1 mol. H_2O), and *silver* salts were obtained. When reduced with sodium amalgam, this acid yields *paracymylglycollic acid*



which forms crystals melting at 124° (uncorr.), and soluble in the usual solvents, except cold water; the *sodium*, *potassium*, *calcium* (with $2\frac{1}{2}$ mols. H_2O), *barium* (with 3 mols. H_2O), *silver*, *copper* (with 8 mols. H_2O), and *lead* salts are described.

By heating paracymyl methyl ketone with ammonium sulphide in a sealed tube *paracymylacetamide* [$\text{Me : Pr : CH}_2\text{CONH}_2 = 1 : 2 : 4$] is

obtained; this crystallises in thin, lustrous scales, melts at 123° (uncorr.), sublimes, and dissolves in the usual solvents, except cold water. *Paracymylacetic acid* is obtained by saponifying the amide; it crystallises in flat, lustrous, colourless needles which melt at 70° (uncorr.), and dissolve in the usual solvents, except cold water; the *sodium* (with 2 mols. H_2O), *potassium* (with $1\frac{1}{2}$ mols. H_2O), *calcium* (with 4 mols. H_2O), *barium* (with 6 mols. H_2O), and *silver* salts are described.

A. G. B.

Benzoic Fluoride. By E. GUENEZ (*Compt. rend.*, **111**, 681—682).—This compound can be prepared by Moissan's reaction. Silver fluoride and benzoic chloride in equivalent proportions are heated in a sealed tube at 190° for five to six hours. The product is distilled from the silver chloride, and even if excess of silver fluoride has been used, the liquid must be heated again in a sealed tube with more silver fluoride, in order to ensure the complete decomposition of the benzoic chloride.

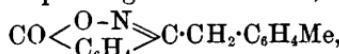
Benzoic fluoride is a colourless liquid with an odour resembling that of benzoic chloride, but much more irritating. It boils at 145° , burns with a smoky flame with a blue edge, is heavier than water, by which it is decomposed into benzoic and hydrofluoric acids, and is rapidly decomposed by solutions of alkalis, especially on heating. Benzoic fluoride attacks glass with great rapidity, with formation of silicon fluoride, an alkaline fluoride, and benzoic anhydride. C. H. B.

Conversion of Cinnamic into Isocinnamic Acid. By E. ERLENMEYER (*Ber.*, **23**, 3130—3131).—Since both α - and β -bromocinnamic acid yield benzaldehyde on oxidation, the bromine atom must be in the α -position in both compounds; it is probable, therefore, that the so-called β -bromocinnamic acid corresponds with isocinnamic acid and the α -bromo-acid with cinnamic acid. This view is rendered very probable by the fact that when the β -acid is treated with hydrogen under certain conditions, it yields isocinnamic acid and variable quantities of cinnamic acid; the iso-acid obtained in this way exhibits all the properties of the natural isocinnamic acid discovered by Liebermann.

F. S. K.

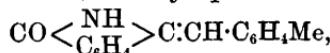
Metaxylalphthalide. By E. HEILMANN (*Ber.*, **23**, 3157—3168).—Metatoluylacetic acid is prepared by heating metatoluylacetone nitrile with three parts of concentrated hydrochloric acid at 100° for 4—5 hours. On fusing metatoluylacetic acid with an equal weight of phthalic anhydride, together with a small quantity of anhydrous sodium acetate, water and carbonic anhydride are eliminated, and a substance with the formula $CO<\overset{O}{\underset{C_6H_4}{\text{C}}}>C:\text{CH}\cdot C_6H_4\text{Me}$ is formed; if the group $CH\cdot C_6H_4\text{Me}$ is termed *xylal*, then this compound would be called *metaxylalphthalide*. It crystallises from alcohol in pale-yellow needles melting at 152 — 153° , and is very sparingly soluble in the ordinary media; the yield is 64 per cent. of the theory. On treatment with potash, xylalphthalide is hydrolysed, and the unsaturated acid which is first formed changes spontaneously into the compound $C_6H_4\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot C_6H_4\cdot\text{COOH}$; this is deposited from alcohol

on the addition of water, in long, lustrous crystals which melt at 111—112°. The corresponding *oximidolactone*,



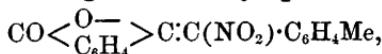
is prepared by the action of hydroxylamine on the acid, and crystallises from dilute alcohol in white, lustrous needles which melt at 133—134°, and are insoluble in alkalis.

By the action of alcoholic ammonia on xylalphthalide, *methyldeoxybenzoïncarboxylamide* is formed; it is difficult to isolate and readily loses the elements of water, *metaxylylphthalimidine*,



being obtained; this crystallises from alcohol in needles which melt at 165°. *Nitro-xylalphthalimidine*, $\text{CO} < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{NH} \end{matrix} > \text{C}\cdot\text{C}(\text{NO}_2)\cdot\text{C}_6\text{H}_4\text{Me}$, is

prepared by the action of nitrous acid on xylalphthalimidine; it crystallises from alcohol in yellow, lustrous needles, and melts at 157—159°. The reaction is explained by assuming that an unstable dinitro-derivative is first formed, from which the mononitro-compound is produced by the elimination of nitrous acid. *Dinitro-xylalphthalide*, $\text{CO} < \begin{matrix} \text{O} \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{NO}_2)\cdot\text{CH}(\text{NO}_2)\cdot\text{C}_6\text{H}_4\text{Me}$, is prepared by the action of nitrous acid on xylalphthalide, and crystallises from acetic acid in white, lustrous, rhombohedral plates, which soften at 125° and melt at 133° with evolution of gas. *Nitro-xylalphthalide*,



is prepared by heating the previous compound with dilute alcohol; it crystallises in yellow, lustrous needles, and melts at 144° with decomposition.

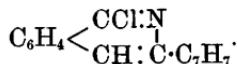
Nitro-xylalphthalide is dissolved in potash, and the solution acidified with hydrochloric acid; the product consists of a mixture of phthalic anhydride and *metatoluylnitromethane*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{NO}_2$; this compound is separated by distillation in a current of steam, and is a yellow, viscid liquid which decomposes on distillation, has a peculiar, offensive smell, and yields *metaxylylamine* on reduction.

Nitro-xylalphthalide is decomposed on heating at 190°, phthalic anhydride and *metatoluyl isocyanate* being formed; the latter is a colourless, oily liquid, which boils at 190—200°, and yields metatoluyl-carbamide on treatment with ammonia; the vapour rapidly attacks the eyes. By the action of phosphorus and hydriodic acid on *nitro-xylalphthalide*, a compound is obtained which is isomeric with xylalphthalide, and is therefore termed *iso-xylalphthalide*; it is slowly deposited from alcohol in long, slender, white crystals, which melt at 92—93°. The constitution of the compound is probably represented

by the formula $\text{C}_6\text{H}_4\cdot\text{CH} \begin{matrix} \text{C}_6\text{H}_4\cdot\text{CH} \\ \text{CO} \end{matrix} > \text{C}\cdot\text{C}_7\text{H}_7$.

Iso-xylalphthalimidine, $\text{C}_6\text{H}_4\cdot\text{CH} \begin{matrix} \text{CO}-\text{NH} \\ \text{C}_6\text{H}_4\cdot\text{CH} \end{matrix} > \text{C}\cdot\text{C}_7\text{H}_7$, is prepared by heating

the previous compound with alcoholic ammonia at 100°; crystallises in small, lustrous needles, melts at 196°, and is very sparingly soluble in the ordinary media. *Metatoluylchloroisouquinoline*,



is obtained by the action of phosphorus oxychloride on the previous compound; it crystallises in white, lustrous needles, and melts at 43—44°. On heating with hydriodic acid at 170°, and treating the product with potash, *metatolylisoquinoline*, $\text{C}_6\text{H}_4 < \begin{matrix} \text{CH:N} \\ | \\ \text{CH:} \end{matrix} \text{C}_6\text{H}_7$, is formed as a colourless, viscid liquid, which crystallises after some time, and melts at 51—52; it is deposited from methyl alcohol in long, lustrous needles. The *picrate*, *hydrochloride*, *sulphate*, and *platinochloride* are all crystalline.

J. B. T.

Isogallic Acid Phenylhydrazide. By C. BÖTTINGER (*Annalen*, 259, 373—377).—The phenylhydrazine derivatives of tannin and gallic acid (Abstr., 1890, 163) are very similar in properties, and have the same reducing power as regards alkaline copper solutions; when the tannin derivative is heated with hydrochloric acid at 120°, it is decomposed into gallic acid, phenylhydrazine, and a very small quantity of a reddish-yellow, crystalline, neutral substance; the author names it, therefore, isogallic acid phenylhydrazide.

Isogallic acid phenylhydrazide is converted into an unstable acetyl derivative on boiling with acetic anhydride; it is completely decomposed by boiling alkalis, a property which it has in common with gallic acid phenylhydrazide.

F. S. K.

Condensation Products of Amido-acids with Benzene-sulphonic Chloride. By S. G. HEDIN (*Ber.*, 23, 3196—3199; see also Hinsberg, this vol., p. 49).—For the preparation of the above condensation products, the amido-acid is dissolved in aqueous potash, and an equivalent quantity of benzenesulphonic chloride added in small portions alternately with caustic potash, warming and shaking well during the process. After filtering, if necessary, the liquid is acidified, and the product, being, as a rule, sparingly soluble in cold water, may then be readily purified.

Alanine yields the compound $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_2\text{H}_4\cdot\text{COOH}$, crystallising from hot water in slender needles; this melts at 126°, but forms an oil under water at 100°, and is readily soluble in hot water, alcohol, ether, and ethyl acetate.

The *leucine* compound, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_5\text{H}_{10}\cdot\text{COOH}$, crystallises in beautiful, long needles which melt at 86°, and are less soluble in water than the foregoing compound, but readily soluble in alcohol, ether, acetic acid, and chloroform.

The *aspartic acid* derivative, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_2\text{H}_3(\text{COOH})$, crystallises in splendid, rhomboïdal crystals melting at 170°.

The *alutamine* compound, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_3\text{H}_5(\text{COOH})_2$, does not

separate on the addition of an acid, but must be extracted with ether, and on the evaporation of this it remains as a syrup which gradually solidifies over sulphuric acid, but is not thus obtained quite pure. It is distinguished from the other condensation products by its ready solubility in water.

Tyrosine yields two compounds, one of which is sparingly, and the other readily, soluble in water. The former has the composition $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{C}_2\text{H}_3(\text{C}_6\text{H}_4\cdot\text{OH})\cdot\text{COOH}$, but the latter has not been obtained pure.

Toluene-parsulphonic chloride also readily forms condensation products with amido-acids. Moreover, fibrin, after treatment with pancreatic juice, combines with benzenesulphonic chloride, forming an oil, but it is uncertain whether this is a mixture or not.

An attempt was made to prepare *benzenesulphoneglycocine*, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, by feeding dogs with sodium benzenesulphonate, a process corresponding to the preparation of hippuric acid from sodium benzoate. The results obtained, however, were negative, as were similar experiments in the human organism. H. G. C.

Benzenesulphinic Acid and Ethylsulphinic Acid. By W. AUTENRIETH (*Annalen*, 259, 362—364).—Pure, dry benzenesulphinic acid does not readily undergo oxidation on exposure to the air; its sodium salt is very stable, and is not decomposed to any appreciable extent when its aqueous solution is heated at 180° for 12 hours.

Ethylsulphinic acid is best prepared by oxidising ethyl mercaptan with potassium permanganate, converting the sulphonic acid thus produced into the chloride, and reducing the latter with zinc-dust in alcoholic solution. The pure acid is unstable, but the dry sodium salt is only slowly oxidised on exposure to the air. F. S. K.

Sulphone Derivatives of the Crotonic Acids. By W. AUTENRIETH (*Annalen*, 259, 332—357).— β -*Phenylsulphoneisocrotonic acid*, $\text{CH}_3\cdot\overset{\text{H}}{\underset{\text{C}}{\text{C}}} \cdot\text{SO}_2\text{Ph}$, can be prepared by heating a moderately concentrated

aqueous solution of sodium β -chlorisocrotonate with sodium benzene-sulphinate at 140 — 150° for six to eight hours, precipitating the acid with sulphuric acid, and then extracting with ether. It can also be obtained by treating ethyl β -diphenylsulphonebutyrate with cold, concentrated potash (compare next abstract); the yield is almost quantitative in both cases. It crystallises from water in needles, melts at 126 — 127° , and decomposes at a higher temperature; it is moderately easily soluble (1 in 20) in boiling, but only sparingly (1 in 390 at 15°) in cold, water. It is decomposed by tin and warm concentrated hydrochloric acid with liberation of mercaptan, and boiling alkalis decompose it completely with elimination of benzenesulphinic acid, but it is not acted on by bromine in boiling chloroform solution. The potassium salt, $\text{C}_{10}\text{H}_8\text{SO}_4\text{K} + 3\text{H}_2\text{O}$, crystallises from water in large, transparent, efflorescent plates, and is readily soluble in water and alcohol. The barium salt, $(\text{C}_{10}\text{H}_8\text{SO}_4)_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$, magnesium salt (with 6 mols. H_2O), and zinc salt (with 6 mols. H_2O) crystallise well, and are moderately easily soluble in water.

The *silver* salt, $C_{10}H_9SO_4Ag$, crystallises from water in well-defined plates, and decomposes suddenly at $240-245^\circ$. The *ethyl* salt, $C_{10}H_9SO_4Et$, is a colourless oil.

β-Phenylsulphonecrotonic acid, $\begin{matrix} SO_2Ph \cdot C \cdot Me \\ || \\ H \cdot C \cdot COOH \end{matrix}$, is prepared by heating an aqueous solution of the sodium salt of β -chlorocrotonic acid with sodium benzenesulphinate at $160-180^\circ$ for eight hours; the yield is quantitative. It crystallises from water in lustrous plates, melts at 158° with previous softening, and is moderately easily soluble in ether, alcohol, and benzene, but only very sparingly in light petroleum; it is soluble in 262 parts of water at 15° and in 3·8 to 4 parts of boiling water. When heated at $200-210^\circ$ for 20 hours, it is completely converted into the isomeride (m. p. 127°) described above, but attempts to bring about this intramolecular change by means of sulphuric acid, iodine, alcohol, and water were unsuccessful. The *potassium* salt, $C_{10}H_9SO_4K + 1\frac{1}{2}H_2O$, is deliquescent, and does not crystallise well. The *barium* salt, $(C_{10}H_9SO_4)_2Ba + H_2O$, is very readily soluble in water. The *magnesium* salt (with 7 mols. H_2O) and the *zinc* salt (with 6 mols. H_2O) separate from water in large, transparent crystals. The *copper* salt forms small crystals containing 1 mol. H_2O . The *silver* salt, $C_{10}H_9SO_4Ag$, crystallises from water in very small needles, and decomposes suddenly at $198-200^\circ$.

β-Ethylsulphoneisocrotonic acid, $\begin{matrix} CH_3C \cdot SO_2Et \\ || \\ H \cdot C \cdot COOH \end{matrix}$, can be prepared by treating ethyl β -diethylsulphonebutyrate (compare Baumann, Abstr., 1887, 123) with potash in the cold, or by heating sodium β -chloroisocrotonate at $140-150^\circ$ with sodium ethylsulphinate in aqueous solution. It separates from cold water in well-defined crystals, melts at 98° , and is readily soluble in alcohol, ether, chloroform, and water, but only moderately easily in benzene. It is slowly decomposed by alkalis into tetrolic acid and ethylsulphinic acid, and when treated with tin and hydrochloric acid it yields mercaptan, but it is not acted on by bromine in boiling chloroform solution. The *silver* salt, $C_8H_9SO_4Ag$, forms large, well-defined crystals, and decomposes on exposure to light; the other metallic salts do not crystallise well. The *ethyl* salt, $C_8H_{14}SO_4$, is a colourless oil which cannot be distilled. The stereochemical isomeride of β -ethylsulphoneisocrotonic acid could not be obtained.

F. S. K.

Sulphur Derivatives of Ethyl Acetoacetate, Ethyl Methylacetoacetate, and Ethyl Ethylacetoacetate. By W. AUTENRIETH (*Annalen*, 259, 365-373).—*Ethyl β-diphenylsulphonebutyrate*, $CMe(SO_2Ph)_2 \cdot CH_2 \cdot COOEt$, can be obtained by adding sulphuric acid and potassium permanganate to a benzene solution of ethyl β -dithiophenylbutyrate (compare Baumann and Escales, Abstr., 1886, 878) until a permanent coloration is produced. It separates from alcohol in well-defined, lustrous crystals, melts at 97° , and is readily soluble in hot alcohol, ether, and benzene, but only sparingly in cold alcohol, and insoluble in water; when treated with potash, it is converted into β -phenylsulphoneisocrotonic acid (compare preceding abstract).

Ethyl α-ethyl-β-diethylsulphonebutyrate, $\text{CMe}(\text{SO}_2\text{Et})_2\cdot\text{CHEt}\cdot\text{COOEt}$, is formed when ethyl α-ethyl-β-dithioethylbutyrate, the condensation product of ethyl mercaptan and ethyl ethylacetooacetate, is oxidised in a similar manner. It crystallises from boiling water in lustrous plates, melts at $87-88^\circ$, and is readily soluble in ether, benzene, and alcohol; it is not acted on by concentrated potash or ammonia in the cold, but on boiling with potash, it is gradually decomposed, yielding small quantities of an acid melting at $102-103^\circ$, the nature of which could not be determined.

Ethyl α-methyl-β-diethylsulphonebutyrate, prepared in like manner, crystallises from water in plates, melts at 79° , and is only sparingly soluble in cold, but readily in hot, water; it is not acted on by cold alkalis, but when boiled therewith, it is completely decomposed.

Ethyl α-ethyl-β-dithiophenylbutyrate, $\text{CMe}(\text{SPh})_2\cdot\text{CHEt}\cdot\text{COOEt}$, is obtained when hydrogen chloride is passed into a mixture of ethyl ethylacetooacetate and phenyl mercaptan. It separates from alcohol in large, transparent crystals, melts at $70-71^\circ$, and is readily soluble in benzene, alcohol, and ether, but insoluble in water.

Ethyl α-ethyl-β-diphenylsulphonebutyrate, $\text{C}_{20}\text{H}_{24}\text{S}_2\text{O}_6$, prepared by oxidising the preceding compound in the manner described above, separates from alcohol in crystals, melts at 111° , and is insoluble in water, but readily soluble in alcohol, benzene, and ether; when boiled with potash, it yields only a trace of an acid.

F. S. K.

Indene and Cinnamene in Coal-tar. By G. KRAEMER and A. SPILKER (*Ber.*, **23**, 3276-3283; compare *Abstr.*, 1890, 496).—The higher fractions of the light oils obtained from coal-tar contain a hydrocarbon of the composition C_9H_8 , to which the authors give the name *indene*, as it has the constitution $\text{C}_6\text{H}_4 < \begin{matrix} \text{CH} \\ \diagup \\ \text{CH}_2 \end{matrix} > \text{CH}$.

This compound is isolated in the following manner from the fractions boiling at $176-182^\circ$, the yield of the pure substance being about 20 per cent. of the crude oil employed:—A quantity of picric acid, sufficient to combine with the unsaturated compounds (determined by titrating a portion of the oil with bromine), is dissolved in the hot liquid, the crystalline precipitate, which contains as impurities all the naphthalene and a little cumarone, is treated with steam, and the indene in the distillate purified by precipitation with picric acid in toluene solution. The picrate is obtained in this way in golden needles melting at 98° ; it decomposes slowly on exposure to the air, but quickly when heated with water, and it explodes when heated in the dry state.

Indene is a colourless oil of sp. gr. 1.04 at 15° , which turns yellowish on keeping, the colour disappearing again on exposure to light; it boils at $179.5-180.5^\circ$ (corr.), is converted into a resinous compound (parindene) by concentrated sulphuric acid in benzene or ethereal solution, and into a very insoluble, infusible substance, which contains a large quantity of sulphur, by energetic treatment with concentrated sulphuric acid. On oxidation with boiling 30 per cent. nitric acid, it yields phthalic acid. The dibromide, $\text{C}_9\text{H}_8\text{Br}_2$, prepared by treating the hydrocarbon with the theoretical quantity of bromine in

etheral solution, forms transparent, prismatic crystals, melts at 43—45°, and is readily soluble in all ordinary solvents except water and light petroleum; it readily undergoes spontaneous decomposition with evolution of hydrogen bromide and formation of a resinous substance.

Indene hydroxybromide, C_9H_9BrO , is formed when the dibromide is warmed with water or boiled with 10 per cent. alcohol; it crystallises in colourless needles, melts at 130—131°, and is soluble in water and alcohol.

Hydrindene, C_9H_{10} , is obtained when indene is reduced with sodium and alcohol; it is a colourless oil of sp. gr. 0·957 at 15°, and boils at 176—176·5° (corr.). It forms a sulphonic acid, the salts and amide of which are very like the corresponding derivatives of benzenesulphonic acid.

Cinnamene can be isolated from coal-tar in the form of the crystalline dibromide, $C_8H_8Br_2$, by treating well-cooled, crude xylene with bromine and evaporating the solution.

The red coloration which is produced on dissolving impure naphthalene in sulphuric acid is due to the presence of indene, and the red coloration observed in the case of phenol is probably due to a similar cause.

F. S. K.

Synthesis of Indigo with Phenylglycocine. By K. HEUMANN (*J. pr. Chem.*, [2], **42**, 520).—The author claims priority as to the method for the synthesis of indigo published by Lederer (this vol., p. 75), he having already patented the method. Lederer is mistaken in supposing that indigo is left when the melt is dissolved in water or dilute sulphuric acid; any that may be formed is only produced by oxidation by the air; some substance like indigo-white is the actual product of the fusion, and oxidation is necessary to convert this into indigo. The author is further investigating the subject.

A. G. B.

Synthesis of Indigo from Anilidoacetic Acid. By A. BIEDERMANN and R. LEPESTIT (*Ber.*, **23**, 3289—3291).—Aniline and chloroacetic acid are mixed together in molecular proportions and fused with 3—4 parts of soda, together with sufficient water to form a paste; as soon as the mass becomes orange-coloured, it is quickly cooled, dissolved in water, and the solution oxidised by means of a current of air; indigo is at once deposited, the yield being 9·5 per cent. It is probable that in the first instance anilidoacetic acid is formed; two molecules then combine together with elimination of water and hydrogen. Indigo may also be obtained by the fusion of anilidoacetic acid and sodium, the product being then oxidised with air as before. Indigo is directly prepared by the fusion of a mixture of oxanilic acid and anilidoacetic acid in molecular proportion with excess of soda; the yield is a little less than with anilidoacetic acid alone.

J. B. T.

Condensation of Cinnamene with Methylbenzene Derivatives. By G. KRAEMER and A. SPILKER (*Ber.*, **23**, 3169—3174).—Crude xylene containing cinnamene is treated with concentrated sulphuric acid, when two layers of liquid are formed, the heavier of which

contains sulphonic acids. The lighter oily portion is separated, washed with soda, and distilled in a current of steam; the residue after fractionation in a vacuum, yields *phenyltoluylpentane*, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$; this is a colourless, viscid liquid which boils at $293-294^\circ$, and has a sp. gr. of 0·987 at 15° . It is probable that in the first instance cinnamene and sulphuric acid combine to form an additive compound, which then condenses with xylene according to the equation $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{SO}_4\text{H} + 2\text{C}_6\text{H}_4\text{Me}_2 = \text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me} + \text{C}_6\text{H}_3\text{Me}_2\cdot\text{SO}_3\text{H} + \text{H}_2\text{O}$. It is found that other methylbenzene derivatives condense with cinnamene in a similar manner, but benzene itself does not react in this way. On passing the vapourised substance through heated tubes, hydrogen and methane are eliminated, and methylanthracene (m. p. 200°) is formed; the yield is 62·5 per cent. of the substance employed.

Corresponding anthracene derivatives are obtained from the condensation products of cinnamene and toluene, metaxylene, and pseudocumene respectively.

The authors point out the bearing of their work on the theories regarding the formation of the higher boiling constituents of coal tar, and conclude with some polemical remarks on the Duismore process for the manufacture of coal gas.

J. B. T.

Cinnamene Derivatives of Aromatic Hydrocarbons and their Conversion into Anthracene and Methylanthracenes. By G. KRAEMER, A. SPILKEE, and P. EBERHARDT (*Ber.*, **23**, 3269—3276; compare preceding abstract).—The compounds formed by the condensation of cinnamene with xylene are most probably $\alpha\beta$ -, and not $\alpha\gamma$ -derivatives of propane as was previously supposed; this view would explain their ready transformation into anthracene derivatives.

Metaxylenecinnamene ($\alpha\beta$ -*phenylmetatoluylpropane*),



prepared by gradually adding concentrated sulphuric acid to a mixture of metaxylene and cinnamene, is a colourless, feebly fluorescent oil of sp. gr. 0·987 at 15° ; it boils at 240° under a pressure of 110 mm., and at $311-312^\circ$ (corr.), and is miscible with alcohol, ether, benzene, and light petroleum, but insoluble in water. When passed through a red-hot tube, it is almost completely converted into methylanthracene (m. p. 207°).

Paraxylenecinnamene ($\alpha\beta$ -*phenylmetatoluylpropane*), $\text{C}_{16}\text{H}_{18}$, obtained from paraxylene in like manner, boils at $302-303^\circ$ (corr.), and resembles the preceding compound very closely.

Ortho-xylencinnamene ($\alpha\beta$ -*phenylorthotoluylpropane*), $\text{C}_{16}\text{H}_{18}$, boils at $316-317^\circ$ (corr.).

Pseudocumene cinnamene ($\alpha\beta$ -*phenylxyllylpropane*),



is obtained by the condensation of cinnamene with trimethylbenzene; it boils at 324° (corr.) and is readily converted into dimethylanthracene (m. p. 235°).

Toluene cinnamene ($\alpha\beta$ -*diphenylpropane*), $\text{CHMePh}\cdot\text{CH}_2\text{Ph}$, pre-

pared from toluene in like manner, is a colourless liquid boiling at 291—293° (corr.) ; when heated strongly, it yields only small quantities of anthracene.

Condensation products of benzene with cinnamene could not be obtained.

F. S. K.

Condensation Products of Paranitrobenzyl Cyanide. By P. REMSE (*Ber.*, **23**, 3133—3136).—A compound of the constitution $\text{CHPh:C(CN)·C}_6\text{H}_4\cdot\text{NO}_2$ is formed when sodium ethoxide is gradually added to a mixture of paranitrobenzyl cyanide (1 mol.) and benzaldehyde (1 mol.) until a blue coloration is produced. It crystallises from alcohol in yellow needles, melts at 175—176°, and is soluble in glacial acetic acid, benzene, and chloroform, but only sparingly in alcohol and ether, and insoluble in water.

The condensation product obtained in like manner from orthonitrobenzaldehyde and paranitrobenzyl cyanide has the composition $\text{C}_{15}\text{H}_9\text{N}_3\text{O}_4$; it crystallises from glacial acetic acid in large, yellowish needles, melts at 184—185°, and is soluble in chloroform, benzene, alcohol, and ether, but insoluble in water.

Metanitrobenzaldehyde and paranitrobenzyl cyanide also condense to form a compound of the composition $\text{C}_{15}\text{H}_9\text{N}_3\text{O}_4$, which crystallises from alcohol in yellow needles, melts at 195°, and is soluble in most ordinary solvents except water.

A compound of the constitution $\text{OMe·C}_6\text{H}_4\cdot\text{CH:C(CN)·C}_6\text{H}_4\cdot\text{NO}_2$ can be obtained by treating anisaldehyde with paranitrobenzyl cyanide as described above; it crystallises from alcohol in yellow needles, melts at 165—166°, and is soluble in ether, benzene, and glacial acetic acid.

The condensation product of cinnamaldehyde and paranitrobenzyl cyanide has the constitution $\text{CHPh:CH·CH:C(CN)·C}_6\text{H}_4\cdot\text{NO}_2$; it crystallises from glacial acetic acid in yellow needles, melts at 205—206°, and is soluble in benzene and chloroform, but more sparingly in alcohol and ether, and insoluble in water.

F. S. K.

Condensation of Unsaturated Hydrocarbons with Phenols. By W. KOENIGS (*Ber.*, **23**, 3144—3146).—When a mixture of isomylene and phenol is treated with a mixture of concentrated sulphuric acid (1 vol.) and glacial acetic acid (9 vols.) at the ordinary temperature for 1 to 2 days, a considerable quantity of parisoamylphenol is formed,

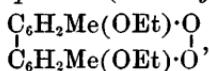
Hydroxydiphenylethane, $\text{CHMePh·C}_6\text{H}_4\cdot\text{OH}$, is obtained when cinnamene is treated with phenol under the same conditions as those described above; the yield is about 40 per cent. The reaction product is submitted to distillation with steam and, as soon as the whole of the phenol has passed over, the receiver is changed, the residue heated to 160—170°, and the hydroxydiphenylmethane distilled with superheated steam; the oily product is then converted into the benzoyl derivative (m. p. 83°) by Baumann's method, and the latter, after recrystallisation from alcohol, hydrolysed with alcoholic potash. The phenol obtained in this way solidifies on cooling, and forms a sodium derivative which crystallises in colourless needles.

Resorcinol seems to yield condensation products with amylenes and with cinnamene just as readily as phenol. F. S. K.

Diphenyl Derivatives from Alkylquinols. By E. NOELTING and P. WERNER (*Ber.*, **23**, 3246—3252).—*Diethyltoluquinol*, $C_6H_3Me(OEt)_2$, can be obtained, together with the monomethyl derivative, by heating toluquinol with ethyl bromide and sodium ethoxide in alcoholic solution for 5 to 6 hours at 130—140°; the two compounds are separated by treating the product with soda, in which the diethyl derivative is insoluble. It is a colourless liquid of sp. gr. 1·0134 at 15°, boils at 247—249° (corr.), and solidifies at a low temperature, melting again at 8—9°; it is insoluble in water, but miscible with alcohol, ether, benzene, and chloroform in all proportions.

Ethyltoluquinol, $C_6H_3Me(OH) \cdot OEt$, is obtained when the alkaline filtrate from the preceding compound is acidified and then extracted with cold benzene; it crystallises from dilute alcohol in plates, melts at 116—117°, and boils at 253—287°.

Diethoxydimethyldiphenylquinone (diethoxyditolylquinone),

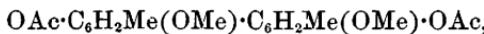


is formed when the diethyl derivative described above is dissolved in a mixture of dilute acetic acid and sulphuric acid and a concentrated solution of sodium dichromate is gradually added. It crystallises from alcohol in greenish-black needles which melt at 139°, and, when crushed, give a reddish-brown powder; it is precipitated from its solution in boiling glacial acetic acid on the addition of water in reddish-brown flocks. It resembles very closely the cedriret-like oxidation product of the dimethyltoluquinol (compare Nietzki, *Abstr.*, 1883, 465), than which it is, however, much more readily soluble in alcohol and glacial acetic acid.

Diethyltetrahydroxyditolyl, $O \cdot OH \cdot C_6H_2Me(OEt) \cdot C_6H_2Me(OEt) \cdot OH$, prepared by reducing the preceding compound with sulphurous anhydride in boiling alcoholic solution, crystallises from dilute alcohol in colourless needles, melts at 132—133°, sublimes with partial decomposition, and readily oxidises on exposure to the air; it is only sparingly soluble in water, but moderately easily in the ordinary organic solvents.

Dimethoxyditolylquinone (compare Nietzki, *loc. cit.*) and diethoxyditolylquinone are reconverted into the corresponding quinols by phenylhydrazine, phenylhydrazine sulphonic acid, and sodium hydrogen sulphite; attempts to convert the quinols into derivatives of diphenylene oxide were unsuccessful.

Diacetyl dimethoxyditolylquinol,



is formed when dimethoxyditolylquinol is boiled with acetic anhydride and sodium acetate; it crystallises in colourless needles, melts at 123°, and is readily soluble in glacial acetic acid, boiling alcohol, and benzene, but insoluble in water and alkalis.

Bromodimethylquinol, $C_6H_3Br(OMe)_2$, can be obtained, together

with the dibromo-derivative and a liquid boiling at 246—260°, which is probably bromomethylquinol, by treating dimethylquinol with bromine (1 mol.) in cold glacial acetic acid solution; it is a colourless oil of sp. gr. 1·445 at 15°, boils at 262—263° (corr.), and is insoluble in water, but readily soluble in the ordinary organic solvents. When treated with potassium dichromate and sulphuric acid under suitable conditions, it yields a very small quantity of a cedriret-like compound, which, on reduction, is converted into a colourless, crystalline leuco-compound. The *nitro*-compound $\text{NO}_2\cdot\text{C}_6\text{H}_2\text{Br}(\text{OMe})_2$, prepared by nitrating with acid of sp. gr. 1·4 in well-cooled acetic acid solution, crystallises from glacial acetic acid in orange-yellow needles, and melts at 152—153°. Warm nitric acid converts dibromodimethylquinol (Habermann, *Ber.*, **11**, 1137) into a nitro-compound, which crystallises in orange prisms and melts at 188°.

Dibromodimethylquinol, nitrobromodimethylquinol, nitrodibromodimethylquinol, and nitrodimethylquinol cannot be converted into cedriret-like compounds.

Dimethylparaxyloquinol, $\text{C}_6\text{H}_2\text{Me}_2(\text{OMe})_2$ [$\text{Me}_2 : (\text{OMe})_2 = 1 : 4 : 2 : 5$], prepared by heating paraxyloquinol with sodium methoxide and methyl iodide in methyl alcoholic solution for 8—10 hours, crystallises from dilute alcohol in colourless plates, melts at 108°, and is soluble in ether, but insoluble in water. The corresponding diethyl derivative melts at 111—112°, and not at 105—106°, as stated by Städel and Hölz.

Diethylmetaxyloquinol is a colourless oil boiling at 240—249°. The corresponding *ortho*-compound, $\text{C}_6\text{H}_2\text{Me}_2(\text{OEt})_2$ [$\text{Me}_2 : (\text{OEt})_2 = 1 : 2 : 3 : 4$], forms colourless plates, melts at 68—69°, and is readily soluble in alcohol, benzene, ether, &c., but insoluble in water. Cedriret-like oxidation products cannot be obtained from the xyloquinol derivatives described above.

F. S. K.

Orthomethylbenzidine. By R. HIRSCH (*Ber.*, **23**, 3222—3226).—Orthomethylbenzidine can be prepared in the following manner (compare D. R.-P. 54112):—A solution of nitrobenzene (1 part) and orthonitrotoluene (4 parts) in alcohol (5 parts) is boiled with sodium hydroxide (about 0·5 part) and zinc-dust added until the solution becomes grey or bright yellow; the alcohol is then evaporated, the residue carefully treated with a quantity of hydrochloric acid just sufficient to dissolve the zinc hydroxide, but not the organic bases, and the solution filtered. The residue, which consists principally of hydrazobenzene and its homologues, is then dissolved in warm dilute hydrochloric acid to convert these compounds into the corresponding benzidines, the excess of acid expelled from the filtered solution, the bases precipitated with sodium sulphate, and the sulphates decomposed with sodium carbonate. The mixture of the three bases (benzidine, orthotoluidine, and orthomethylbenzidine) obtained in this way is repeatedly extracted with boiling water, and the combined extracts carefully treated with dilute sulphuric acid to precipitate the sulphates of benzidine and orthomethylbenzidine; these salts are decomposed, and the mixture of bases again extracted (5 times)

with boiling water (20 parts), when pure orthomethylbenzidine is deposited from the first two extracts, on cooling, in lustrous plates melting at 115°. It melts at about 90° under water, forms a diacetyl derivative melting at 310°, and a benzylidene derivative, which crystallises from alcohol in yellow plates, and melts at 217°.

F. S. K.

Diphenyl Bases. By E. NOELTING and P. WERNER (*Ber.*, **23**, 3252—3266).—*Ditolyline hydrochloride*, $C_{14}H_{14}N_2 \cdot 2HCl$, is obtained, together with tolidine hydrochloride and other compounds, when orthohydrazotoluene is treated with warm concentrated hydrochloric acid (4 parts). The solution is heated to boiling, then allowed to cool, the tolidine hydrochloride and azotoluene separated by filtration, and the filtrate concentrated by evaporation; after filtering again, the solution is rendered alkaline, extracted with ether, the ether evaporated, and the residue heated at 250° until free from orthotoluidine; it is then dissolved in hydrochloric acid, the ditolyline reprecipitated from the filtered solution, extracted with ether, and converted into the hydrochloride by passing hydrogen chloride into the dried ethereal solution. This salt crystallises in colourless needles, and is very readily soluble in water, but only sparingly in hydrochloric acid; in its aqueous solutions, bromine-water produces a slight, dirty-green coloration which changes to violet. The free base is a colourless, flocculent compound which rapidly oxidises on exposure to the air. The sulphate is very readily soluble. The colouring matters obtained from ditolyline do not dye cotton fibre.

Parabromazobenzene (m. p. 82°), identical with the compound obtained by Janovsky and Erb (*Abstr.*, 1887, 478) by brominating azobenzene, can be prepared from amidoazobenzene by Sandmeyer's method; when treated with stannous chloride in alcoholic solution, it is converted into bromodiphenyline (bromobenzidine).

Pariodazobenzene, $C_{12}H_9N_2I$, prepared in like manner, crystallises from alcohol in yellowish-brown needles, melts at 105°, and is soluble in ether and benzene, but insoluble in water. The corresponding hydrazo-compound crystallises in colourless needles melting at 105—106°.

Iododiphenyline hydrochloride, prepared by treating the azo-compound with stannous chloride in alcoholic solution, crystallises in colourless needles, and is readily soluble in water, but only sparingly in concentrated hydrochloric acid. Bromo- and iodo-diphenyline yield coloured azo-compounds which impart to unmordanted cotton only a very slight coloration.

When metadiiodazobenzene is treated with hot concentrated hydrochloric acid, it yields iodazobenzene and large quantities of benzidine. Azobenzeneparasulphonic acid is converted into hydrazobenzene-parasulphonic acid by hydrogen sulphide in ammoniacal solution, and not into benzidinesulphonic acid as stated by Griess (*Annalen*, **154**, 213); on treating the ammoniacal solution with hydrochloric acid, benzidine sulphate is precipitated.

Ethoxyazobenzene, $NPh:N \cdot C_6H_4 \cdot OEt$, is converted into a base of the constitution $NH_2 \cdot C_6H_4 \cdot C_6H_3(OEt) \cdot NH_2$, when it is treated with

the theoretical quantity of stannous chloride and hydrochloric acid in alcoholic solution; the colouring matters obtained from this base do not dye unmordanted cotton.

Orthotolylazophenol, $C_6H_4Me \cdot N \cdot N \cdot C_6H_3 \cdot OH$, prepared by treating diazorthotolyl chloride (1 mol.) with an alkaline solution of phenol (1 mol.) and precipitating the product with an acid, crystallises from a mixture of benzene and light petroleum in dark-red or orange-yellow plates, melts at $102-103^\circ$, and is very readily soluble in alcohol, ether, benzene, and alcohol, but only sparingly in water and light petroleum.

Orthotolyldisazophenol, $(C_6H_4Me \cdot N_2)_2C_6H_3 \cdot OH$, is obtained when a larger quantity (2 mols.) of the diazochloride is employed in the above reaction; it crystallises from alcoholic chloroform in slender, brown needles, melts at 146° , and is readily soluble in chloroform, but insoluble in water.

Orthotolylazophenetöil, $C_6H_4Me \cdot N_2 \cdot C_6H_4 \cdot OEt$, prepared by treating the phenol with sodium ethoxide and ethyl bromide, crystallises from alcohol in orange plates, melts at 53° , and is only sparingly soluble in water, but readily in alcohol, ether, benzene, and chloroform; stannous chloride, in alcoholic solution, converts it into a diphenyl base from which fast dyes cannot be obtained.

Paratolylazophenetöil, $C_{15}H_{14}N_2O$, crystallises from alcohol in large, golden plates, melts at $121-122^\circ$, and is insoluble in water and alcohol, but moderately easily soluble in cold alcohol, and readily in boiling alcohol, chloroform, &c.

Paratolylydrazophenetöil, $C_{15}H_{18}N_2O$, prepared by reducing the preceding compound with hydrogen sulphide in ammoniacal alcoholic solution, crystallises in colourless needles, and readily oxidises on exposure to the air; it is insoluble in water, but readily soluble in boiling alcohol. Acids do not convert it into a diphenyl base, but decompose it into toluidine and amidophenetöil.

Phenylazorthocresetöil, $NPh \cdot N \cdot C_6H_3Me \cdot OEt$, prepared from phenylazorthocresol, crystallises from alcohol in slender, orange needles or prisms, melts at 59° , and is soluble in benzene and ether, but insoluble in water. The corresponding *hydrazo*-compound, $C_{15}H_{18}N_2O$, crystallises in colourless plates, melts at 76° , and is readily soluble in hot alcohol, but insoluble in water; it readily oxidises on exposure to the air, and it is decomposed by hydrochloric acid yielding a diphenyl base from which fast azo-dyes cannot be obtained.

Orthotolylazorthocresol, $C_6H_4Me \cdot N \cdot N \cdot C_6H_3Me \cdot OH$, crystallises from alcohol in red prisms, melts at 132° , and is soluble in benzene and ether, but insoluble in water. The *hydrazo*-compound, $C_{16}H_{20}N_2O$, is a colourless, crystalline substance which melts at 75° , and readily oxidises on exposure to the air; the diphenyl base, produced from the *hydrazo*-compound by intramolecular change under the influence of hydrochloric acid, does not yield any colouring matters which dye unmordanted cotton fibre.

Orthotolyldisazorthocresol, $(C_6H_4Me \cdot N_2)_2C_6H_2Me \cdot OH$, crystallises in slender, brown needles, melts at 148.5° , and is insoluble in water,

but soluble in alcohol, benzene, chloroform, and alcoholic soda. The *ethyl* derivative, $C_{23}H_{24}N_2O_2$, prepared by treating the phenol with sodium ethoxide and ethyl bromide, crystallises in golden needles, melts at 102° , and is soluble in chloroform, benzene, and ether, but insoluble in water and alkalis.

Paratolylazorthocresol, $C_6H_4Me \cdot N \cdot N^{\cdot} \overset{4}{C_6H_3} \overset{1}{Me} \overset{1}{OH} \overset{3}{\cdot} \overset{4}{O}$, forms orange crystals, melts at 163° , and is insoluble in water, but readily soluble in alcohol, ether, chloroform, and alkalis. The *ethyl* derivative, $C_{16}H_{18}N_2O$, crystallises in orange needles, melts at $73-74^\circ$, and is readily soluble in alcohol, ether, and benzene, but insoluble in water. The *hydrazo*-compound, $C_{16}H_{20}N_2O$, prepared by reducing the *ethyl* derivative, crystallises in colourless needles, melts at 87° , and is readily soluble in alcohol, but insoluble in water; it readily oxidises on exposure to the air, and when treated with hydrochloric acid it does not yield a diphenyl base, but is decomposed into an azo-compound and an amido-compound.

Paratolydisazorthocresol; $C_{21}H_{20}N_4O$, forms small, prismatic crystals, melts at 164.5° , and is insoluble in water, and only sparingly soluble in alcohol. The *ethyl* derivative, $C_{23}H_{24}N_4O$, crystallises in yellow, microscopic needles, melts at $107-108^\circ$, and is soluble in hot ether, benzene, and chloroform, but insoluble in water and alkalis.

Phenylazoparacresetoil, $NPh \cdot N \cdot C_6H_3Me \cdot OEt$, prepared by heating the corresponding phenol with ethyl iodide and sodium ethoxide in alcoholic solution, crystallises from alcohol in red plates, melts at 48° , and is soluble in ether and benzene, but insoluble in water and alkalis. The *hydrazo*-compound, $C_{16}H_{18}N_2O$, crystallises in colourless needles, melts at 105° , and is soluble in alcohol, benzene, &c., but insoluble in water.

Methylethoxybenzidine, $NH_2 \cdot C_6H_4 \cdot C_6H_2Me(OEt) \cdot NH_2$, is formed when phenylhydrazoparacresetoil is treated with moderately concentrated hydrochloric acid, and the hydrochloride produced decomposed with ammonia. It crystallises from light petroleum in slender, colourless needles, melts at 107° , and is very sparingly soluble in water, but readily in ether and alcohol; its azo-derivatives dye unmordanted cotton, but not so readily as the corresponding benzidine derivatives.

Orthotolylazoparacresol, $C_{14}H_{14}N_2O$, forms red needles with a blue reflex, melts at 98° , and is soluble in alcohol and chloroform, but insoluble in water and dilute alkalis. The *ethyl* derivative, $C_{16}H_{18}N_2O$, crystallises in red prisms with a blue reflex, melts at $82-83^\circ$, and resembles the preceding compound in its behaviour with solvents. The *hydrazo*-compound, $C_{16}H_{20}N_2O$, prepared by reducing the *ethyl* derivative with hydrogen sulphide in ammoniacal alcoholic solution, crystallises in colourless plates, melts at 138° , and is insoluble in water, but soluble in alcohol.

Dimethylethoxybenzidine, $NH_2 \cdot C_6H_3Me \cdot C_6H_3Me(OEt) \cdot NH_2$, is formed, together with a small quantity of the azo-compound, when the *hydrazo*-compound just described is treated with hot dilute sulphuric acid; it crystallises from dilute alcohol in colourless needles, melts at 75° , and is readily soluble in alcohol, ether, and chloroform,

but only sparingly in water; it yields coloured azo-compounds which dye unmordanted cotton fibre.

Paratolylazoparacresetoil, $C_{16}H_{18}N_2O$, crystallises from alcohol in red needles, melts at 171° , and is readily soluble in ether and benzene. The corresponding *hydrazo*-compound, $C_{16}H_{20}N_2O$, forms colourless needles, melts at 153° , and is insoluble in water, but soluble in alcohol, benzene, &c.; when treated with hydrochloric acid, it yields a base which is analogous to diphenyline, and from which azo-compounds, having only a very feeble colouring power, are obtained.

F. S. K.

Orthonitrophenylcinnamic Acid and Phenylhydrocarbo-styryl. By A. OGLIALORO and E. ROSINI (*Gazzetta*, 20, 396—402).—*Orthonitrophenylcinnamic acid*, $C_{15}H_{11}NO_4$, is prepared by heating a mixture of dry sodium phenylacetate (1 mol.), orthonitrobenzaldehyde (1 mol.), and acetic anhydride (4 mols.) for six hours at 160° . The impure acid obtained is partially purified and then converted into the *barium salt*, $(C_{15}H_{11}NO_4)_2Ba \cdot 5H_2O$, which crystallises in tufts of pale-yellow needles. The pure acid crystallises in small, pale-yellow prisms, begins to soften at 192° , and melts at 195 — 196° . It is sparingly soluble in water, but freely in hot alcohol; it also dissolves in ether and in benzene. From some of the alcoholic solutions obtained in the preparation of this acid, another barium salt may be obtained containing 8 mols. H_2O .

On reducing a diluted alcoholic solution of the acid with sodium amalgam, the product consists of a mixture of several substances which may be separated by fractional solution in water, dilute and absolute alcohol. The portion extracted by dilute alcohol crystallises in yellowish needles, melts at 173 — 174° , and has the composition of *phenylhydrocarbo-styryl*, $C_{15}H_{13}NO$. It is very soluble in hot alcohol, moderately in chloroform and benzene, but only sparingly in ether and light petroleum. Attempts made to prepare hydrophenylinole from this compound by fusing it with potash were unsuccessful.

S. B. A. A.

Naphthyl Methyl Ketones. By A. CLAUS and H. TERSTEEGEN (*J. pr. Chem.* [2], 42, 517—519).—The crystals obtained by prolonged cooling of α -naphthyl methyl ketone below 0° (Abstr., 1887, 271) are β -naphthyl methyl ketone.

β -*Naphthyl methyl ketone* is best obtained by acetylisng naphthalene in the cold and with exclusion of direct sunlight; the process is slow and the yield poor; it is freed from the α -ketone by crystallisation and pressure; it sublimes with steam in small, transparent leaflets, melts at 51.5 — 52° (uncorr.), boils undecomposed at 301 — 303° (uncorr.), and dissolves freely in alcohol, ether, and chloroform. The *oxime* forms colourless crystals which melt at 145° (uncorr.), and the *acetyl compound* of this melts at 134° . The *phenylhydrazide* melts at 171° (uncorr.).

α -Naphthyl methyl acetoxime melts at 114° , and α -naphthyl methyl ketone hydrazide at 146° (uncorr.; compare Abstr., 1887, 271).

β -*Naphthylglyoxylic* (β -*naphthoylformic*) *acid*, obtained by oxidising the ketone with potassium permanganate, is a greenish-yellow oil which slowly crystallises and melts at 75° (?); it is pretty freely

soluble in water; the *barium salt* is anhydrous; the *potassium* and *calcium salts* crystallise with 1 mol. H_2O . By reduction, it yields β -naphthylglycollic acid, which crystallises in small needles, sublimes in long needles, and melts at 176° (uncorr.); it is little soluble in water; its *barium salt* is anhydrous. α -Naphthylglycollic acid melts at 163° (uncorr.).

β -Naphthylacetic acid is obtained by reducing the glycollic acid with hydriodic acid; it crystallises in lustrous, silvery leaflets which melt at 142° (uncorr.); its *amide* melts at 200° (uncorr.). A. G. B.

Naphthasultonsulphonic Acids and α -Naphtholsulphonamidosulphonic Acids. By A. BERNTHSEN (*Ber.*, 23, 3088—3096).

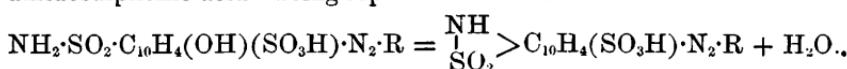
—When naphthasultone, the "naphtholsulphonic acid-S." of the Schöllkopf Aniline and Chemical Co.'s Germ. Pat. 40571, is sulphonated with concentrated sulphuric acid, and the melt poured into water, α -naphthol- δ -disulphonic acid ("S. acid") $[OH : SO_3H : SO_3H = 1 : 4 : 1']$ is obtained (Schöllkopf Co., *loc. cit.*). The author finds that this acid is not the immediate product of sulphonation, but results from hydration of the initially-formed naphthasultonsulphonic acid- δ .

Naphthasultonsulphonic acid δ is obtained as sodium salt when 1 part of naphthasultone is gradually stirred into 8 parts of cooled 5 per cent. anhydrosulphuric acid, left for about an hour until a portion is found to be completely soluble in water, and then stirred into an externally-cooled mixture of 12 parts of ice and 16 parts of saturated brine. The sodium salt, $\text{C}_{10}\text{H}_5\overset{\text{O}}{\underset{\text{SO}_2}{\text{--}}} \text{SO}_3\text{Na} + 3\text{H}_2\text{O}$, which separates after some time, crystallises in thin scales or tables, is much more soluble in water than the sodium salt of naphthasultonsulphonic acid ϵ (*Abstr.*, 1890, 387), and in aqueous solution gives no colour reaction with ferric chloride. On treatment with alkalis or alkaline carbonates, or by boiling with dilute (5 per cent.) sulphuric acid, or prolonged boiling with water, it is converted into sodium 1 : 4 : 1'- α -naphtholdisulphonate, whilst the latter, on treatment with suitable dehydrating agents, such as concentrated sulphuric acid at 100° , yields the naphthasultonsulphonate. The solution in concentrated ammonia, on addition of hydrochloric acid, gives a precipitate of the sodium salt of naphtholsulphonamidosulphonic acid δ , $\text{OH}\cdot\text{C}_{10}\text{H}_5(\text{SO}_2\text{NH}_2)\cdot\text{SO}_3\text{Na} + 2\text{H}_2\text{O}$, which crystallises in rhomb-like scales or plates, resembles the ϵ -compound (*loc. cit.*) in properties, and forms similar azo-dyes.

The azo-dyes obtained from the salts of naphtholsulphonamido-sulphonic acid ϵ give much bluer or redder shades, are less soluble in water, and crystallise better than those from α -naphtholdisulphonic acid ϵ . The dyes formed by the action of diazotised xylidine, α -naphthylamine, and benzidine give respectively very blue-claret, wine-red, and bluish-violet shades, are scarcely affected by acids, and, on reduction with stannous chloride and hydrochloric acid, yield the sodium hydrogen salt of an amidonaphtholdisulphonic acid (probably $\text{OH} : \text{NH}_2 : \text{SO}_3\text{H} : \text{SO}_3\text{H} = 1 : 2 : 3 : 1'$).

The azo-dyes obtained with diazotised xylidine dissolve in concen-

trated sulphuric acid with a magenta colour, which, after a short time, changes to yellow; a corresponding colour-change occurs also with the other dyes named, and is due to hydrolysis of the $\text{SO}_2\text{-NH}_2$ radicle with the production of ammonia and the corresponding azo-colouring matters derived from α -naphtholdisulphonic acid ϵ . A more remarkable change is that brought about by alkalis. The bluish-red azo-dye obtained with diazotised xyldine, when warmed for a short time with alkalis or alkaline carbonates, changes colour to a bright reddish-yellow, and a corresponding change to yellow or red shades ensues under like conditions with the other dye stuffs named. The azo-dyes formed can be salted out from solution, and, unlike the parent colours, are very sensitive towards acids, changing colour to blue or violet, and thus resemble many of the amidoazo-dyes. Moreover, they crystallise well, are very soluble in water containing some alkali, and in an acid bath produce shades on wool which are distinctly bluer than those from the parent dyes. On reduction with stannous chloride and hydrochloric acid, the "altered" xyldine dye, which gives a cochineal shade on wool in an acid bath, yields a sparingly soluble compound, $\text{C}_{10}\text{H}_8\text{N}_2\text{S}_2\text{O}_5 + 2\text{H}_2\text{O}$, crystallising in long, flat needles. This compound dissolves readily in alkalis, is precipitated from the alkaline solutions by acids, and by prolonged boiling with phenanthraquinol in acetic acid solution, forms an azine. It is a derivative of, but not identical with, $1:2:3:1'$ -orthonaphthylenediaminedisulphonic acid, and is regarded by the author as the *anhydride*, $\text{NH}_2\text{SO}_2>\text{C}_{10}\text{H}_4(\text{NH}_2)\cdot\text{SO}_3\text{H}$, of this compound, the action of alkalis on the azo-dyes obtained from naphtholsulphonamidosulphonic acid ϵ being represented thus:—



Sodium hydrogen 1 : 2 : 3 : 1'-orthonaphthylenediaminedisulphonate, $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_4(\text{NH}_2)_2\cdot\text{SO}_3\text{Na} + 3\text{H}_2\text{O}$, crystallises in small needles, is much more soluble than the salt of the anhydride, and forms an azine on treatment with phenanthraquinone. W. P. W.

Dinaphthyl Picrates. By R. WEGSCHEIDER (*Ber.*, **23**, 3199—3201).—Of the dinaphthyl picrates, only the $\alpha\alpha$ -compound has previously been prepared. $\alpha\beta$ -Dinaphthyl picrate, $\text{C}_{20}\text{H}_{14} + \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, may be readily obtained by mixing boiling alcoholic solutions of the hydrocarbon and picric acid, and crystallises in golden-yellow needles melting at $155-156^\circ$. For the preparation of $\beta\beta$ -dinaphthyl picrate, the constituents must be dissolved in boiling benzene; the salt separates out on cooling in microscopic, orange prisms, which have the composition $\text{C}_{20}\text{H}_{14}, 2\text{C}_6\text{H}_3\text{N}_3\text{O}_7$. The author regards the hydrocarbon obtained by Bischoff, by the action of methyl chloride on naphthalene in presence of aluminium chloride (*Abstr.*, 1890, 1145), as probably identical with $\beta\beta$ -dinaphthyl. H. G. C.

Chrysidines. By A. PICRET and S. ERLICH (*Chem. Centr.*, 1890, ii, 350—351; from *Arch. sci. phys. nat., Genève* [3], **23**, 552).—The

authors have pursued the investigations already commenced by Pictet (*Abstr.*, 1890, 390), and have studied the action of heat on the two benzylidenenaphthylamines, which are obtained by heating benzaldehyde with the two naphthylamines. By passing the vapour of these compounds through a red-hot tube, two new bases, of the formula $C_{17}H_{11}N$, are obtained, the constitutional formula being, probably, $C_6H_4\overset{||}{CH}_2C_6H_6N$. These bases, which correspond with the phen-anthridines, and are similar to them in their properties, are, therefore, α - and β -chrysidine. Their alkaline solutions have a blue fluorescence, they form yellow salts with acids, and the solutions of the latter have a green fluorescence. Reduction with tin and hydrochloric acid converts them into secondary bases. α -Chrysidine melts at 108° , β -chrysidine at 126° .

J. W. L.

Turpentine. By R. G. DUNWODY (*Chem. Centr.*, 1890, ii, 241—242; from *Amer. J. Pharm.*, June, 1890).—The author finds very considerable variations in the specific rotatory power and the specific gravity of oil of turpentine. In 12 samples, the former varied from 2.60° to 36.64° in a 200 mm. tube, before rectification, and from 3.90° to 38.62° after rectification. The specific gravity at 15° varied from 0.856 to 0.876 before, and from 0.851 to 0.873 after rectification. The oils commenced to boil at 155 — 159° , and the last portions distilled between 165° and 170° ; the principal part distilled at 160 — 162° . The author has not found Allen's test with castor-oil, for the detection of petroleum in turpentine, of much value, since an admixture of 65 per cent. of the former escaped detection by means of this test. In pure glacial acetic acid both petroleum and turpentine are perfectly miscible, but of acetic acid containing 1 per cent. of water, more and more is required for complete solution, the greater the proportion of petroleum which is present, as is shown in the following table:—

Petroleum	1	2	3	4	5	7	8 c.c.
Oil of turpentine.....	9	8	7	6	5	3	2 „
Acetic acid + 1 per cent H_2O	40	60	80	110	150	230	270 „

From the pitch remaining in the retort, after the distillation of the turpentine, the author has separated, with light petroleum, two well crystallised substances, the one being abietic acid, melting at 131° , and the other, a new substance, having the composition 72—72.8 per cent. carbon, 9.75—9.50 per cent. hydrogen, 18.25—17.70 per cent. oxygen; and melting at 125 — 126° .

J. W. L.

Terpenes and Ethereal Oils. By O. WALLACH (*Annalen*, 259, 309—324).—*Pinole glycol diacetate*, $C_{10}H_{16}O(OAc)_2$, is formed, together with pinole and pinole glycol, when pinole dibromide is warmed with sodium or silver acetate in glacial acetic acid solution; the product is purified by fractional distillation under a pressure of 13 mm. It crystallises well from water, and melts at 97 — 98° .

Pinole glycol, $C_{10}H_{16}O(OH)_2$, can be prepared by boiling the VOL. IX.

diacetate with very dilute sulphuric acid, or by treating the bromide with freshly precipitated silver oxide; it crystallises from light petroleum in needles, melts at 125°, is very readily soluble in chloroform, and is converted into the diacetate by boiling acetic anhydride.

Pinole hydrate, $C_{10}H_{18}O_2$, is obtained, together with cymene, when a well-cooled glacial acetic acid solution of crude pinole is saturated with hydrogen bromide, and then shaken with very dilute soda in the cold, in order to decompose the additive product; after separating the cymene by distilling with steam, the hydrate is extracted from the alkaline solution by shaking with ether. Pinole hydrate crystallises in needles or plates, melts at 131°, and is moderately easily soluble (1 in 30 at 15°) in water, but more readily in alcohol; it crystallises unchanged from boiling glacial acetic acid, but when warmed with dilute sulphuric acid, it is converted into pure pinole. It is identical with the crystalline substance which was formed, as was first observed by Sobrero (*Annalen*, **80**, 106), when oil of turpentine is exposed to direct sunlight in presence of oxygen (compare Armstrong, *Proc.*, 1890, 99). Pinole, on oxidation with potassium permanganate, yields terebic acid and considerable quantities of oxalic acid and carbonic acid; pinole hydrate, under the same conditions, gives terpenylic acid, carbonic acid, and oxalic acid; pinole glycol seems to give the same oxidation products as the hydrate.

Pure pinole is easily prepared by boiling a benzene solution of pinole dibromide with the theoretical quantity of sodium, in the form of fine wire, until decomposition is complete; the filtered solution is evaporated, and the residual pinole purified by fractional distillation.

Pinole tribromide, $C_{10}H_{15}OBr_3$, is obtained in small quantities in the preparation of the dibromide from crude pinole; it crystallises from ethyl acetate in needles, and melts at 160° with decomposition.

F. S. K.

Fenchole, an Isomeride of Camphor. By O. WALLACH and F. HARTMANN (*Annalen*, **259**, 324—331).—A liquid of sp. gr. 0·934, possessing a strong odour of camphor, and boiling at 190—193°, can be isolated from oil of fennel; it has the composition $C_{10}H_{16}O$, and is named by the authors *fenchole*. The whole chemical behaviour of fenchole is that of a position-isomeride of camphor, as will be seen from the experiments described below; it combines with bromine in well-cooled light petroleum solution, yielding a bright-red, crystalline, unstable additive product, which is reconverted into fenchole on treatment with soda; it also yields with sodium, a solid compound, which seems to be converted into an acid by carbonic anhydride.

Fenchole oxime, $C_{10}H_{16}\cdot N\cdot OH$, crystallises from alcohol in slender needles, and from ethyl acetate in well-defined crystals, $a : b : c = 1\cdot3047 : 1 : 0\cdot55259$, $\beta = 76^\circ 20'$, which melt at 148—149°, and are very like those of camphor oxime in appearance. The *hydrochloride*, $C_{10}H_{17}NO\cdot HCl$, melts at 118—119°, and is decomposed by alcohol. The *anhydride*, $C_{10}H_{15}N$, prepared by dissolving the oxime in dilute sulphuric acid, is a colourless liquid, boiling at 217—219°; it can be distinguished from the anhydride of camphor oxime by the fact that it yields a crystalline *hydrobromide*, $C_{10}H_{15}N\cdot HBr$, which is, however, very unstable.

Isofenchole oxime, $C_{10}H_{17}NO$, is formed when fenchole oxime anhydride is boiled with alcoholic potash for five to six hours; it crystallises from alcohol in plates, melts at $113-114^\circ$, and is readily soluble in alcohol, ether, and acids, and moderately soluble in water.

Fencholenic acid, $C_{10}H_{16}O_2$, is obtained when isofenchole oxime is boiled with alcoholic potash for four days, but some of the oxime remains unchanged. It is an almost colourless liquid, boils at $257-260^\circ$, and forms a sparingly soluble silver salt and a deliquescent ammonium salt.

F. S. K.

Rose-oil. By V. MARKOVNIKOFF (*Ber.*, **23**, 3191).—Rose-oil consists, as is well known, of liquid constituents and stearoptene. The latter melts at 36.5° , and has all the properties of a paraffin; it is perfectly inodorous, and is, therefore, of no value with regard to the quality of the oil. The liquid portion or eleoptene boils within narrow limits, and appears to be a mixture of two substances, $C_{10}H_{20}O$ and $C_{10}H_{18}O$, one of which is an alcohol, and forms the chief constituent of rose-oil.

H. G. C.

β -Methylpyridine. By C. STOEHR (*Ber.*, **23**, 3151—3157).—The product obtained by the distillation of strychnine or of brucine is not homogeneous. After purification, however, it yields β -methylpyridine, which boils at $142-143^\circ$, and is identical with the synthetical product from glycerol, acetamide, and phosphoric anhydride. The mercurochloride melts at $145-146^\circ$, the platinosochloride at $257-257.5^\circ$, and the platinochloride at $201-202^\circ$. Ladenburg (*Abstr.*, 1890, 1432) gives three melting points for this last compound (from synthetical β -methylpyridine), which range between 191° and 198° and it is suggested that he had to deal with varying mixtures of the two platinum compounds. Ladenburg's theory of the constitution of pyridine, so far as it is based on the existence of two β -methyl derivatives, is thus proved to be erroneous.

J. B. T.

A New Class of Acridines: Phenylcarbazacridine. By D. BIZZARRI (*Gazzetta*, **20**, 407—417).—*Phenylcarbazacridine*, $C_{19}H_{11}N$, is formed when a mixture of pure carbazole (20 grams) with benzoic acid (15 grams) and fused zinc chloride (45 grams) is heated for five hours at $120-130^\circ$, and the alcoholic solution of the product precipitated with strong aqueous ammonia. The product when pure crystallises from alcohol in minute, white scales, turns green on heating to 150° , and melts at 186.5° . It dissolves in most of the ordinary solvents, but only sparingly in absolute alcohol, and not at all in water. It crystallises from benzene in groups of rectangular laminæ, and from xylene in peculiar, spherical tufts. With acetic acid, it forms an intense green solution, which is dichroic when concentrated (0.25 per cent.), appearing emerald-green by reflected, and garnet-red by transmitted light. It is not affected by boiling with alkalis, and only partially decomposed by heating with soda-lime. It is dissolved by benzoic chloride, but not further affected.

The *methiodide*, $C_{19}H_{11}N\cdot MeI$, prepared by heating the base with methyl iodide at 140° , crystallises in brownish-yellow plates, soluble in

q 2

alcohol and acetic acid. From these solutions, the base is reprecipitated on the addition of water. Boiling alcoholic potash decomposes it into the free base, methyl alcohol, and potassium iodide. On gently heating, it is similarly split up into the base and methyl iodide.

The hydrochloride forms emerald-green scales, soluble in acetic acid and in alcohol, but not in water. It dissociates even in alcoholic solution, and is only stable in presence of an excess of free hydrochloric acid. It is completely decomposed by boiling water. The sulphate forms a green, shining mass, soluble in acetic acid and in alcohol, but not in water. It is gradually decomposed by boiling water, and the alcoholic solution is unstable in the absence of free sulphuric acid. The picrate and hydrioxide crystallise in green plates decomposed by water, and forming unstable alcoholic solutions. The chromate crystallises in scales decomposed by water and alcohol.

Benzoylcarbazole, $C_{19}H_{13}NO$, is obtained by heating carbazole with benzoic anhydride at 240° . It crystallises from alcohol in white, acicular prisms, melts at $95\cdot5^\circ$, dissolves in benzene, ether, &c., but only sparingly in alcohol. It is decomposed by alcoholic potash into carbazole and benzoic acid. Its formation and decomposition, together with the analogy to acetylcarbazole, establish for this compound the constitution $C_{12}H_8NBz$. On heating it with zinc chloride at $130-150^\circ$, phenylcarbazacridine is formed.



prepared by reducing phenylcarbazacridine with zinc-dust, crystallises in yellowish leaves which turn brown and melt at 172° , and dissolves in acetic acid, alcohol, and ether, but not in water. It reduces silver nitrate in alcoholic solution, and picric acid imparts to it an orange coloration. It has no basic properties, but acids and potassium permanganate convert it into phenylcarbazacridine.

When carbazole is heated with benzoic acid and zinc chloride at $150-160^\circ$, there is formed, besides the acridine described and resinous products, a compound of unknown constitution, which crystallises from boiling alcohol in tables which melt at 210° , and are stained yellow by picric acid. At $200-210^\circ$, no phenylcarbazacridine is formed, the products consisting mainly of resins. At 280° , the mass is gradually carbonised.

S. B. A. A.

Thiazoles. By K. HUBACHER (*Annalen*, **259**, 228-253; compare Hantzsch, Abstr., 1889, 413, 723, and 1890, 1238).—*Thiopropionamide*, C_3H_7NS , can be prepared by treating propionamide with phosphorus pentasulphide, as described by Hantzsch (*loc. cit.*) in the case of thiacetamide; the yield is, at the most, 10 per cent. of the amide employed. It crystallises in yellowish plates, melts at $42-43^\circ$, and is very readily soluble in benzene, but only sparingly in ether, alcohol, and water.

z.-Methyl- μ -ethylthiazole, $\text{CH}-\text{S}\left[\begin{smallmatrix} \text{CMe} \\ || \\ \text{N} \end{smallmatrix}\right]\text{CEt}$, is obtained when thiopropionamide is treated with chloroacetone in alcoholic solution, and the

product decomposed with soda. It is a colourless liquid, boils at 159·5—160° (728·5 mm.), has an odour of pyridine, and is miscible with alcohol and ether, but is only sparingly soluble in cold water. The *platinochloride*, $(C_6H_9NS)_2H_2PtCl_6$, forms small, yellowish-red crystals, and melts at 177° with decomposition.

α-t-phenyl-μ-ethylthiazole, $C_{11}H_{11}NS$, is formed when thiopropionamide is treated with bromacetophenone in like manner; the product is dissolved in dilute hydrobromic acid, and the crystalline hydrobromide, which is deposited from the filtered solution, decomposed with soda. The base is a colourless oil, of agreeable odour, boils at 295° (729 mm.), and is insoluble in water, but miscible with alcohol and ether. The *platinochloride*, $(C_{11}H_{11}NS)_2H_2PtCl_6$, forms light-yellow, microscopic crystals, and melts at 128—129° with decomposition. The *hydrobromide*, $C_{11}H_{11}NS \cdot HBr$, crystallises in colourless needles, melts at 68—70°, and is decomposed by cold water or when kept over sulphuric acid.

μ-Phenylthiazole, C_9H_9NS , is formed when thiobenzamide is heated at 100° for several hours with dichlorether and sodium acetate in alcoholic solution; the dark, resinous product is extracted with dilute hydrochloric acid, the base liberated with soda, and distilled. It is a colourless oil boiling at 266—268° (732 mm.). The *hydrochloride*, $C_9H_9NS \cdot HCl + 2H_2O$, crystallises from dilute hydrochloric acid in plates, melts at 61—62°, loses its water over sulphuric acid, and is immediately decomposed by water. The *platinochloride*, $(C_9H_9NS)_2H_2PtCl_6 + 2H_2O$, is a yellow, crystalline compound melting at 173—175° with decomposition; it loses its water at 110°. The picrate crystallises in yellow needles, melts at 124—125°, and is only very sparingly soluble in water, but readily in hot alcohol.

α-Methyl-μ-phenylthiazole, $C_{10}H_9NS$, prepared by treating thiobenzamide with chloracetone in alcoholic solution, is an oil boiling at 277·5—278° (724 mm.).

αμ-Diphenylthiazole, $C_{15}H_{11}NS$, obtained from thiobenzamide and bromacetophenone in like manner, crystallises from alcohol in colourless plates, melts at 92—93°, boils above 360° without decomposition, and is readily soluble in alcohol and ether; it is a very feeble base, but its salts are unstable and cannot be obtained in a pure condition.

Ethyl α-methyl-μ-phenylthiazolecarboxylate, $\begin{array}{c} \text{CPh}\cdot\text{S} \\ || \\ \text{N}\cdot\text{CMe} \end{array} >\text{C}\cdot\text{COOEt}$, is obtained when thiobenzamide is warmed with ethyl chloracetoacetate, and the salt thus produced decomposed with soda; it crystallises from ether in yellow needles, and melts at 43°. The corresponding acid, $C_{11}H_9NS$, prepared by hydrolysing the ethereal salt with alcoholic potash, crystallises in colourless needles, melts at 202—204·5°, and, when heated more strongly, sublimes in long needles, being at the same time partially decomposed into carbonic anhydride and methylphenylthiazole. It is readily soluble in alcohol, but only sparingly in ether, and almost insoluble in water; in its neutral solutions many metallic salts produce a precipitation.

A mixture of various compounds, which contains *α-chloropropalde-*

hyde, can be obtained by gradually adding sulphuryl chloride to an ethereal solution of propaldehyde in which barium carbonate is suspended; the ethereal solution is washed with water and sodium carbonate consecutively, dried, and then submitted to fractional distillation; the portion passing over between 60° and 150° was employed in some of the experiments described below.

$\beta\mu\text{-D.methylthiazole}$, $\text{CH}\cdot\text{N} \geqslant \text{CMe}\text{S}$, is formed in small quantities

when crude α -chloropropaldehyde is warmed with thiacetamide, the product boiled with hydrochloric acid, and then treated with soda; it is purified by distilling with steam, and then submitted to fractional distillation. It is a colourless liquid, boils at 148—150° (734 mm.), and is sparingly soluble in water, but readily in ether and alcohol. The *platinumchloride*, $(\text{C}_6\text{H}_5\text{NS})_2\text{H}_2\text{PtCl}_6$, crystallises in prisms and melts at 202°; the picrate crystallises in small, yellow needles, melts at 165—167°, and is sparingly soluble in water.

$\beta\text{-Methyl-}\mu\text{-amidothiazole}$, $\text{C}_4\text{H}_6\text{N}_2\text{S}$, is obtained by heating crude α -chloropropaldehyde with thiocarbamide; it crystallises from water in yellowish plates, melts at 94—95°, and is readily soluble in alcohol, but less readily in ether, and only sparingly in cold water. The *platinumchloride* forms nodular, crystalline aggregates, and melts at 181—182° with decomposition.

$\alpha\beta\text{-Diphenyl-}\mu\text{-amidothiazole}$, $\text{C}_{15}\text{H}_{12}\text{N}_2\text{S}$, can be prepared by warming bromodeoxybenzoin with thiocarbamide and decomposing the product with dilute sodium carbonate. It crystallises from alcohol in yellowish needles, melts at 185—186°, and is readily soluble in alcohol, but only sparingly in ether, and insoluble in water. The *hydrobromide*, $\text{C}_{15}\text{H}_{21}\text{N}_2\text{S}\cdot\text{HBr}$, crystallises in needles, melts at 215—217° with partial decomposition, and is only sparingly soluble in dilute hydrobromic acid.

$\alpha\beta\text{-Diphenyl-}\mu\text{-methylthiazole}$, $\text{C}_{16}\text{H}_{13}\text{NS}$, can be obtained by treating an alcoholic solution of thiacetamide with bromodeoxybenzoin; it is purified by means of the hydrochloride, a crystalline compound melting at 96—97°. The base crystallises in colourless needles, melts at 51—52°, and is insoluble in water, but readily soluble in alcohol and ether.

Triphenylthiazole, $\text{C}_{21}\text{H}_{15}\text{NS}$, prepared from thiobenzamide and bromodeoxybenzoin, crystallises in colourless, well-defined prisms, melts at 86—87°, and is readily soluble in ether, but more sparingly in alcohol, and insoluble in water. It crystallises unchanged from hot concentrated hydrochloric acid, in which it is only very sparingly soluble.

Phenylhydroxythiazole (m. p. 204°) is formed when bromacetophenone is treated with xanthogenamide under various conditions. The *ethyl derivative* of phenyloxypseudothiazole is obtained when phenylhydroxythiazole is treated with sodium ethoxide and ethyl iodide at 140—150°. It crystallises from ether in colourless plates, melts at 71°, and is decomposed by concentrated hydrochloric acid at 220° yielding ethylamine; it has, therefore, the constitution expressed

by the formula $\text{CPh}\cdot\text{NET} >$.

F. S. K.

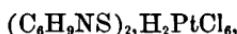
Trimethylthiazole, Methylthethylthiazole, and Thiazolecarboxylic Acids. By T. ROUBLEFF (*Annalen*, **259**, 253–276).—*Ethyl α-chloromethylacetacetate*, $\text{COMe}\cdot\text{CMeCl}\cdot\text{COOEt}$, is obtained when sulphuryl chloride is gradually added to well-cooled ethyl methylacetacetate. It is a colourless liquid of sp. gr. 1·0591 at 16·5°, with a pleasant, rather pungent odour, and boils at 192–194° (corr.). It does not yield a salt with copper acetate under any conditions; the corresponding bromo-compound, obtained by brominating ethyl methylacetacetate, gives a copper salt, and can be readily converted into thiazole derivatives. It is evident, therefore, that chlorine and bromine, at the ordinary temperature, displace different hydrogen atoms in ethyl methylacetacetate (compare Hantzsch, *Abstr.*, 1890, 1238; it has, however, been stated by Genvresse (*Compt. rend.*, **107**, 187) that both α- and γ-chloro-derivatives are formed when ethyl acetacetate is treated with chlorine at 170°.

Trimethylthiazole, $\text{CMe}=\text{S} \begin{matrix} \parallel \\ \text{CMe-N} \end{math} \text{CMe}$, is formed when crude methyl chlōrethyl ketone, prepared by hydrolysing ethyl α-chlormethylacetacetate with 40 per cent. hydrochloric acid, or by chlorinating methyl ethyl ketone with sulphuryl chloride, is warmed with thiacetamide; the product is boiled with dilute hydrochloric acid, the filtered solution mixed with soda, and the precipitated oil extracted with ether. Trimethylthiazole can also be obtained by brominating methyl ethyl ketone in ethereal solution, and treating the methyl bromethyl ketone produced with thiacetamide. It is a colourless liquid of sp. gr. 1·0130 at 16°, boils at 166·5–167·5° (corr.), and is moderately easily soluble in cold water. The *platinochloride*, $(\text{C}_6\text{H}_9\text{NS})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in orange prisms, and melts at 232–233° with decomposition. The *hydrochloride* is a crystalline, deliquescent compound melting at 173–174°. The *aurochloride* is sparingly soluble in boiling water, from which it crystallises in yellow needles melting at 155–156°. The *picrate* crystallises from hot water in yellow prisms melting at 133°, and the *mercurochloride* crystallises in small plates melting at 118–119°.

Ethyl bromomethylacetacetate, $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{COOEt}$, prepared by brominating ethyl methylacetacetate, is an oil of sp. gr. 1·1981 at 16·5°, with a disagreeable, pungent odour; its alcoholic solution gives a reddish-violet coloration with ferric chloride, and a green, crystalline precipitate with copper acetate.

Ethyl methylthiazolepropionate, $\text{CMe}=\text{N} \begin{matrix} \parallel \\ \text{S}-\text{CH} \end{math} \text{C}\cdot\text{CHMe}\cdot\text{COOEt}$, is formed when thiacetamide is treated with ethyl bromomethylacetacetate; it is a thick, dark-brown oil, and on hydrolysis with alcoholic soda, it yields an oily acid which, when distilled with lime, is converted into μ-methyl-α-ethylthiazole.

μ-Methyl-α-ethylthiazole, $\text{C}_6\text{H}_9\text{NS}$, purified by fractional distillation, is an oil boiling at 169–171° (corr.). The *platinochloride*,



forms reddish-yellow prisms, and melts at 182–183° with decom-

position. The *picroate* crystallises from water in well-defined, lemon-yellow prisms, melting at 114—115°, and the *mercurochloride* crystallises in prisms melting at 138—139°.

$\alpha\mu\text{-Dimethylthiazole-}\beta\text{-carboxylic acid}$, $\text{CMe} \begin{matrix} \text{N-CMe} \\ \parallel \\ \text{CMe-S} \end{matrix} \text{C-COOH}$, is obtained

when the ethyl salt (compare Hantzsch, Abstr., 1889, 724) is hydrolysed with alcoholic potash. It crystallises from hot water in long, colourless needles or small prisms, melts at 227° with evolution of gas, sublimes without decomposition, and is only moderately easily soluble in hot water, but more readily in alcohol and ether. The salts of the alkaline earths are readily soluble in water, but in neutral solutions of the ammonium salt, many metallic salts produce a precipitation. The silver salt, $\text{C}_6\text{H}_5\text{NS-COOAg}$, crystallises from boiling water in colourless needles, and quickly darkens on exposure to light. The *hydrochloride*, $\text{C}_6\text{H}_5\text{O}_2\text{NS-HCl}$, crystallises from cold dilute hydrochloric acid in transparent plates, and is decomposed by water, or when heated at 70°. The acid is completely destroyed by potassium permanganate, but it is not acted on by boiling concentrated nitric acid.

$\mu\text{-Methylthiazoledicarboxylic acid}$, $\text{CMe} \begin{matrix} \text{S-COOH} \\ \parallel \\ \text{N-COOH} \end{matrix}$, can be ob-

tained by warming ethyl chloroxalacetate, prepared by treating ethyl oxalacetate with sulphuryl chloride, with thiacetamide, and hydrolysing the product with alcoholic soda. It crystallises from warm water in long, colourless needles with 1 mol. H_2O , sublimes below 100°, melts at 169° with evolution of carbonic anhydride, and is readily soluble in cold water and alcohol, but very sparingly in ether, carbon bisulphide, benzene, &c. The *barium salt*, $\text{C}_6\text{H}_5\text{NSO}_4\text{Ba} + 2\text{H}_2\text{O}$, crystallises in colourless needles, and loses the whole of its water at 130°. The *mercury salt*, $\text{C}_6\text{H}_5\text{NSO}_4\text{Hg} + 3\frac{1}{2}\text{H}_2\text{O}$, is colourless and crystalline, and loses its water at 115°. Most of the other salts, except those of calcium, magnesium, and the alkalis, are sparingly soluble in water.

$\mu\text{-Methylthiazole-}\beta\text{-carboxylic acid}$, $\text{C}_6\text{H}_5\text{O}_2\text{NS}$, is formed with evolution of carbonic anhydride, when the dicarboxylic acid just described is heated for some time at 170—172°. It crystallises from water in small, colourless needles or prisms containing 1 mol. H_2O , loses its water at 70—80°, and melts at 144—145°; it is readily soluble in cold water, but more sparingly in alcohol, ether, and chloroform, and almost insoluble in carbon bisulphide and benzene. The salts are all readily soluble, except those of silver, copper, and mercury.

Ethyl $\mu\text{-amidothiazoledicarboxylate}$, $\text{C}_9\text{H}_{12}\text{O}_4\text{N}_2\text{S}$, is obtained in the form of the hydrochloride when ethyl chloroxalacetate is mixed with thiocarbamide; when the crystalline salt, which is only very sparingly soluble in water, is treated with potassium carbonate, the base is liberated, and can be purified by crystallisation from ether-alcohol. It forms well-defined prisms which contain $\frac{1}{2}$ mol. $\text{C}_2\text{H}_6\text{O}$, and melt at 90°, the alcohol-free compound melting at 112°.

$\mu\text{-Amidothiazoledicarboxylic acid}$, $\text{C}_6\text{H}_4\text{N}_2\text{SO}_4$, prepared by hydrolysing the ethyl salt with alcoholic soda, crystallises from hot water

in yellowish needles with 1 mol. H₂O, loses its water at 150°, melts at 229—230° with complete decomposition, and is only sparingly soluble in most ordinary neutral solvents. Attempts to convert this acid and its ethyl salt into $\alpha\beta$ -thiazoledicarboxylic acid by means of nitrous acid were unsuccessful.

F. S. K.

Diazo-compounds of the Thiazole Series. By M. WOHMANN (*Annalen*, 259, 277—300).—A compound of the composition C₇H₈N₃O₃S, which seems from its behaviour to be the diazo-hydrate of ethyl methylthiazolecarboxylate, COOEt·C=S—C≡N·OH
CMe₂N, is formed when ethyl methylamidothiazolecarboxylate (10 grams), prepared as described by Zürcher (Abstr., 1889, 725), is dissolved in a mixture of 33 per cent. hydrochloric acid (30 c.c.) and water (200 c.c.), and sodium nitrite (25 grams), dissolved in water (100 c.c.), gradually added to the cooled solution; after expelling the nitrous acid with a stream of air, the precipitate is quickly separated by filtration, washed with very dilute nitric acid, alcohol, and ether consecutively, and then recrystallised from cold ether, from which it separates in small, yellowish plates. It melts and explodes at 99—100°, is rather unstable, gives Liebermann's reaction, and is moderately easily soluble in glacial acetic acid, alcohol, benzene, and light petroleum, but more sparingly in ether. In some respects, it behaves like an aromatic diazo-compound, being soluble in alkalis and cold concentrated acids, and giving dyes with phenols; in others, it behaves like a nitroso-derivative, and, when treated with most ordinary reducing agents, is reconverted into the amido-compound.

Ethyl hydrazomethylthiazolecarboxylate is obtained in an impure condition by carefully reducing the diazo-compound described above with zinc-dust and dilute ammonia. It is a crystalline, very unstable compound, which reduces Fehling's solution in the cold, and combines readily with aldehydes and ketones in acetic acid solution, yielding crystalline compounds; the condensation product obtained with acetone forms bright-yellow needles and is unstable.

Ethyl methylchlorothiazolecarboxylate, C₇H₈O₂NSCl, can be prepared by gradually adding the diazo-compound to warm 15 to 18 per cent. hydrochloric acid, and heating the mixture until the evolution of nitrogen ceases; the solution is then diluted with water, the product distilled with steam in order to separate it from the azimido-compound described below, and then treated with dilute hydrochloric acid to free it from ethyl methylamidothiazolecarboxylate. It crystallises from alcohol in transparent prisms, melts at 50—51°, has a sweet, sharp taste, and a fruity odour; it is soluble in concentrated hydrochloric acid and dissolves freely in most ordinary organic solvents, but is insoluble in water.

Ethyl methylbromothiazolecarboxylate, C₇H₈O₂NSBr, prepared by treating the diazo-compound with hydrobromic acid in a similar manner, crystallises from alcohol in large, colourless plates, melts at 70—71°, and resembles the chloro-derivative in chemical and physical properties. The corresponding *iodo*-compound, C₇H₈O₂NSI, is formed

in small quantity when the diazo-compound is treated with 2 to 3 per cent. hydriodic acid, the principal product, however, being regenerated amido-compound; it separates from alcohol and glacial acetic acid in crystals melting at 86—87°, and resembles the chlorinated derivative very closely. The yield of the iodo-compound is only 5 to 10 per cent., whereas in the case of the chlorinated and brominated derivatives the yield is 60—70 per cent. of the ethyl methylamidothiazolecarboxylate employed.

Ethyl methylazimidothiazolecarboxylate, $C_{14}H_{17}O_4N_5S_2$, is gradually deposited in orange-red needles when the diazo-compound is boiled with alcohol or heated for a long time with almost any neutral solvent. It separates from alcohol and glacial acetic acid in crystals, melts at 224—225°, and is moderately easily soluble in benzene and light petroleum, but more sparingly in ether; it dissolves freely in mineral acids, but it is only very sparingly soluble in, and is decomposed by, alkalis. On reduction with zinc-dust and hydrochloric acid, it is converted into ethyl methylamidothiazolecarboxylate, and on hydrolysis with alcoholic potash it is converted into the corresponding acid, $C_{10}H_9O_4N_5S_2$, which crystallises in slender, yellowish-red needles, melts at 214° with decomposition, and is almost insoluble in all ordinary neutral solvents.

Methylchlorothiazolecarboxylic acid, $C_5H_4O_2NSCl$, is obtained when the ethyl salt described above is hydrolysed with cold alcoholic potash, but the product is always mixed with some methylhydroxythiazolecarboxylic acid, from which it can only be imperfectly separated by fractional crystallisation. It seems to melt at about 144—148°, and is very readily soluble in all organic solvents, but only moderately easily in hot water. The silver salt, $C_5H_3O_2NSClAg$, crystallises in colourless needles.

The *bromo-acid*, $C_5H_4O_2NSBr$, and the *iodo-acid*, $C_5H_4O_2NSI$, were also obtained in an impure condition; the former seems to melt at about 162—164°, the latter at about 174—176°, with decomposition.

Methylhydroxythiazolecarboxylic acid, $C_5H_5O_3NS$, is formed when methylchlorothiazolecarboxylic acid is heated at 170°, but it is best prepared by fusing the ethyl salt of the chlorinated acid with concentrated potash. It crystallises from alcohol in small needles, melts at 222° with decomposition, and is moderately easily soluble in alcohol and hot water, but only sparingly in ether, and almost insoluble in benzene and light petroleum. The ammonium salt, $C_5H_8O_3N_2S$, crystallises from water in large prisms with 3 mols. H_2O , and melts at 138° with liberation of carbonic anhydride, being transformed into methylhydroxythiazole (m. p. 102°); this hydroxy-compound is also obtained when the acid is carefully heated.

Ethyl methylthiazolecarboxylate, $C_7H_9O_2NS$, can be easily prepared by treating the chlorinated derivative with zinc-dust and acetic acid at a temperature below 50°. It crystallises in transparent prisms, melts at 27—28°, boils at 232—233° (726 mm., thermometer entirely in vapour), is volatile with steam, and is very readily soluble in all ordinary solvents except water. The corresponding acid, $C_6H_8O_2NS$, prepared by hydrolysing the ethyl salt with alcoholic potash, crystallises from hot water in nacreous plates, and from alcohol in small

needles, melts at 257° with decomposition, and is almost insoluble in benzene and light petroleum; most of the salts of the heavy metals are insoluble.

F. S. K.

Synthesis of a Diamidocarbazole from Benzidine. By E. TÄUBER (*Ber.*, **23**, 3266—3269).—*Diamidocarbazole sulphate*, $C_{12}H_{11}N_3H_2SO_4$, can be obtained by heating metadiamidobenzidine hydrochloride (compare *Abstr.*, 1890, 782) with 18 per cent. hydrochloric acid (6 parts) for 10 hours at 180—190°, and treating the filtered solution of the product with excess of hot dilute sulphuric acid; it crystallises in colourless needles and is almost insoluble in boiling water. The base, $C_{12}H_{11}N_3$, crystallises from hot alcohol in flat, lustrous needles, and turns black at 200°, but without melting; it is not identical with the diamidocarbazole obtained by nitrating carbazole and reducing the product (compare *D. R.-P.*, No. 46438). The hydrochloride is moderately easily soluble in water but is precipitated from the solution in crystals on the addition of hydrochloric acid. The tetrazo-derivatives of the base dye unmordanted cotton very readily, the shades being the same as those obtained with the corresponding benzidine dyes.

F. S. K.

Tritopine and other Rare Opium Bases. By E. KAUDER (*Arch. Pharm.*, **228**, 419—431).—The rarer alkaloids were sought for in large quantities of the mother liquor, obtained in the preparation of morphine, &c., on a manufacturing scale. The results largely confirm and extend those previously obtained by Hesse. After removing the relatively large quantities of morphine, codeïne, narceïne, thebaïne, papaverine, and narcotine still present in the mother liquor, a considerable amount of cryptopine was the first product. The mother liquor, diluted with water, warmed to 60°, and poured into water containing excess of sodium hydroxide, gave a dark, resinous precipitate. The filtrate, further treated with hydrochloric acid, ammonia, &c., gave only narcotine and laudanine. Lanthopine and codamine were not detected. Laudanine, whilst soluble in sodium hydroxide, can also be methylated, so that it ranges with morphine. The methyl ether of laudanine, melting at 113°, is not identical with laudanosine. The dark, resinous precipitate above described was dissolved in a little alcohol, treated with ether until precipitation ceased, the ether filtered off, and treated with acetic acid water. Excess of potassium iodide added to this solution precipitates almost the whole of the alkaloids, with much resin. After 24 hours, the mother liquor was poured off, the residue mixed with a little alcohol and set aside for several days. Large quantities of iodides thus crystallised out, which were pressed and washed with a little alcohol. No more crystals could be obtained from the tenacious mother liquor containing most of the resin. The iodides were converted into the free bases, and these dissolved in hydrochloric acid and concentrated. After the addition of an equal volume of alcohol and then alcoholic ammonia, crystals of protopine, and a new base, tritopine, separated. The filtrate from these was treated with much ether, the ether agitated with oxalic acid water, the aqueous solution concentrated and treated with more oxalic acid.

After 24 hours, a few hard crystals of protopine and cryptopine binoxalate had formed. Further treatment of the mother liquor with potassium iodide, &c., separated small quantities of cryptopine, protopine, and tritopine, whilst still further concentration yielded laudanosine, easily purified by crystallising from light petroleum. *Tritopine*, $C_{42}H_{54}N_2O_4$, melts at 182° . It is easily soluble in chloroform, slightly in ether; 1 part dissolves in 40 parts of boiling alcohol, from which it crystallises in transparent prisms. Several salts of this base are described. The relative amounts of the bases found were approximately, laudanosine, 1; tritopine, 2; protopine, 3·5; laudanine, 20; cryptopine, 70.

J. T.

Atropamine. By O. HESSE (*Chem. Centr.*, 1890, ii, 446—447; from *Pharm. Zeit.*, 35, 471).—The author has separated an alkaloid from the roots of *Atropa belladonna*, which he has named *atropamine*. At ordinary temperatures, it is solid, but is quite liquid at 60° . It is precipitated from solutions of its salts by potash or soda as an oil; it is readily soluble in alcohol, ether, and chloroform. It has the formula $C_{17}H_{21}NO_2$; it contains 1 mol. H_2O less than atropine, hyoscyamine, and hyoscine, and is isomeric with belladonnine. It forms haloid salts, which crystallise very beautifully; this distinguishes it from belladonnine and other *atropa* alkaloids.

It is optically inactive. A 2 per cent. solution of the hydrochloride has, according to Berlin, no mydriatic action. Protracted boiling with alcoholic solution of barium hydroxide causes a decomposition with formation of tropine and an acid which is neither tropic, atropic, nor isatropic acid. By the action of hydrochloric acid, atropamine is converted into belladonnine, and is then further transformed as by heating with alcoholic barium hydroxide. Atropamine is very readily decomposed by acids, and hence it has been overlooked in the past. The acid above referred to, the nature of which has not been determined, sometimes causes a smell of bitter almond oil if mixed with potassium permanganate, a reaction which is not produced with atropamine.

J. W. L.

Root Constituents of Scopolia atropoïdes. By E. SCHMIDT (*Arch. Pharm.*, 228, 435—441).—A new investigation, in which the bases were precipitated as aurochlorides, yielded hyoscyamine, but only a very small amount of atropine, and a minute quantity of aurochloride, which agreed as to its melting point, 198—199°, and analysis with the hyoscine compound. Scopoletin has been proved to be identical with methylæsculetin by Takahashi (*Abstr.*, 1889, 255). F. Schmidt has found by the application of Zeisel's method (heating with hydriodic acid, &c.) that scopoletin contains only one methoxyl group. The æsculetin produced by this reaction was isolated and analysed. The methylæsculetin of Tie-mann and Will melts at 184° , whilst scopoletin melts at $199—200^\circ$, so that one is probably the α - and the other the β -methylæsculetin; but which is which has not been determined.

J. T.

Alkaloids of Chelidonium majus. By F. SELLE (*Arch. Pharm.*, **228**, 441—462).—Besides the two alkaloids chelidonine and chelerythrine, E. Schmidt found strong evidence of the presence of α -homochelidonine, β -homochelidonine, and a third base seemingly identical with protopine, an alkaloid obtained by Hesse from opium. The author has separated and investigated these three new bases. The following general method is used to extract the bases from the root of the plant. The dried and pulverised material is repeatedly extracted with alcohol containing acetic acid; after filtration and dilution with water, the alcohol is distilled off and the resin separated is removed by another filtration. The filtrate is treated with ammonia and shaken up with chloroform; the chloroform solution on evaporation leaves a residue which is dissolved in the least possible amount of alcohol containing hydrochloric acid. After cooling, the alcoholic solution is separated by filtration from the undissolved and crystalline portion, consisting of chelidonine and protopine hydrochlorides. The alcoholic solution is diluted with water, freed from alcohol, strongly diluted with hydrochloric acid water, filtered, and treated with ammonia in excess. The filtrate contains β -homochelidonine, which may be extracted by shaking up with alcohol. The precipitate contains α -homochelidonine and chelerythrine; the latter can be obtained by long digestion with ether.

β -Homochelidonine, $C_{19}H_{15}(OMe)_2NO_3$, appears as well formed, colourless, seemingly monoclinic crystals, which melt at 159° . A solution (1 : 100) gives a white precipitate with mercury chloride, phosphotungstic acid, and potassium cadmium iodide; yellowish-white with potassium mercury iodide and phosphomolybdic acid; yellow with bromine-water; reddish-yellow with potassium bismutho-iodide. Concentrated sulphuric acid gives a beautiful violet coloration. Froehde's reagent yields a transient yellow, violet, and green coloration, which becomes a beautiful blue, and finally an intense moss-green. Erdman's reagent gives a yellow, passing quickly to a beautiful violet, which gradually becomes dirty-violet. Concentrated nitric acid produces a yellow colour. Vanadium sulphuric acid gives yellow, violet, and intense blue; after a time this become green. The alkaloid is easily soluble in hydrochloric, sulphuric, nitric, and acetic acids. The hydrochloride, platinochloride, and aurochloride are described.

α -Homochelidonine, $C_{19}H_{15}(OMe)_2NO_3$, forms large, rhombic crystals, when recrystallised from its solution in ethyl acetate, which melt at 182° . Its solution (1 : 100) yields precipitates similar to those given by the β -base, with the addition that tannin gives a white precipitate, soluble in excess. Concentrated sulphuric acid dissolves the base, with the gradual formation of pale-yellow streaks. Concentrated nitric acid gives a yellow coloration. Froehde's reagent produces a dirty brownish-green and then brownish-yellow tint. Erdmann's reagent and vanadium sulphuric acid yield a reddish-yellow coloration. The hydrochloride, platinochloride, and aurochloride are described and analysed.

Protopine (?) was finally obtained in colourless crystals from its solution in a mixture of much chloroform with little ethyl acetate; its melting point is 207° . The amount obtained was insufficient to

admit of a determination of its formula, but $C_{20}H_{17}NO_5$ is indicated, and Zeisel's method does not indicate the presence of methoxyl groups. Its reactions with precipitants are the same as those given for α -homochelidonine.

J. T.

Alkaloids of the Rhizome of Veratrum album. By G. SALZBERGER (*Arch. Pharm.*, 228, 462—483).—Besides the three crystallisable bases, jervine, rubijervine, and pseudojervine already known, the author has isolated two new ones, *protoveratrine*, an extremely powerful poison, and *protoveratridine*. Two methods of extraction were followed: one, the baryta method, is relatively rapid, and gives jervine, rubijervine, and protoveratridine, but no protoveratrine; the other, the metaphosphoric acid method, yields protoveratrine and pseudojervine, with small amounts of jervine and rubijervine. The yield varies considerably, and the method of drying the rhizome is not without influence on the result. The moderately pulverised rhizome was mixed with barium hydroxide and water, and extracted with ether. The extract was freed from ether at the lowest possible temperature in a gentle current of hydrogen. The dark-green syrup thus obtained gave a crop of crystals mainly consisting of jervine. Recrystallisation from alcohol separated a little protoveratridine, and further treatment by Wright and Luff's process with dilute sulphuric acid yielded a small amount of rubijervine. The mother liquor from the crude jervine by further treatment yielded a little more protoveratridine and rubijervine, and other uncrystallisable and decomposition products. Protoveratrine can be easily extracted from the drug by cold water, but cannot be obtained in a crystalline form by this means. To obtain the crystalline base, the rhizome is freed from fatty and resinous compounds by treatment with ether, and an alcoholic extract of the residue is prepared. This extract is freed from alcohol in a vacuum, mixed with much acetic acid water, quickly filtered from the insoluble residue, and treated with solid metaphosphoric acid, until no further precipitate appears. The voluminous precipitate contains much amorphous matter, besides insoluble compounds of jervine and rubijervine. The filtrate is treated with excess of ammonia, filtered, and shaken up with ether, and from the ether extract the protoveratrine crystallises out when the ether is distilled off. By recrystallisation from strong alcohol, the base is purified and separated from some little remaining rubijervine and jervine. The yield was about 0·3 gram per kilo. The ammoniacal solution, after removal of ether, was further treated with chloroform, when pseudojervine was obtained. Protoveratridine is not obtained by this metaphosphoric acid process, which would indicate this base to be a decomposition product of protoveratrine.

Protoveratrine, $C_{22}H_{31}NO_{11}$, crystallises from dilute solutions in microscopic four-sided plates, which melt with charring at 245—250°. The base is insoluble in water, benzene, and light petroleum; chloroform and boiling 96 per cent. alcohol dissolve it somewhat; cold ether scarcely touches it, boiling ether takes up a little more. Dilute acids, with the exception of acetic acid, dissolve it. The base is exceedingly poisonous; a minute amount applied to the nose causes violent

sneezing. Concentrated sulphuric acid dissolves the alkaloid slowly with the production of a greenish colour, which passes to cornflower blue, and after some hours becomes violet. With the same acid and sugar, the first formed greenish colour becomes olive-green, then dirty green and finally dark brown; this is very different from the colours yielded by veratrine. When warmed with the strong acid, the solution is first light, then dark cherry-red, and exhales the odour of isobutyric acid. Concentrated hydrochloric and phosphoric acids give the same reaction. Dilute solutions of salts of this base are quantitatively precipitated by ammonia; precipitates are also produced by Nessler's test, gold chloride, potassium mercury iodide, potassium cadmium iodide, phosphotungstic acid, and picric acid, whilst no precipitate is produced by tannin, platinic chloride, or mercuric chloride. The aurochloride, a golden-yellow, amorphous compound, was obtained and analysed.

Protoveratridine, $C_{26}H_{45}NO_8$, occurs as colourless, four-sided plates, which melt at 265° . It is almost insoluble in alcohol, chloroform, methyl alcohol, and acetone, and insoluble in benzene, light petroleum, and ether. It is not poisonous, and does not cause sneezing, but its solution in dilute acids has a very bitter taste. Concentrated sulphuric acid gives first a violet, then a cherry-red colour. Its solution in concentrated hydrochloric acid becomes light-red on warming, as is the case with veratrine, but with a decided odour of isobutyric acid. Dilute acids readily dissolve the base, and the solutions give crystalline precipitates with ammonia. The sulphuric acid solution gives copious precipitates with phosphotungstic, picric, and tannic acids, and with potassium mercury iodide, but gives no precipitate with platinum chloride, potassium cadmium iodide, or with Millon's reagent. *Protoveratridine platinochloride*, $(C_{26}H_{45}NO_8)_2H_2PtCl_6 + 6H_2O$, was precipitated as large, six-sided plates on adding alcohol to a mixed solution of platinum chloride and a salt of the base. Pseudojervine has been already described by Wright and Luff; they found its melting point to be 299° ; the author makes it 300° to 307° . Jervine, $C_{26}H_{37}NO_3$, melts at 238° to 242° , Wright and Luff found 237° . The hydrochloride, nitrate, platinochloride, and aurochloride are described. Wright and Luff's formula is confirmed, and not the one given by Tobien. Rubijervine, $C_{26}H_{43}NO_2 + H_2O$, melts at 240° to 246° ; Wright and Luff found 236° . Five basic compounds have thus been determined with certainty in white hellebore root.

J. T.

Cytisine. By A. PARTHEIL (*Ber.* **23**, 3201—3203).—The alkaloid prepared by Husemann and Marmé from the seeds of the laburnum and other kinds of *Cytisus*, to which they gave the name of cytisine, may be readily obtained in the following manner. The coarsely-powdered seeds are extracted with alcohol containing hydrochloric acid, the alcohol distilled off, the residue treated with water, and filtered through a wet filter to remove any fatty oil, the filtrate treated with lead acetate, and after separating the precipitated colouring matter, made alkaline with caustic potash, and shaken with amyl alcohol. The latter solution is then extracted with dilute hydrochloric acid, the solution evaporated, the crude cytisine hydrochloride

thus obtained treated with dilute alcohol to remove colouring matters, and recrystallised several times from water. The salt then forms well-developed, colourless, transparent prisms. Its *platinochloride* crystallises in golden-yellow needles, which have the composition $C_{11}H_{14}N_2O \cdot H_2PtCl_6 + 2\frac{1}{2}H_2O$, are tolerably soluble in water, and decompose on heating without melting. The *aurochloride*, $C_{11}H_{14}N_2O \cdot HAuCl_4$, crystallises in short, reddish-brown, hook-shaped needles, which melt at 212—213° (uncorr.) with evolution of gas. From the analyses of these double salts, it follows that cytisine has the composition $C_{11}H_{14}N_2O$, and not $C_{20}H_{27}N_3O$ as given by Husemann and Marmé. The same formula has already been given by Gerrard to ulexine, obtained from the seeds of *Ulex europaeus* (Abstr., 1886, 1048), which, as Koberth as already suggested, on physiological grounds (*Deutsch. Med. Wochenschr.*, 1890, 406) may be identical with cytisine. Both compounds are being at present further investigated.

H. G. C.

Products of the Artificial Digestion of Glue. By F. KLUG (*Chem. Centr.*, 1890, ii, 318—319; from *Centr. Physiol.*, 4, 189—191).—Glue, obtained from the refining of fine French gelatin, is precipitated from its solution by picric acid, chromic acid, tannin, platinic chloride, mercuric chloride and iodide, potassium iodide, and hydrochloric acid. These precipitates dissolve in hot water, and are reprecipitated on cooling. Alcohol, phosphotungstic acid, and hydrochloric acid, basic lead acetate, and ammonium sulphate also precipitate it, the precipitates being, however, insoluble in hot water. With sodium hydroxide and copper sulphate, its solution is coloured violet-blue. Acetic acid and potassium ferrocyanide cause no precipitation. Millon's reagent causes a flocculent precipitate, soluble in the hot liquid; if the solution be boiled, it is coloured red. Nitric acid and sodium hydroxide colour hot glue solutions slightly yellow; copper sulphate causes a blue coloration. Glue, therefore, may be distinguished from egg albumin by the precipitate obtained with picric acid dissolving on heating and by the biuret reaction, whereas with nitric acid neither precipitation nor yellow coloration ensues. It is to be noted, however, that concentrated solutions of sodium chloride, ammonium sulphate, and gallic acid form precipitates with picric acid which dissolve in warm liquids. By artificial digestion, glue becomes converted into three substances, *glutose* and *glutinopeptone*, which dissolve, and *apoglutin*, which remains in the liquid as a flocculent residue, to the amount of 5·69 per cent.

Apoglutin dissolves completely in sulphuric acid, but only imperfectly in the other mineral acids and in acetic acid. When boiled with nitric acid, it becomes coloured yellow; sodium hydroxide and copper sulphate colour it violet; boiled with Millon's reagent, it is coloured red; it is not digested by pancreatic juice.

Glutose is precipitated from the solution of digested glue by the addition of ammonium sulphate or alcohol, and it may be precipitated, after re-solution in water, by addition of sodium chloride, and then acetic acid and concentrated solution of sodium chloride. That part which is precipitated by salt has been named by the author *protoglutose*; the remaining portion, which is separated on the addition of acetic acid

and sodium chloride, he names *deuteroglucose*. Glutose, precipitated by 95 per cent. alcohol, separates as a sticky, white mass. It is also precipitated by picric and chromic acids, phosphotungstic acid and hydrochloric acid, mercuric iodide, potassium iodide and hydrochloric acid, platinic chloride, and mercuric chloride; all these precipitates, that by phosphotungstic acid excepted, are dissolved on warming the solutions, and are again precipitated on cooling. When boiled with nitric acid, it is neither precipitated nor coloured yellow; but if sodium hydroxide is added, the solution becomes yellow. Sodium hydroxide and dilute copper sulphate colour the solution violet-red; copper sulphate alone colours it blue.

Glutinopeptone is also obtained by the digestion of glutose, and may be precipitated by means of a mixture of alcohol and ether. When dried on the water-bath and in the desiccator, it appears as a yellow, brittle mass, very readily soluble in water, which distinguishes it readily from glutose. Picric acid causes a precipitate only with concentrated solutions, which redissolves in an excess of the reagent, and also by heating; chromic acid and platinic chloride cause no precipitation; sodium hydroxide and highly dilute copper sulphate solution cause a rose-red coloration; copper sulphate alone, a green coloration; Millon's reagent causes a milkiness, which redissolves on boiling. It becomes precipitated by saturating the solution with either sodium chloride or ammonium sulphate. The following are the elementary analyses of glue, apoglutin, and glutose.

	C.	H.	N.	O and S.	Ash.
Glue.....	42.75	7.00	15.61	34.64	0.88
Apoglutin ...	48.39	7.50	14.02	30.09	5.22
Glutose	40.06	7.02	15.86	37.06	2.14

J. W. L.