

## Organic Chemistry.

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**Notes on Mine Gas Problems.** GEORGE A. BURRELL (*J. Ind. Eng. Chem.*, 1913, 5, 181—186).—The author gives an account of the various problems met with in connexion with mine gases, interpolating from time to time some of the data accumulated by the Bureau of Mines with respect to the explosibility and physiological effects of mine atmospheres, and to flame extinction and after-damp.

The lower explosive limit of mixtures of air and methane is confirmed to be 5·5% methane. The presence of carbon dioxide alters this explosive limit, but even 10% of carbon dioxide raises it only to 6·6%. Reduction in the volume percentage of oxygen also raises the explosive limit. Harger has suggested that a small reduction in the oxygen percentage and a small increase in the carbon dioxide percentage in mine air will suffice to produce an atmosphere incapable of supporting combustion, and consequently an atmosphere in which explosions and gob fires cannot occur, but the data obtained by the Bureau of Mines indicate that the figures given by Harger are much too low, both with respect to the increase in carbon dioxide and diminution in oxygen.

When acetylene is used in the miner's lamp, the flame resembles the ordinary wick flame burning in pure air, when the oxygen content of the air decreases to 16—16·5%; this behaviour of the flame can be used as a guide to men venturing into workings containing black damp and less oxygen than the percentage given. The ordinary miner's lamp is extinguished when the oxygen falls to about 16·5—17%; the extinguishing of the flame is shown to be due to deficiency in oxygen and not to the presence of carbon dioxide.

Reference is made to the following subjects: Effect of vitiated air on the luminosity of miner's lamps (compare Haldane, *Colliery Guardian*, Oct. 25th, 1912); high velocity of air currents in mines; distribution of after-damp; intrusion of natural gas into mines, etc. Analyses are also given of mine-gas mixtures containing explosive and other proportions of methane, and of samples of after-damp atmospheres which show the large amount of carbon monoxide (white-damp) present shortly after an explosion.

T. S. P.

**Solvents for Acetylene.** JOSEPH H. JAMES (*J. Ind. Eng. Chem.*, 1913, 5, 115—120).—An investigation of the solvent powers for acetylene of a number of organic liquids shows that those containing the carbonyl group are generally the best solvents. Organic acids must be excluded, however, the hydroxyl in the carboxyl group seeming to inhibit the solvent action of the carbonyl. The presence of the carbonyl group is not sufficient, of itself, to account for the solubility, since methylal and acetal are very good solvents.

It is found that acetaldehyde fulfils all the industrial requirements for an acetylene solvent.

T. S. P.

**Preparation of Dimethylacetylene [Crotynylene] and Ethyl-acetylene from Carbides.** CARL WILLI SCHLECHTER (D.R.-P. 253802).—When methyl alcohol is heated with an alkaline earth carbide during four days at 60—120° under a pressure of 50 atmospheres, or during six days in a closed tube at 200° it yields a mixture of crotynylene ( $\Delta^\beta$ -butinene), CMe:CH<sub>2</sub>, b. p. 28°, and ethylacetylene [ $\Delta^\alpha$ -butinene], CEt:CH, b. p. 18°. F. M. G. M.

**$\Delta^{\alpha\gamma\epsilon}$ -Heptatriene and Related Substances.** CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, **10**, 187—189. Compare this vol., i, 243).—A discussion of the influence of structure on the possibility of solidifying unsaturated hydrocarbons. By cooling with liquid air several butadienes and related substances have been converted into the solid state. A. J. W.

**Vinylacetylene.** RICHARD WILLSTÄTTER and THEODOR WIRTH (*Ber.*, 1913, **46**, 535—538).—By the action of dimethylamine in benzene solution on the dibromide of butadiene,  $\alpha\delta$ -tetramethyl-diamino- $\Delta^\beta$ -butylene, NMe<sub>2</sub>·CH<sub>2</sub>·CH:CH·CH<sub>2</sub>·NMe<sub>2</sub>, is obtained. The use of an indifferent solvent, such as benzene, is essential; with alcohol numerous secondary reactions take place.

When the corresponding diquaternary ammonium base is distilled in a vacuum it is decomposed, and vinylacetylene, CH:C·CH:CH<sub>2</sub>, is obtained.

**$\alpha\delta$ -Tetramethyldiaminobutylene** is a colourless oil with a narcotic odour, b. p. 171—172°/723 mm., 65—65.5°/17 mm., D<sub>4</sub><sup>o</sup> 0.8198. The *picrate* forms needles, m. p. 222—223°; the *aurichloride* separates in crystalline needles, m. p. 201° (decomp.); the *platinichloride*, 2H<sub>2</sub>O, crystallises in long, rhombohedric prisms, m. p. 227—228°, whilst the *dimethiodide* forms prisms, decomp. 270°.

**Vinylacetylene** [ $\Delta^{\alpha\gamma}$ -buteninene] melts to a colourless liquid, b. p. 2—3°/729 mm., and has an odour like acetylene. It forms a greenish-yellow copper salt and a colourless, crystalline silver salt, which explodes when heated. E. F. A.

**A Catalytic Method of Isomerisation of Alkyl Chlorides and Bromides.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 658—659. Compare A., 1905, i, 677).—Barium chloride or thorium chloride at 250° causes the decomposition of primary alkyl chlorides or bromides into ethylene hydrocarbons and hydrogen chloride or bromide. These then recombine, when passed over pumice stone at 200°, giving, not the original haloid, but the isomeric chloride or bromide. The resulting liquid is submitted to fractional distillation, thus separating any of the original unchanged substance. W. G.

**Trichloroethylene and Some of its Derivatives.** JACOB BÖESEKEN [with C. E. KLAMER and J. G. DE VOOGT] (*Rec. trav. chim.*, 1913, **32**, 15—22).—Unsuccessful attempts have been made to bring trichloroethylene and tetrachloroethylene into reaction with benzoyl chloride, sulphur chloride, phosphorus chloride, thionyl chloride, and

sulphuryl chloride respectively in the presence of aluminium chloride. Charred products were obtained, except in the case of tetrachloroethylene and sulphuryl chloride, when hexachloroethane was isolated, owing to the decomposition of sulphuryl chloride into sulphur dioxide and chlorine and union of the latter with tetrachloroethylene.

Barium monochlorosulphoacetate,  $C_2H_5O_5ClSBa$ , was isolated from the product of the action of fuming sulphuric acid (containing 10%  $SO_3$ ) on trichloroethylene at 88°.

When trichloroethylene was added drop by drop to a mixture of nitric acid (D 1·5) and concentrated sulphuric acid, cooled by a freezing mixture of salt and ice, and the action interrupted as soon as the temperature of the product rose but slowly when removed from the freezing mixture, dichloroacetic acid was obtained, together with a substance,  $C_2H_5O_3N_2Cl_3$ , b. p. 32°/36 mm., which, when preserved, became converted into colourless, very hygroscopic needles, which were insoluble in, or decomposed by, the ordinary solvents, and had mol. wt. 194 in nitrobenzene solution. When heated with hydrochloric acid, this substance yielded small amounts of nitric oxide and carbon dioxide, but neither hydroxylamine nor oxalic acid could be detected. Alcoholic potassium hydroxide decomposed it according to the equation:  $C_2H_5O_3N_2Cl_3 + 7KOH = \begin{matrix} | \\ Cl_2C-O-N \\ | \\ O' \\ | \\ ClO-O-NH \end{matrix} + 3KCl + 2K_2CO_3 + 4H_2O + N_2$ . With zinc and cold dilute sulphuric acid it gave a quantitative yield of ammonia. It did not give Liebermann's reaction. In view of the above properties, the annexed formula is tentatively proposed for it.

H. W.

**Elimination of Water from Pinacolyl Alcohol. Tertiary Butylethylene.** W. FOMIN and N. SOCHANSKI (*Ber.*, 1913, **46**, 244—248).—Pinacolyl alcohol was converted by Couturier (A., 1893, i, 245) into a bromide, which, when treated with solid potassium hydroxide, gave a mixture of  $\beta\gamma$ -dimethyl- $\Delta\beta$ -butylene (compare Zelinsky and Zelikov, A., 1902, i, 2) with a small quantity of a hydrocarbon, b. p. 56—59°, which was described as *tert*.-butyl ethylene. The latter compound has now been prepared from pinacolyl alcohol by Tschugaev's method and has other properties.

The potassium derivative is prepared by adding the alcohol to potassium *tert*.-amyloxide (compare Tschugaev, A., 1905, i, 167) and then treated with carbon disulphide and methyl iodide. The *methyl pinacolyl xanthate*,  $C_6H_{13}\cdot O\cdot CS\cdot SMe$ , b. p. 100°/12 mm.,  $D_4^{18}$  1·0228, decomposes at 160—175°, and the purified *tert*.-butylethylene [ $\gamma\gamma$ -dimethyl- $\Delta\alpha$ -butylene],  $CMe_3\cdot CH\cdot CH_2$ , is a colourless liquid, having b. p. 41·2°/760 mm.,  $D_4^{18}$  0·6549, and  $n_D$  1·37667. On oxidation with permanganate, acetone is not obtained, the chief product being *aa*-dimethylpropionic acid, whilst reduction with hydrogen in presence of platinum black results in the formation of  $\beta\beta$ -dimethylbutane.

J. C. W.

**Decomposition of Heptyl Alcohol at 220° in the Presence of Finely Divided Nickel.** JACOB BÖESEKEN and G. H. VAN SENDEN (*Rec. trav. chim.*, 1913, **32**, 23—38).—The authors have repeated the

experiments described by van Beresteyn (A., 1911, i, 761), who obtained heptyl alcohol and a substance which he regarded as *n*-hexylene, by the reduction of heptaldehyde according to the general method of Sabatier and Senderens. Heptyl alcohol, under similar circumstances, was found to yield *n*-hexylene, carbon monoxide, and hydrogen, the course of the actions being represented by the equations:  $C_6H_{13}\cdot CHO + H_2 = C_7H_{15}\cdot OH$ .  $C_7H_{15}\cdot OH = C_6H_{12} + CH_3\cdot OH$ .  $CH_3\cdot OH = CO + 2H_2$ . On theoretical grounds, the authors consider this interpretation to be improbable, and are led to the conclusions: (1) that heptyl alcohol, in the presence of finely divided nickel at  $220^\circ$ , is decomposed into heptaldehyde and hydrogen; (2) that, particularly in the presence of an inert gas, the heptaldehyde is converted into *n*-hexylene, hydrogen, and carbon monoxide; (3) that *n*-hexylene combines with a considerable proportion of the liberated hydrogen to form *n*-hexane, and that, in the presence of an excess of hydrogen, all the *n*-hexylene undergoes reduction; (4) that heptaldehyde is not reduced in the presence of carbon dioxide, and only slightly reduced in an atmosphere of hydrogen; (5) that *n*-hexylene (mixed with *n*-hexane) is best obtained by the decomposition of heptaldehyde by nickel at  $220^\circ$  in a current of carbon dioxide, and (6) that *n*-hexane is obtained by the catalytic decomposition of heptyl alcohol or heptaldehyde by nickel at  $220^\circ$  in a current of hydrogen.

Heptyl alcohol was obtained by the reduction of heptaldehyde dissolved in glacial acetic acid by means of sodium amalgam. Small quantities of *s-di-n-hexylethylene glycol* [*n-tetradecane-ηθ-diol*], b. p.  $218^\circ/14$  mm., m. p.  $69-70^\circ$ , were obtained as by-product.

Heptyl alcohol, when passed over nickel at  $220^\circ$  in a current of hydrogen, yielded about 62% *n*-hexane, 17% of a mixture of heptyl alcohol and heptaldehyde, and carbon monoxide. In a current of carbon dioxide, however, it yielded about 14.5% *n*-hexylene, 31% *n*-hexane, 24% of a mixture of heptyl alcohol with a little heptaldehyde, carbon monoxide, and hydrogen, the change being represented by the equation:  $3C_7H_{15}\cdot OH = 2C_6H_{14} + C_6H_{12} + 3CO + 4H_2$ .

Heptaldehyde, at  $220^\circ$  in a current of carbon dioxide, gave about 24% *n*-hexylene, 29% *n*-hexane, 16% unchanged heptaldehyde, carbon monoxide, hydrogen, and possibly a trace of formaldehyde. The quantities of the products obtained agreed with the equation:  $100C_6H_{13}\cdot CHO = 45C_6H_{12} + 55C_6H_{14} + 100CO + 45H_2$ . At  $180^\circ$ , the course of the reaction was similar.

*n*-Hexane was not affected when passed over nickel at  $220^\circ$  in a current of carbon dioxide.

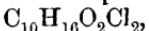
H. W.

*αδ-Oxide from Undecyl Alcohol.* N. A. LOGGINOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 136—145).—The action of zinc chloride or 50% sulphuric acid on undecyl alcohol results in displacement of the double linking of the alcohol and formation of the *αδ-oxide*,  $CH_3\cdot[CH_2]_6\cdot CH<\begin{matrix} CH:CH \\ | \\ O—CH_2 \end{matrix}$ , b. p.  $219-222^\circ$ ,  $D_0^0 0.8641$  (or  $0.8667$ ),  $D_0^{17} 0.8522$ ,  $D_0^{18} 0.8538$ .

When zinc chloride is used, the oxide is accompanied by an unsaturated alcohol,  $C_{11}H_{22}O$ , b. p. 243—246°, which forms a crystalline phenylurethane,  $C_{18}H_{27}O_2N$ , m. p. 49·5°, and is being further investigated.

T. H. P.

**Action of  $\alpha\beta$ -Dichloroethyl Ether on Mixed Magnesium Derivatives.** ROBERT LESPIEAU and BRESCH (*Compt. rend.*, 1913, 156, 710—712).— $\alpha\beta$ -Dichloroethyl ether condenses readily with magnesium derivatives of ethyl and allyl bromides and acetylene, giving products somewhat difficult to purify. The compound,



obtained from the acetylene derivative is a colourless liquid, b. p. 136—137°/12 mm., and is probably a mixture of two *cis*- and *trans*-isomerides (compare Dupont, A., 1910, i, 85). On bromination in chloroform, it yields two *dibromides*,  $C_{10}H_{16}O_2Cl_2Br_2$ , separable by their varying solubility, the less soluble one having m. p. 107—108°, and the other m. p. 71—72°. These are also probably *cis*- and *trans*-isomerides.

W. G.

**Compounds of Ethyl Phosphite with Silver Haloids.** ALEXANDER E. AREBUZOV and A. V. KARTASCHOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 79—81).—Derivatives of tervalent phosphorus of the form  $PR_3$  or  $P(OR)_3$  form compounds with cuprous and platinous haloids, and the authors find that ethyl phosphite forms similar compounds with silver haloids. These compounds form colourless, ribbon-like crystals, their melting points being:  $P(OEt)_3, AgCl$ , 4·5—5·5°;  $P(OEt)_3, AgBr$ , 40—40·5°;  $P(OEt)_3, AgI$ , 81—83°.

T. H. P.

**Uranium Formate.** WILLIAM OECHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], 13, 221—223).—Uranium formate is a deliquescent, yellow salt, readily soluble in water. Attempts to estimate the water of crystallisation were unsuccessful, owing to the ready loss of formic acid from the salt on prolonged desiccation. When calcined in a closed vessel, the salt leaves a residue of pure uranous oxide, but, if an open vessel is used, traces of a higher oxide are formed. Similar results were previously obtained with uranium oxalate (A., 1912, i, 535).

When boiled with a large quantity of water, uranium formate is hydrolysed, hydrated uranium trioxide,  $UO_3 \cdot 2H_2O$ , separating as a yellow precipitate, which is converted by calcination into the green oxide,  $U_3O_8$ .

Uranium formate was exposed to diffused daylight during three months in the presence of methyl alcohol. A brown deposit of uranium oxide was thereby obtained, and the strongly acid methyl alcoholic solution was found to contain methyl formate.

Very little decomposition occurred in similar circumstances in the presence of ethyl alcohol. Very little formic acid was liberated, whilst the residue contained only small amounts of mono- and di-hydrated uranium trioxide mixed with unchanged uranium formate.

H. W.

**Preparation of Halogen Formic Esters.** EMANUEL MERCK (D.R.-P. 254471).—The following halogen formic esters in addition to those previously described (this vol., i, 5) have now been prepared. *Dimethylethylcarbinyl chloro-formate*, a liquid which decomposes at 20° and cannot be distilled in a vacuum; the homologous *methyl-diethyl-carbinyl chloro-formate* has similar properties. F. M. G. M.

**Distillation and Sublimation of Ammonium Salts under Diminished Pressure.** RICHARD ESCALES and HANS KOEPKE (*J. pr. Chem.*, 1913, [ii], 87, 258—279).—Of the normal salts examined the formate (*s*, 90—140°), acetate (*s*, 90°), thiocyanate (*d*, 165°), cyanate (*s*, 160—190°), nitrite (*s*, 70°), and sulphite (*s*, 70—120°) distil or sublime under a pressure of 10 mm. without decomposition, whilst the propionate (*d*, 70—75°), butyrate (*d*, 70—80°), glycollate (*d*, 160°), lactate (*d*, 140—150°), benzoate (*s*, 60—130°), and salicylate (*s*, 90—150°) are converted into the corresponding acid salts,  $\text{NH}_4\text{HX}_2$ ; the temperatures at which distillation or sublimation occurs are given in brackets (*s* denotes sublimation; *d*, distillation). When heated to 300°/10 mm., ammonium sulphate and persulphate lose ammonia, yielding the acid salts; ammonium thiosulphate sublimes at 70°/10 mm., the sublimate consisting of ammonium sulphite. Ammonium carbonate undergoes complete dissociation, whilst carbamide and thiocarbamide sublime in the form of ammonium cyanate and thiocyanate respectively. Of the acid salts,  $\text{NH}_4\text{HX}_2$ , the acetate (*d*, 67°), propionate (*d*, 73°), butyrate (*d*, 78°), glycollate (*d*, 160°), lactate (*d*, 145°), benzoate (*s*, 60—130°), salicylate (*s*, 90—150°), and hydrogen carbonate distil or sublime unchanged at 10 mm.

A mixture of normal or acid ammonium acetate and propionic acid in molecular proportions distils at 66—68°/10 mm., yielding the acid ammonium salt,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{NH}_4\cdot\text{C}_2\text{H}_5\cdot\text{CO}_2\text{H}$ , which forms very deliquescent crystals, m. p. 42—43°, and is converted by distillation with butyric acid into the ammonium salt,  $\text{CH}_3\cdot\text{CO}_2\cdot\text{NH}_4\cdot\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$ . This has m. p. 41°, b. p. 72—74°/10 mm., and is also obtained by distilling normal or acid ammonium acetate with butyric acid. F. B.

**Decomposition of Certain Acid Chlorides by Aluminium Chloride.** JACOB BÖESEKEN (*Rec. trav. chim.*, 1913, 32, 1—14).—In continuation of the work of Böeseken and Prins (A., 1910, i, 152; 1911, i, 173), the action of aluminium chloride on the chlorides or sulphonyl chlorides of a number of halogenated acids has been investigated. Normal results were obtained with acid chlorides which did not contain hydrogen or a benzene group, but, in the presence of the latter, the reaction appeared to be complex, giving resinous products from which no definite compound could be isolated.

[With P. HASSELBACH.]—Monochloroacetyl chloride and aluminium chloride yielded a hygroscopic, crystalline compound,

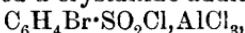


which, when heated alone or with carbon tetrachloride, evolved hydrogen chloride, leaving a charred residue. Carbon monoxide could not be detected in the gas evolved. When heated in chloroform solution at 80°, a small quantity of a substance, m. p. about 175°, was obtained, to

which no definite composition could be assigned. Similarly, aluminium chloride and chlorofumaryl chloride or  $\alpha:\beta:\beta:\beta$ -tetrachloropropionyl chloride yielded only charred or resinous products, from which a definite compound could not be separated.

[With (Mlle.) S. VAN DER TAS.]—*p*-Chlorobenzenesulphonyl chloride and aluminium chloride gave resinous products. The gases evolved contained hydrogen chloride and, generally, sulphur dioxide.

[With W. J. P. PELLE.]—*p*-Bromobenzenesulphonyl chloride and aluminium chloride yielded a crystalline additive product,



which, when heated at  $150\text{--}200^\circ$ , evolved sulphur dioxide and hydrogen chloride, and left a brown resin.

[With P. HASSELBACH.]—*Trichloroacrylyl chloride*, b. p.  $158^\circ/760$  mm., was obtained by the action of thionyl chloride on trichloroacrylic acid. When mixed with aluminium chloride in carbon disulphide solution, it yielded the compound,  $\text{CCl}_2\cdot\text{CCl}\cdot\text{COCl}, \text{AlCl}_3$ , which, when heated in a current of dry air, gave only trichloroacrylyl chloride mixed with a little aluminium chloride, but no carbon monoxide. In the presence of aluminium chloride, trichloroacrylyl chloride reacted with benzene and its homologues to form quantitative yields of ketones of the type  $\text{R}\cdot\text{CO}\cdot\text{CCl}_2\cdot\text{CCl}_2$ , only the chlorine atom attached to the carbonyl group being replaced.

*Pentachloropropionyl chloride*, m. p.  $42^\circ$ , obtained from the preceding chloride by the action of chlorine in sunlight, when heated with aluminium chloride at  $60^\circ$  evolved carbon monoxide and carbonyl chloride, leaving a residue from which hexachloroethane and tetrachloroethylene were isolated, decomposition occurring according to the equations : (I)  $\text{CCl}_3\cdot\text{CCl}_2\cdot\text{COCl} = \text{CO} + \text{C}_2\text{Cl}_6$ . (II)  $\text{CCl}_3\cdot\text{CCl}_2\cdot\text{COCl} = \text{COCl}_2 + \text{C}_2\text{Cl}_4$ . When treated with aluminium chloride in the presence of benzene, *pentachloropropiophenone*,  $\text{COPh}\cdot\text{CCl}_2\cdot\text{CCl}_3$ , m. p.  $83^\circ$ , was obtained when the reaction was continued until one molecule of hydrogen chloride had been evolved. When, however, reaction was continued until two molecules of hydrogen chloride had been evolved, tetrachloroethylene and benzophenone were formed. The presence of the latter may be due to dissociation of pentachloropropionyl chloride into tetrachloroethylene and carbonyl chloride, and condensation of the latter with benzene, or pentachloropropiophenone may be decomposed by aluminium chloride into tetrachloroethylene and benzoyl chloride. The odour of the latter is perceptible when pentachloropropiophenone is warmed with a little aluminium chloride. H. W.

**Montanic Acid and its Derivatives.** HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1913, **30**, 97—105. Compare A., 1909, i, 629).—The authors have prepared a series of derivatives of montanic acid, the formulae of which are in agreement with the formula,  $\text{C}_{28}\text{H}_{56}\text{O}_2$ , for montanic acid itself, thus confirming the previous work of Ryan and Dillon (A., 1909, i, 629), and Easterfield and Taylor (T., 1911, **99**, 2302), in contrast to that of Hell (*Zeitsch angew. Chem.*, 1900, **13**, 556), von Boyen (A., 1902, i, 72), and Eisenreich.

*Methyl montanate*, prepared by boiling montanic acid with methyl

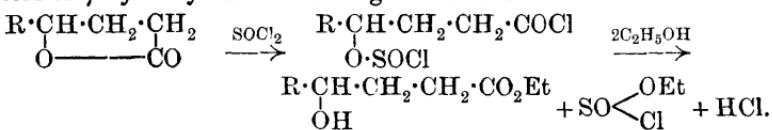
alcohol in the presence of sulphuric acid, crystallises in white, curved needles, m. p. 66°. The similarly crystallised *ethyl* and *n-propyl* esters have m. p. 64—65° and 63·5° respectively.

*Dimethylheptacosylcarbinol*,  $C_{27}H_{55}\cdot CMe_2\cdot OH$ , obtained from methyl montanate and magnesium methyl iodide, has m. p. 63—64°, whilst the corresponding *diethyl* and *diphenyl* derivatives melt respectively at 59—60° and 58°. When ethyl montanate is treated with *p*-bromo-toluene and the resulting product subjected to steam distillation, the residue is found to consist of the unsaturated hydrocarbon,  $C_{27}H_{54}\cdot C(C_6H_4Me)_2$ , m. p. 47°. When, however, the steam distillation is omitted and the product purified by repeated crystallisation from alcohol, it can be separated into two portions, the major part consisting of the above hydrocarbon, the minor part of *di-p-tolylheptacosylcarbinol*, m. p. 51—52°. The action of an ethereal solution of magnesium  $\alpha$ -naphthyl bromide on ethyl montanate appears to yield a mixture of *di- $\alpha$ -naphthylheptacosylcarbinol*, m. p. 57—58°, and, probably,  $\alpha$ -naphthyl-heptacosyl ketone,  $C_{27}H_{55}\cdot CO\cdot C_{10}H_7$ , m. p. 51—53°. These substances can be readily separated, since the former dissolves very sparingly in hot methyl alcohol, in which the latter is readily soluble.

Unsuccessful attempts were made to isolate *montanyl chloride* in the pure state by the action of phosphorus tri- or penta-chloride on montanic acid. The product obtained had m. p. 63—65°. It was transformed by concentrated aqueous ammonia into *montanamide*, m. p. 109°, small quantities of a substance, probably montanonitrile, m. p. 60—65°, being simultaneously formed.

Attempts to prepare ceryl alcohol from montanic acid were unsuccessful, owing to the difficulty of isolating *heptacosylmethylurethane* from the product of the successive action of bromine and sodium methoxide on montanamide. The converse operation (the preparation of montanic acid from ceryl alcohol by the malonic ester synthesis) could not be effected, since cerylmalonic ester could not be obtained from ceryl iodide and sodium malonic ester under the most varied conditions. *Ceryl iodide*,  $C_{26}H_{53}I$ , m. p. 55—56°, was obtained by the action of iodine and red phosphorus on ceryl alcohol. H. W.

**Action of Thionyl Chloride on Certain Lactones.** PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 223—229).—A critical survey of the action of thionyl chloride on organic substances is given. The authors have investigated the effect of boiling certain  $\gamma$ -lactones (1 mol.) in benzene solution with thionyl chloride (1·1 mol.). The product of the reaction was poured into excess of methyl or ethyl alcohol and subsequently examined in the form of its methyl or ethyl ester. In these circumstances, thionyl chloride transforms the  $\gamma$ -lactones employed (except coumarin) into esters of  $\gamma$ -hydroxy-acids according to the scheme:



$\gamma$ -Valerolactone was transformed into ethyl  $\gamma$ -hydroxyvalerate,

b. p. 80—81°/12 mm. (compare Neugebauer, A., 1885, 651), from which a phenylurethane could not be obtained.

$\gamma$ -Phenyl- $\gamma$ -butyrolactone, m. p. 37—38°, b. p. 175—176°/11 mm. (Jayne, A., 1883, 472; Fittig and Leoni, A., 1898, i, 196), was prepared by the condensation of bromoacetophenone with ethyl sodiomalonate and saponification of the crude product with alcoholic sodium hydroxide at 160°. At the high temperature employed, the latter substance probably acted as a reducing agent. In addition, small quantities of benzoylpropionic acid and of a neutral *substance*, m. p. 190—192°, probably a dilactone (annexed formula), were obtained. When acted on successively by thionyl chloride and ethyl alcohol,  $\gamma$ -phenyl- $\gamma$ -butyrolactone yielded *ethyl*  $\gamma$ -hydroxy- $\gamma$ -phenylbutyrate, b. p. 158—160°/17 mm.

Coumarin did not react with thionyl chloride under the conditions employed.

H. W.

**Action of Thionyl Chloride on Certain Lactonic Acids.**  
PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 229—236. Compare preceding abstract).—The experimental conditions chosen were the same as those previously described (*loc. cit.*). In these circumstances, thionyl chloride does not cause a rupture of the lactonic grouping, the product of the reaction being the lactonic acid chloride. This result is not influenced by the use of an excess of thionyl chloride.

Methylparaconyl chloride, b. p. about 142°/10 mm., obtained by the action of thionyl chloride on methylparaconic acid, was converted by methyl alcohol into *methyl methylparaconate*, b. p. 145—146°/11 mm.

In similar circumstances, terebic acid slowly yielded the corresponding chloride, b. p. 143°/12 mm., from which *methyl terebate*, b. p. 148—149°/17 mm., was obtained.

$\beta\beta$ -Dimethylbutyrolactone- $\gamma$ -carboxylic acid (Perkin and Thorpe, T., 1899, 75, 56) gave the corresponding chloride, which, when treated with methyl alcohol, yielded the *methyl ester*, b. p. 149—150°/12 mm.

Similarly, terpenylic acid formed terpenyl chloride, methyl terpenylate, b. p. 145—147°/15 mm., and ethyl terpenylate, m. p. 37.5°, b. p. 174—177°/15 mm. Fittig and Levy (A., 1890, 873) give b. p. 305°/ordinary pressure, whereas Simonsen (T., 1907, 91, 187) found 169—171°/15 mm.

Phenylparaconyl chloride, prepared by the action of thionyl chloride on anhydrous phenylparaconic acid, m. p. 106°, 115°, or 121° (compare Jayne, A., 1883, 473; Fittig and Röders, A., 1890, 621) yielded, when decomposed by water, the acid, m. p. 99°. With methyl alcohol it yielded *methyl phenylparaconate*, m. p. 69—70°, b. p. 211°/14 mm. In the case of phenylparaconic acid, small quantities of polyphenylcrotonic acid, m. p. 179°, were also isolated.

The authors have attempted unsuccessfully to repeat the previously recorded transformation of terebic and phenylparaconic acids into the

anhydrides of *cis*-3 : 3-dimethylcyclopropane-1 : 2-dicarboxylic acid and *cis*-3-phenylcyclopropane-1 : 2-dicarboxylic acid (A., 1911, i, 722) under the action of thionyl chloride. They now attribute this result to the presence of some impurity in the specimen of thionyl chloride used, and point out that the substance is frequently contaminated with phosphoryl chloride, stannic chloride, sulphur trioxide, etc., to the presence of which the irregular results frequently obtained by the application of the reagent are ascribed.

H. W.

*γγγ*-Trichloro- $\beta$ -hydroxybutyric Acid and *γγγ*-Trichloro-crotonic Acid. KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, **46**, 487—494. See following abstract).—*γγγ*-Trichloro- $\beta$ -hydroxybutyric acid, m. p. 118—119° (von Thurnlackh, A., 1892, 429), is best obtained by gently boiling a mixture of malonic acid, chloral, and acetic acid for several hours; a certain specimen of malonic acid, although apparently normal in all other respects, always failed to give this reaction. The substance can be distilled almost undecomposed in small quantities, b. p. 181—188°/17 mm.; methyl ester, rhombohedral crystals, m. p. 61—62°, b. p. 135—136°/13 mm.; ethyl ester, silky needles, m. p. 56—57°, b. p. 143—144°/12 mm.; the *acetyl* derivative, needles, m. p. 97—99°, gives an oily *methyl* ester, b. p. 130°/13 mm.,  $D_4^{14.3}$  1·3937,  $n_D^{14.5}$  1·46815, and an oily *ethyl* ester, b. p. 134°/10 mm.,  $D_4^{14.1}$  1·3395,  $n_D^{14.1}$  1·46458. All endeavours to produce a substance,  $\text{OH} \cdot \text{CH} \cdot \text{CCl}_2 > \text{O}$ , by elimination of hydrogen chloride from the tri-chlorohydroxybutyric acid were fruitless.

The method described by Kötz (A., 1907, i, 707) for the preparation of *γγγ*-trichlorocrotonic acid is found to yield the above trichlorohydroxybutyric acid, and the m. p. given for the substance (*loc. cit.*) agrees with that of this acid. It is now found that the elements of water can be eliminated from trichlorohydroxybutyric acid by heating with acetic anhydride and sodium acetate; the resultant *γγγ*-trichloro-crotonic acid forms needles, m. p. 113—114°, b. p. 143—146°/18 mm.; it immediately reduces potassium permanganate in the cold, and is rapidly decomposed by hot water with formation of hydrochloric acid. The *potassium* and *silver* salts were prepared, the latter of which when heated in benzene on the water-bath eliminates silver chloride with the formation of a mixture of substances mainly complex, but possibly containing a little of the lactone,  $\text{CH} \cdot \text{CCl}_2 > \text{O}$ . The acid forms an oily *methyl* ester, b. p. 85·4°/12 mm.,  $D_4^{21.4}$  1·3968,  $n_D^{21.2}$  1·48975, and an oily *ethyl* ester, b. p. 100·5°/13 mm.,  $D_4^{14.2}$  1·3375,  $n_D^{14.2}$  1·48693.

From the above results it follows that the group  $-\text{CCl}_3$  exerts no special spectrochemical influence.

D. F. T.

**The Constitution of the Chlorides of 1:2- and 1:3-Dicarboxylic Acids.** KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, **46**, 457—487).—The consideration of the spectrochemical effect of chlorine in organic substances (von Auwers, A., 1912, ii, 1015) is extended to the question of the structure of such acid dichlorides

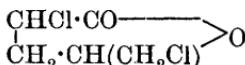
as succinyl and phthalyl chlorides (compare Scheiber, A., 1912, i, 559; Scheiber and Knothe, A., 1912, i, 701; Bredt, A., 1912, i, 411; Ott, A., 1912, i, 828). The decision of Brühl as to the symmetrical structure of phthalyl chloride (*Ber.*, 1907, **40**, 884, 896) is based on too little experimental evidence to be entirely satisfactory; an investigation of the specific exaltations of the refractivity and dispersive power of various acid chlorides nevertheless indicates the correctness of this view.

A comparison of the chlorides and ethyl esters of crotonic, benzoic, and cinnamic acid shows that the exaltations in specific refractivity stand in the order acid > chloride > ester, whilst for the dispersion the exaltation is least for the ester, the free acid and the chloride being approximately equal. Phthalyl chloride shows no exceptional exaltation when compared with ethyl phthalate, the values in fact being in good agreement with those for the corresponding derivatives of benzoic acid; the results, however, when compared with those calculated for the unsymmetrical formula  $C_6H_4\begin{array}{l} \text{CCl}_2 \\ \diagup \\ \text{CO} \end{array}\text{O}$  would indicate an improbably large exaltation.

The ethyl ester and chloride of fumaric acid exhibit exaltations approximately equal to those of the corresponding phthalic acid compounds; isophthalic ester and chloride have exaltations appreciably higher, but this is probably to be attributed to the effects of structure isomerism. Maleyl chloride could not be obtained sufficiently pure for spectrochemical investigation.

In order to throw further light on this question, most of the chlorides of the oxalic series of acids were examined from oxalic to sebacic acid, and no exaltation was observed except a trace in the case of oxalyl chloride which may be attributed to the  $-\text{CO}\cdot\text{CO}-$  group. Succinyl and glutaryl chloride must therefore be entirely of the symmetrical dichloride structure.

In the absence of pure, simple derivatives of the dichlorolactone molecule  $\begin{array}{c} \text{CH}\cdot\text{CCl}_2 \\ \diagup \\ \text{CH}-\text{CO} \end{array}\text{O}$ ,  $\alpha\delta$ -dichloro- $\gamma$ -valerolactone,



(Leuchs and Giua, A., 1912, i, 603, 604), was investigated and compared with the lactones of  $\delta$ -methoxy- and  $\delta$ -ethoxy- $\gamma$ -hydroxyvaleric acids, and with methyl  $\alpha\beta$ -butyleneoxide- $\delta$ -carboxylate. All were found to be optically normal. It is therefore probable that the hypothetical dichlorolactonic structure for succinyl and phthalyl chlorides would also be optically normal.

*d-cis*-Camphoryl, *l-trans*-camphoryl, *d*-chlorocamphoryl, and dehydrocamphoryl chlorides from their spectrochemical behaviour are probably all normal acid chlorides. The first and third named certainly exhibit a certain negative exaltation, but as this is also to be observed with the corresponding esters it probably arises from the *gem*-dimethyl groups (see this vol., ii, 261).

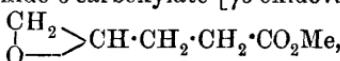
A comparison of the chlorides and esters of chlorofumaric and fumaric acids shows a similar exaltation in the chloride and ester

of each acid, thus indicating the normal symmetrical structure of the chlorides. With chloromaleyl chloride, however, the molecular refraction is below that of the isomeric chlorofumaryl chloride, and is in agreement with that calculated on theoretical grounds for the structure  $\text{CH} \cdot \text{CCl}_2 > \text{O}$ ; the lactonic formula is also favoured by a consideration of the molecular volume (Ott, *loc. cit.*). The structure of phthalyl chloride, on the other hand, is almost certainly the symmetrical one, as is indicated by recent chemical and physicochemical investigations (Scheiber, *loc. cit.*; Ott, *loc. cit.*) and by the present confirmation of Brühl's results. The constitution of the chlorides of the isomeric camphoric acids, chlorocamphoric acid, and dehydrocamphoric acid is also decided in favour of the symmetrical acid chloride form (compare Scheiber and Knothe, *loc. cit.*).

Succinyl chloride gave curiously variable results for density, refraction, and dispersion, probably due to some difficultly removable impurity; a specimen regarded as pure, indicated a true acid chloride structure, as already suggested by Ott.

The following substances were examined, but only the refraction for sodium light is quoted below; the original paper gives the values for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -lines also.

Acetyl chloride, b. p. 51—52°,  $D_4^{20.6}$  1·1039,  $n_D^{20.8}$  1·38831; *isovaleryl chloride*, b. p. 114·5—115·5°/771 mm.,  $D_4^{24.3}$  0·9854,  $n_D^{24.3}$  1·41361; *crotonyl chloride*, b. p. 117—120°/754 mm.,  $D_4^{17.4}$  1·0822,  $n_D^{17.9}$  1·46001; *methyl  $\alpha\beta$ -butyleneoxide- $\delta$ -carboxylate* [ $\gamma\delta$ -oxidovalerate],



$D_4^{24.1}$  1·0731,  $n_D^{24.7}$  1·42589;  $\delta$ -methoxy- $\gamma$ -valerolactone,  $D_4^{22.6}$  1·1205,  $n_D^{22.2}$  1·44533;  $\delta$ -ethoxy- $\gamma$ -valerolactone,  $D_4^{24.5}$  1·0718,  $n_D^{24.9}$  1·44082;  $\alpha\beta$ -dichloro- $\gamma$ -valerolactone,  $D_4^{24.2}$  1·4367,  $n_D^{24.6}$  1·49624; *oxalyl chloride*, b. p. 60—61°,  $D_4^{13.4}$  1·4884,  $n_D^{12.9}$  1·43395; *malonyl chloride*, b. p. 58°/26 mm.,  $D_4^{22.9}$  1·4505,  $n_D^{23.4}$  1·45973; *succinyl chloride*, b. p. 88·8°/19 mm.,  $D_4^{15.2}$  1·3948,  $n_D^{15.2}$  1·47348; *glutaryl chloride*, b. p. 107—108°/16 mm.,  $D_4^{21.8}$  1·3221,  $n_D^{20.2}$  1·47281; *suberyl chloride*, b. p. 149—150°/12 mm.,  $D_4^{20.8}$  1·1718,  $n_D^{20.6}$  1·46847; *sebacyl chloride*, b. p. 168—170°/16 mm.,  $n_D^{18.3}$  1·46836; *fumaryl chloride*, b. p. 158—160°,  $D_4^{16.8}$  1·4117,  $n_D^{18.1}$  1·50038; *chlorofumaryl chloride*, b. p. 87—87·5°/28 mm.,  $D_4^{16.2}$  1·5653,  $n_D^{17.6}$  1·52172; *ethyl chlorofumarate*, b. p. 135—136°/17 mm.,  $D_4^{18.7}$  1·1886,  $n_D^{18.3}$  1·45782; *uns chloromaleyl chloride* ( $\text{CH} \cdot \text{CCl}_2 > \text{O}$ , Ott, *loc. cit.*), b. p. 82·2—82·5°/26 mm.,  $D_4^{17.7}$  1·6055,  $n_D^{18.1}$  1·51362.

*Benzoyl chloride*,  $D_4^{20.9}$  1·2105,  $n_D^{20.9}$  1·55376; *cinnamoyl chloride*, b. p. 131°/20 mm.,  $D_4^{45.3}$  1·1617,  $n_D^{42.5}$  1·61364; *phthalyl chloride*, b. p. 156—157°/23 mm.,  $D_4^{15.2}$  1·4081,  $n_D^{15.5}$  1·57099; *ethyl phthalate*, b. p. 162—163°/7 mm.,  $D_4^{17.8}$  1·1202,  $n_D^{17.7}$  1·50293; *isophthalyl chloride*, m. p. 40—41°,  $D_4^{47.3}$  1·3880,  $n_D^{46.9}$  1·56999; *ethyl isophthalate*, b. p. 170—170·5°/24 mm.,  $D_4^{16.7}$  1·1239,  $n_D^{17.5}$  1·50815; *d-cis-camphoryl chloride*, b. p. 144·5—145·5°/17 mm.,  $D_4^{20.2}$  1·2446,  $n_D^{19.9}$  1·50133; *ethyl d-cis-camphorate*, b. p. 150—152°/8 mm.,  $D_4^{19.2}$  1·0318,  $n_D^{19.1}$  1·45613;

*l-trans*-camphoryl chloride, b. p. 153—154°/24 mm.,  $D_4^{20.6}$  1.2270,  $n_D^{20.7}$  1.49880; ethyl *l-trans*-camphorate, b. p. 155—157°/20 mm.,  $D_4^{22}$  1.0282,  $n_D^{21.6}$  1.45454; *d*-chlorocamphoryl chloride, b. p. 152—152.5°/17 mm.,  $D_4^{31.5}$  1.3219,  $n_D^{31.3}$  1.50797; *d*-dehydrocamphoryl chloride, b. p. 160—161°/32 mm.,  $D_4^{49.3}$  1.2176,  $n_D^{48}$  1.50433. D. F. T.

**Preparation of Terpenylic and Terebic Acids.** RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 166—169).—Tiemann and his collaborators (A., 1895, i, 548; 1896, i, 385; 1897, i, 81) have suggested that methoethylheptanonolide yields terpenylic acid on oxidation by chromic acid, and terebic acid when oxidised by nitric acid, and may be used as a source of these two acids. The author finds that on oxidation by nitric acid, terpenylic acid is the chief product (58.2% of the theoretical), the yield of terebic acid (18.6% of the theoretical) being small. The preparation and separation of the two acids are described.

T. A. H.

**Attempts to Synthesise Monosubstituted Paraconic Acids.** PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 161—166. Compare A., 1911, i, 708)—The only method hitherto available for the preparation of these acids is that of Fittig (A., 1890, i, 583), which gives poor yields when aliphatic aldehydes are used. The authors have modified Reformatsky's reaction for the production of  $\beta$ -hydroxy-acids (A., 1896, i, 128) with a view to preparing mono-substituted paraconic acids by this means, but the yields are poor, only 7% of the theoretical yield of isopropylparaconic acid being obtained, and 12% of the calculated yield of hexylparaconic acid. The latter acid had m. p. 79—80°, which is 10° below that recorded by Schnegans.

T. A. H.

**Preparation of Strontium Cholate.** KNOLL & Co. (D.R.-P. 254530).—*Strontium cholate*,  $(C_{24}H_{39}O_5)_2Sr \cdot 10H_2O$ , colourless, hair-like tufts is readily obtained when an alcoholic solution of cholic acid is heated with an aqueous solution (or suspension) of strontium hydroxide; it has an important therapeutic action.

F. M. G. M.

**Oxidation of Aldehydes by an Aqueous Solution of Bromine.** ERNEST ANDERSON (*Amer. Chem. J.*, 1913, 49, 179—184).—It is usually supposed that the method used for converting aldoses into the corresponding acids by oxidation with aqueous solution of bromine is not applicable to the ordinary aldehydes. In order to test this question, several aldehydes have been subjected to the action of bromine, and the oxidation products isolated. The results show that whilst benzaldehyde, acetaldehyde, paraldehyde, and formic acid give good yields of the corresponding acids, namely, benzoic, acetic, and carbonic, formaldehyde and aldol are oxidised to only a small extent, and salicylaldehyde and chloral not at all.

Acetaldehyde was found to give 71% of the theoretical yield of acetic acid; benzaldehyde, 80% of benzoic acid; paracetaldehyde, 86% of acetic acid; and formic acid, 80% of carbonic acid.

E. G.

**Glyoxal.** CARL D. HARRIES (*Ber.*, 1913, **46**, 294—296. Compare A., 1907, i, 183).—Polymerisation of glyoxal is accelerated by the presence of moisture. When technical glyoxal which has been dried over phosphoric oxide at 95° is distilled alone, the unimolecular compound is obtained. It is claimed that Meisenheimer's depolymerisation of methylglyoxal (A., 1912, i, 831) was foreshadowed in the above-mentioned paper.

J. C. W.

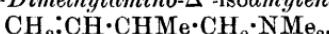
**Catalytic Preparation of Ketones.** JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1913, [viii], **28**, 243—344).—A résumé of work already published (A., 1909, i, 286, 627; 1910, i, 11, 179, 489; 1911, i, 134, 302; 1912, i, 537).

H. W.

**The Synthesis of Sugars by means of Radioactive Emanations.** JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Compt. rend.*, 1913, **156**, 646—648. Compare A., 1911, i, 178, 769).—As with ultra-violet rays, so under the influence of radium emanation hydrogen and carbon dioxide react in the presence of potassium hydrogen carbonate, giving formaldehyde, which in the presence of potassium hydroxide polymerises and gives reducing sugars. No formates could be detected during the reaction. The sugars formed are a mixture of hexoses giving phenylosazones, separable into two fractions, one, m. p. 198—199°, and the other, m. p. 178°. Unlike the sugars obtained in the photochemical synthesis under the influence of ultra-violet rays (compare A., 1912, i, 606), these sugars are optically active and have  $[\alpha]_D + 17.58^\circ$ . By distillation with hydrochloric acid indications of the presence of a pentose were obtained.

W. G.

**Preparation of  $\delta$ -Dimethylamino- $\Delta^a$ -isoamylene and  $\delta$ -Dimethylamino- $\Delta^a$ -butylene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254529. Compare A., 1912, i, 742, 781; and Euler, A., 1897, i, 585).— $\delta$ -Dimethylamino- $\Delta^a$ -isoamylene,



a colourless liquid, b. p. 113—116°, and identical with the so-called “ $\beta$ -methyldimethylpyrrolidine” (Euler, *loc. cit.*), can be prepared by heating  $\gamma$ -hydroxy- $\beta$ -methylbutyldimethylamine with concentrated sulphuric acid (3 parts) during three to four hours at 100°, or with 50% sulphuric acid (5—10 parts) during ten hours at 150—160°.

$\delta$ -Dimethylamino- $\Delta^a$ -butylene,  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , a colourless liquid, b. p. 94—96°, is obtained in a similar manner from  $\gamma$ -hydroxybutyldimethylamine with 20—30% sulphuric acid (5 parts) at 200° during ten hours.

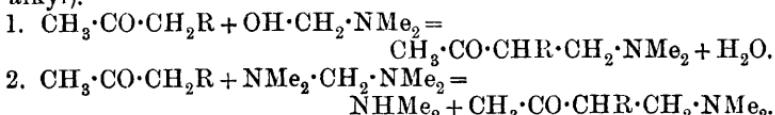
These compounds have an odour of coniine, and find employment in the preparation of isoprene and erythene.

F. M. G. M.

**Preparation of  $\delta$ -Dimethylamino- $\gamma$ -dimethylbutan- $\beta$ -ol.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254713).—When methyl tetramethylaminoisopropyl ketone (following abstract) is boiled during one hour with 20% sulphuric acid (4—6 parts), it furnishes dimethylamino- $\beta$ -acetylallylene,  $\text{CH}_2\cdot\text{C}\text{Ac}\cdot\text{CH}_2\cdot\text{NMe}_2$ , which

on reduction gives rise to  $\delta$ -dimethylamino- $\gamma$ -methylbutan- $\beta$ -ol (A., 1911, i, 598), a colourless oil, b. p. 67—69°/17 mm. F. M. G. M.

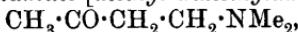
**Preparation of Amino- and Diamino-ketones of the Aliphatic Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254714. Compare A., 1911, i, 598, and preceding abstract).—When dimethylaminomethyl alcohol,  $\text{OH}\cdot\text{CH}_2\cdot\text{NMe}_2$ , or tetramethyldiaminomethane,  $\text{Me}_2\text{N}\cdot\text{CH}_2\cdot\text{NMe}_2$ , are condensed with acetone (or its homologues), the following reactions take place ( $\text{R}$  = hydrogen or alkyl).



The following compounds are described: dimethyl- $\beta$ -acetylpropylamine (*loc. cit.*), b. p. 51—51.5°/13 mm.

$\beta\beta$ -Acetyltrimethylenetetramethyldiamine [*methyl tetramethyldiaminotert-butyl ketone*],  $\text{CH}_3\cdot\text{CO}\cdot\text{CMe}(\text{CH}_2\cdot\text{NMe}_2)_2$ , a colourless, viscous oil, b. p. 110—112°/18 mm., from methyl ethyl ketone and dimethylaminomethyl alcohol.

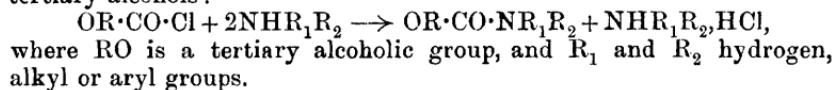
$\beta$ -Acetylethyltrimethylamine [*methyl dimethylaminoethyl ketone*].



a colourless oil with a strong ammoniacal odour, b. p. 57—58°/18 mm.; and  $\beta$ -acetyltrimethylenetetramethyldiamine [*methyl tetramethyldiaminoisopropyl ketone*],  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_2)_2$ , a colourless, odourless, viscous oil, b. p. 96—98°/16 mm.

These compounds are employed in the preparation of erythrene and isoprene. F. M. G. M.

**Preparation of Urethanes of Tertiary Alcohols.** EMANUEL MERCK (D.R.-P. 254472. Compare this vol., i, 5).—It is found that the halogen formyl esters described previously can be readily converted by the action of ammonia or substituted amonias into urethanes of tertiary alcohols:



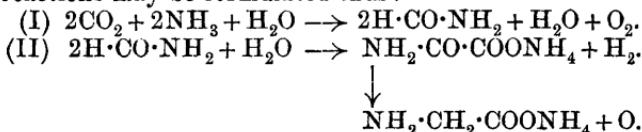
Dimethylethylcarbinyl chloro-formate with alcoholic ammonia furnishes a *urethane*, colourless needles, m. p. 85—87°; an *ethyl urethane*, a colourless oil, b. p. 89°/13 mm., and 86°/11 mm.; a *phenylurethane*, colourless crystals, m. p. 44—47°, b. p. 146°/9 mm.; a *methyl-phenylurethane*, a colourless oil, b. p. 133°/13 mm., and with *p*-phenetidine a *p-ethoxyphenylurethane*, colourless needles, m. p. 88—90°, whilst methyldiethylcarbinol gives rise to a *urethane*, colourless needles, m. p. 61°, and a *phenylurethane*. F. M. G. M.

**Behaviour of Formamide Under the Influence of the Silent Electric Discharge. The Question of Nitrogen Assimilation.** WALTHER LÖB (*Ber.*, 1913, 46, 684—697).—In the course of some experiments on the influence of the silent electric discharge on various combinations of moist carbon dioxide, carbon monoxide,

alcohol and ammonia, with or without oxygen or air, the only compound obtained which could be regarded as of interest to the problem of nitrogen assimilation was hexamethylenetetramine (A., 1909, i, 769). Further investigations on the behaviour of this compound towards oxidising and reducing agents, and towards living yeast, showed that it had no relation to the amino-acids, and, therefore, throws no light on the general question. The discovery of Losanitsch and Jovitschitsch (A., 1897, i, 179) that ammonia and carbon monoxide produce formamide led the author to regard this compound as an intermediate stage, and to try the effect of the silent discharge on the dry substance and on an aqueous solution, both boiling under reduced pressure. In the former case, oxamide was deposited on the sides of the discharge tube, and in the latter, as would be expected, ammonium oxamate. Some reduction was therefore necessary in order to arrive at glycine. Previous experience had shown that water itself is a reducing agent under these conditions (A., 1906, ii, 324), whilst the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$  had also to be considered. The resolution of some formamide into carbon monoxide and ammonia was to be expected, and, indeed, an examination of the gases liberated during the experiment proved the presence of these substances. The existence of glycine in the product, after the removal of ammonia, was unquestionably demonstrated by the formaldehyde test of Sörensen, the "deaminising" method of van Slyke, the reaction with triketohydrindene hydrate, and the formation of the naphthalenesulphonyl compound (E. Fischer and Bergell, A., 1903, i, 24).

The presence of glycine could also be observed on repeating the experiment with moist carbon monoxide and ammonia. The formation of glycine from carbon dioxide (which breaks down into carbon monoxide under the influence of the silent discharge), ammonia, and water is therefore a process of reduction, and the oxidation of glycine should lead to these or intermediate products. Halsey has shown that the products of the action of permanganate do, indeed, include formamide and oxamic acid (A., 1898, ii, 529).

The reactions may be formulated thus:



Reference must be made to the original paper for the experimental details, but it may be said that the amount of oxamide accumulated during twenty hours from 20 grams of dry formamide, boiling at  $110^\circ/15$  mm., was about 0·05–0·08 gram, whilst about 0·01 gram of ammonium oxamate was obtained from a 5–10% solution during the same time, the glycine present being comparable with a 0·01% solution.

J. C. W.

The Diamide of Sulphoisobutyric Acid. JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1913, 32, 90-96. Compare A., 1905, i, 16).—Sulphoisobutyrodiamide,  $\text{NH}_2\cdot\text{SO}_2\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}_2$ , was obtained by passing ammonia into a cold methyl-alcoholic solution of methyl

chlorosulphoisobutyrate. It decomposed without melting at about  $340^{\circ}$ . At  $17^{\circ}$ , one part of diamide dissolved in 201.8 parts of water, whilst at  $100^{\circ}$  the solubility was one part in 24.9. It was insoluble in the other usual solvents. Attempts to condense it with carbonyl chloride, in the presence or absence of a catalyst, were unsuccessful. Similarly, oxalyl chloride, alone or in benzene solution, was without action on it.

To determine whether it was possible to cause a sulphonamide to react with oxalyl chloride, a solution of benzenesulphonamide and oxalyl chloride in benzene was boiled during two and a-half days. Hydrogen chloride was slowly evolved, and *diphenylsulphonoxamide*,  $C_2O_2(NH \cdot SO_2Ph)_2$ , formed. It had m. p.  $256^{\circ}$  (corr., slight decomp.).

H. W.

**Extraction of Glutamic Acid Hydrochloride and Betaine Hydrochloride from Molasses Residue.** HUGO STOLTZENBERG (*Ber.*, 1913, **46**, 557—566. Compare *A.*, 1912, i, 680).—Molasses residue is mixed with hydrochloric acid and subsequently saturated with hydrogen chloride. The crude hydrochlorides which are precipitated are treated with alcohol and hydrogen chloride, whereby glutamic acid hydrochloride is converted into the readily soluble ester hydrochloride. The solution of the latter is concentrated to a syrup, the residue boiled with water, the solution filtered from humin, decolorised, and concentrated until crystallisation begins, when it is again saturated with hydrogen chloride, whereby glutamic acid hydrochloride is precipitated. This has m. p.  $213^{\circ}$  when rapidly heated, and is shown to be partly racemised, the highest observed value for  $[\alpha]_D^{15}$  being  $+26.15^{\circ}$  in 10% hydrochloric acid solution, whereas Siegfried and Schutt (*A.*, 1912, i, 952) observed  $+34.89^{\circ}$ . Purification by transformation into the barium salt and subsequent reprecipitation of the hydrochloride effected no improvement. The filtrates obtained after removal of glutamic acid hydrochloride deposited, on evaporation, betaine hydrochloride, and contained also a strongly acid substance, which could not be obtained in the crystalline state.

The remainder of the paper consists of a reply to the criticisms brought by Ehrlich (*A.*, 1912, i, 835) against the previous work of the author (*loc. cit.*). Stoltzenberg's process of isolating betaine hydrochloride from molasses differs essentially from that of Ehrlich (1904, D.R.-P. 157173), in that hydrochloric acid and alcohol are employed in the given order in the former process, in the inverse order in the latter. In the second method, the chemical nature of the residue is not affected by agitation with alcohol, and the hydrogen chloride is only used to precipitate the hygroscopic betaine. In the first method, however, the composition of the residue itself is greatly altered by the action of the hydrogen chloride. Ehrlich's statement that the alcohol consumption is less in his process than in that of the author is incorrect.

The paper concludes with a critical survey of the historical development of the subject as described by Ehrlich. H. W.

**Action of Sodium Hypobromite on Semicarbazide.** ROBERT STOLLE (*Ber.*, 1913, **46**, 260. Compare Linch, T., 1912, **101**, 1755).

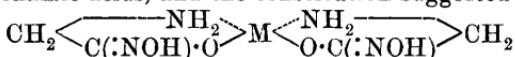
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—The product of the action of sodium hypobromite on semicarbazide is hydrazodicarbonamide, and not *p*-urazine as described by Linch. The compound obtained on oxidation with chromic acid is therefore azodicarbonamide (Thiele, A., 1892, 1295 and 1430), and not a stable tetrazine.

J. C. W.

**Salt- and Complex Salt-Formation with Amino- and Hydroxy-acetohydroxamic Acids.** HEINRICH LEY and F. MÄNNCHEN (*Ber.*, 1913, **46**, 751—758).—On account of the similarity in structure between the carboxylic and hydroxamic acids, the authors have investigated certain derivatives of the latter in which the formation of complex salts was to be expected. It is found that internally complex salts are obtainable from amino- and hydroxy-hydroxamic acids somewhat analogous to those obtained from the simple amino-acids. To the normal copper salts is attributed the structure  $R \cdot C \begin{array}{l} \text{NO} \\ \diagdown \\ \text{O} \end{array} Cu$ ; acid salts could be obtained only from substituted hydroxamic acids, and the constitution suggested is



(compare Ley, A., 1909, i, 138), where M represents a bivalent metal atom. Complex salts containing a bivalent metal together with an alkali metal could be obtained both from the unsubstituted and substituted acids; the heavy metal is present as part of a complex ion, but from the colour of the salts of the amino- and hydroxy-substituted acids the conclusion is drawn that this atom is also linked with the anion complex by supplementary partial valencies.

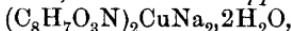
*Aminoacetohydroxamic acid*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{C(OH)} \cdot \text{N-OH}$ , was obtained by the interaction of equimolecular quantities of hydroxylamine, ethyl aminoacetate, and sodium ethoxide in alcoholic solution; it was precipitated as the copper salt and recovered by the action of hydrogen sulphide; it is a colourless, crystalline solid, m. p.  $107^\circ$  (approx.); normal *copper* salt, green, amorphous powder, obtained by mixing aqueous solutions of the acid and copper acetate; *acid copper* salt, obtained by adding copper acetate to a solution of the sodium salt, separates in violet crystals; *acid nickel* salt, prepared by the addition of dilute sodium hydroxide solution to a solution of nickel acetate with a bimolecular quantity of the acid, forms deep red crystals; the complex *sodium nickel* salt,  $(\text{C}_2\text{H}_4\text{O}_2\text{N}_2)_2 \text{NiNaH}_2\text{O}$ , yellowish-red, rhombic tablets, was obtained by treating a solution of the sodium salt with nickel acetate and sodium hydroxide.

*Anilinoacetohydroxamic acid*,  $\text{NHPh} \cdot \text{CH}_2 \cdot \text{C(OH)} \cdot \text{N-OH}$ , colourless needles, m. p.  $126^\circ$  (decomp.), separates in the form of the *sodium* salt when ethyl anilinoacetate is treated in alcoholic solution with an equimolecular quantity of hydroxylamine; *copper* salt, green, amorphous solid.

*Phenylglycolohydroxamic acid*,  $\text{OH} \cdot \text{CHPh} \cdot \text{C(OH)} \cdot \text{N-OH}$ , colourless, rhombic leaflets, m. p.  $132^\circ$ , was prepared in a similar manner to the last; *sodium* salt, needles; the green *copper* salt, like that of the last acid, gives a violet solution in aqueous sodium hydroxide; the  *salt could be obtained only as a reddish-yellow solution.*

The free acid soon decomposes in solution with the formation of benzaldehyde.

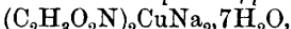
*Phenoxyacetohydroxamic acid*,  $\text{OPh}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\text{N}\cdot\text{OH}$ , prepared in an analogous manner from ethyl phenoxyacetate, forms colourless leaves, m. p.  $114^\circ$ ; the addition of copper acetate and sodium hydroxide solution to the solution of the sodium salt causes the formation of the crystalline, bluish-violet *copper sodium salt*,



which is converted by water into the green *copper salt*.

The interaction of equimolecular quantities of hydroxylamine, ethyl lactate, and sodium ethoxide in alcoholic solution produces unstable *sodium lactohydroxamate*,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}(\text{ONa})\cdot\text{NOH}$ .

An aqueous solution of acetohydroxamic acid (Miolati, A., 1892, 699) when treated with copper acetate and sodium hydroxide, after some days, deposits blue crystals of a complex *copper sodium salt*,



which is converted by water into the ordinary green *copper salt*.

D. F. T.

#### New Method of Preparing Nitriles of the Aliphatic Series.

ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 74—79).

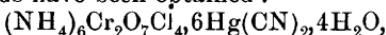
—Catalytic decomposition of the hydrazones of aliphatic aldehydes in presence of cuprous chloride, platinous chloride, or zinc chloride always yields nitriles to some extent, although the yield varies considerably. In general, hydrazones containing small radicles give very small proportions of nitriles, the decomposition then yielding principally substituted indoles and other compounds (see this vol., i, 388). On the other hand, hydrazones containing large radicles, such as *isovaleraldehydophenylhydrazone*, undergo nitrilic decomposition almost exclusively:  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{NHPh} = \text{NH}_2\text{Ph} + \text{C}_5\text{H}_9\text{N}$ .

*isoValeronitrile*, thus obtained in 56% yield, is a colourless, mobile liquid, b. p.  $128.5^\circ$ , or  $52.5-53^\circ/50$  mm.,  $D_0^{20} 0.7884$ ,  $D_0^{20} 0.8054$  (compare Erlenmeyer, *Annalen*, 1871, 160, 266).

*isoButyronitrile* is similarly obtained from *isobutaldehydophenylhydrazone* in 37% yield, and *n-heptonitrile*, b. p.  $183.5^\circ$ ,  $D_0^{20} 0.8107$  (compare Henry, A., 1905, i, 561), from *n-heptaldehydophenylhydrazone*.

T. H. P.

**Chromates and Mercuric Cyanide.** DANIEL STRÖMHLOM (*Zeitsch. anorg. Chem.*, 1913, 80, 155—160. Compare A., 1912, ii, 648).—The following compounds have been obtained :



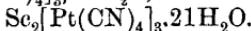
long, reddish-yellow crystals, with only a narrow range of stability;  $2\text{K}_2\text{CrO}_4\cdot 3\text{Hg}(\text{CN})_2\cdot 2\text{H}_2\text{O}$ . A chloride-chromate salt has not been obtained in the case of potassium.

C. H. D.

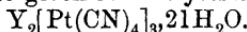
**Potassium  $\beta$ -Ferricyanide.** HORACE L. WELLS (*Amer. Chem. J.*, 1913, 49, 205—206).—Hauser and Biesalski (this vol., i, 26) have stated that the potassium  $\beta$ -ferricyanide described by Locke and Edwards (A., 1899, i, 407) is merely the ordinary salt, contaminated with colloidal Prussian-blue. It is now shown that this view is incorrect, and that Hauser and Biesalski have overlooked the fact that the

$\beta$ -ferricyanide does not yield a precipitate with bismuth nitrate, and is thus readily distinguished from the ordinary salt. E. G.

**Crystalline Form of Two Scandium Platinocyanides.** PETR N. TSCHIRVINSKI (*Zeitsch. Kryst. Min.*, 1913, 52, 44—47).—The crystalline form, as observed under the microscope, is described for the yellow salt,  $\text{Sc}_2[\text{Pt}(\text{CN})_4]_3 \cdot 18\text{H}_2\text{O}$ , and for the red salt,



New observations are also given for the yttrium salt,



L. J. S.

**Magnesium Methyl Iodide.** PIERRE JOLIBOIS (*Compt. rend.*, 1913, 156, 712—714. Compare A., 1912, i, 675, 753).—The action of methyl iodide on magnesium in dry ether is a simple one, there being practically no secondary reaction under any conditions. The magnesium methyl iodide, so obtained, when heated in a vacuum, first loses its ether of constitution at  $130^\circ$ , and at  $240^\circ$  methane is evolved, according to the equation :  $2\text{MgMe}_2\text{MgI}_2 = 3\text{CH}_4 + \text{Mg}_2\text{C}_2\text{MgI}_2$ .

By raising the temperature to  $600^\circ$  no more gas is evolved. The residue is a voluminous, yellow mass, from which only a definite portion of the iodine can be extracted in the form of magnesium iodide by dry ether, leaving a compound, having the definite composition  $\text{Mg}_2\text{C}_2\text{MgI}_2$ , which is violently decomposed by water with development of light and heat, and, on controlled decomposition by moist ether, yields practically pure methane. W. G.

**The Catalytic Hydrogenation of Camphorone. Some New cycloPentane Hydrocarbons.** MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, 156, 470—473).—Camphorone on hydrogenation in the presence of reduced nickel at  $130^\circ$  yields dihydrocamphorone (compare Semmler, A., 1904, i, 260). If the reduction is carried out at  $280^\circ$ , the product obtained is 1-methyl-3-isopropylcyclopentane,  $\text{C}_5\text{H}_8\text{MePr}^2$ , a liquid with a terpene-like odour, b. p.  $132$ — $134^\circ$ ,  $D^{19} 0.773$ ,  $n_D^{19} 1.4250$ . The same compound is obtained by dehydrating 1-methyl-3-isopropylcyclopentane-2-ol with zinc chloride, which furnishes a mixture of two isomeric unsaturated hydrocarbons, b. p.  $143$ — $145^\circ$ ,  $D^{18} 0.786$ ,  $n_D^{18} 1.4465$ , non-separable, but which on hydrogenation at  $170^\circ$  are converted into the pentane hydrocarbon.

Dihydrocamphorone reacts with magnesium methyl iodide, giving a mixture of 1:2-dimethyl-3-isopropyl- $\Delta^1$ - and - $\Delta^2$ -cyclopentenes, b. p.  $150$ — $155^\circ$ ,  $D^{17} 0.812$ ,  $n_D^{17} 1.4500$ , which on hydrogenation at  $180^\circ$  are transformed into 1:2-dimethyl-3-isopropylcyclopentane, b. p.  $146$ — $148^\circ$ ,  $D^{16} 0.786$ ,  $n_D^{16} 1.4337$ . Similarly by using magnesium isopropyl iodide a mixture of 1-dimethyl-2:3-diisopropyl- $\Delta^1$ - and - $\Delta^2$ -cyclopentene, b. p.  $160$ — $168^\circ$ ,  $D^{18} 0.812$ ,  $n_D^{18} 1.4509$ , is obtained, yielding on hydrogenation at  $180^\circ$ , 1-methyl-2:3-diisopropylcyclopentane, b. p.  $150$ — $152^\circ$ ,  $D^{17} 0.781$ ,  $n_D^{17} 1.4318$ . W. G.

**The cycloOctane Series. VI. cycloOctatetraene.** RICHARD WILLSTÄTTER and MICHAEL HEIDELBERGER (*Ber.*, 1913, 46, 517—527. Compare Willstätter and Waser, A., 1912, i, 17).—The previous

observations with *cyclooctatetraene* have been repeated and extended. The quaternary ammonium base is now distilled in a still lower vacuum and at a correspondingly lower temperature (30—45°). On cooling, the hydrocarbon solidifies to a pale yellow, crystalline mass, m. p. —27°. It forms an additive compound with bromine, taking up two atoms only. The *dibromide*,  $C_8H_8Br_2$ , crystallises in lustrous, snow-white needles, m. p. 70—71.5° (corr.). It decolorises permanganate instantaneously and tends to take up more bromine, but hydrogen bromide is then eliminated, and a *substance*,  $C_8H_7Br_3$ , m. p. 53—55°, is obtained instead of the tetrabromide.

The tetraene reacts immediately with chlorine, and hydrogen chloride is eliminated; an oily *chloride* is obtained, and can be separated into two fractions, both of which have the composition  $C_8H_7Cl_3$ .

With hydrogen bromide in acetic acid solution the tetraene forms a *hydrobromide*,  $C_8H_9Br$ , which is an almost colourless oil with a sweet odour, b. p. 85—87°/12.5 mm. It slowly decomposes in presence of oxygen, and gives an orange coloration with concentrated sulphuric acid.

The molecular refraction of *cyclooctatetraene* shows little or no exaltation. Similarly, the molecular dispersion ( $\beta-a$ ) shows no marked exaltation, although in consequence of the greater dispersion in the ultra-violet the molecular dispersion,  $M_\gamma - M_\alpha$ , shows a larger exaltation.

The tetraene behaves, like benzene, optically normal in regions where it is free from absorption; the dispersion is, however, abnormal in the region where selective absorption takes place.

Such selective exaltation of the molecular dispersion is even more marked in the case of the yellow fulvenes; data are quoted for methylmethyfulvene and dimethylfulvene, as well as *cyclooctatriene*.

When *cyclooctatetraene* is hydrogenated by the platinum method the yellow colour disappears after the addition of 1.5 molecules of hydrogen. The first three molecules appeared to be absorbed in approximately equal times and the fourth more slowly, the actual figures being 35, 40, 40, and 95 minutes respectively.

Methylmethyfulvene does not lose the yellow colour until reduction is nearly complete. The three molecules of hydrogen were absorbed in 7, 7, and 10 minutes.

The product, *sec.-butylcyclopentane*, is a mobile liquid, with an odour like limonene, b. p. 152—154°/725 mm.,  $D_4^0$  0.810.

The *cyclooctane* formed even from pure *cyclooctatetraene* is not pure, and probably contains an isomeride.

Pure *cyclooctatetraene* may be kept for several months without decomposition. E. F. A.

[Preparation of *cyclohexene*.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 254473. Compare A., 1899, i, 22; 1902, i, 2, and T., 1898, 73, 941).—When the vapour of chlorocyclohexane at 350—450°/15—20 mm. is conducted over a catalytic agent (such as barium chloride, aluminium oxide, or nickel chloride), it gives rise to *cyclohexene*. F. M. G. M.

**Rational Preparation of Some Benzene Homologues. II.** FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1913, [ii], 87, 227—236).—A continuation of previous work (this vol., i, 29) on the preparation of benzene homologues by the interaction of alkyl esters of chloro-formic acid with aromatic hydrocarbons in the presence of aluminium chloride.

Methyl chloro-formate reacts with benzene to form toluene and *m*-xylene; with toluene it yields *p*-xylene and  $\psi$ -cumene.

The interaction of ethyl chloro-formate with benzene and toluene yields respectively *p*-diethylbenzene and 1-methyl-3:4-diethylbenzene, b. p. 200—203°, the constitution of which has been established by its oxidation to 4-methylphthalic acid.

*m*-Xylene reacts with ethyl chloro-formate, yielding 1:3-dimethyl-5-ethylbenzene, b. p. 182—188°, and with *p*-xylene to form 1:4-dimethyl-2-ethylbenzene, b. p. 183—185°.

The interaction of cumene with methyl and ethyl carbonates yields dimethylisopropylbenzene, b. p. 195—210°, and diethylisopropylbenzene, b. p. 250—256° respectively.

The addition of *isobutyl* chloro-formate to a mixture of aluminium chloride and benzene gives rise to *tert*.-butylbenzene, whilst the addition of aluminium chloride to a mixture of the ester with benzene yields *di*-(*tert*. ?)-butylbenzene, b. p. 225—235°, and *tri*-(*tert*. ?)-butylbenzene.

The preparation of a *p*(?)-methylbutylbenzene, b. p. 190—195°, and a methyldibutylbenzene, b. p. 241—247°, from toluene and *isobutyl* chloro-formate, and *p*-methylamylbenzene, b. p. 205—210°, from amyl chloro-formate and toluene is also described.

F. B.

**Chemical Action of Light. XXV. Autoxidations. III.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1913, 46, 417—422\*).—A continuation of the investigation of the autoxidation of aromatic hydrocarbons (A., 1912, i, 174, 645). The results are in accordance with those of Suida (A., 1912, i, 957), but as the present authors gave prolonged exposure to light and investigated only the final products, indications of peroxides were but rarely observed.

Benzene in contact with water and oxygen is completely unaltered after several months' exposure to sunlight (compare Suida, *loc. cit.*).

Ethylbenzene under similar conditions gives a yellow aqueous layer, and after neutralisation with sodium carbonate, ether extracts acetophenone with some unchanged ethylbenzene; the former was characterised by its semicarbazone; this, it was observed, separates from methyl alcohol with one molecule of alcohol of crystallisation, which is lost on drying over sulphuric acid. The alkaline solution, which had been extracted with ether, was found to contain formic and benzoic acids.

Mesitylene, when treated similarly, gave a strongly acidic mixture, which after neutralisation yielded an ethereal extract containing mainly unchanged hydrocarbon, together with a small quantity of a non-volatile substance and a trace of an aldehyde. The aqueous liquid on acidification gave formic acid, mesitylenic acid, a substance probably

\* and *Atti. R. Accad. Lincei*, 1913, [v], 22, i, 127—132.

a polycarboxylic acid which sublimed near 300°, and some resinous matter.

The oxidation product of  $\psi$ -cumene contained as its neutral constituents only unchanged hydrocarbon and a trace of an aldehydic substance; the acidic constituents comprised formic acid, together with 3 : 4-dimethylbenzoic acid, 2 : 4-dimethylbenzoic acid, and a difficultly volatile, crystalline substance; the presence of 2 : 5-dimethylbenzoic acid could not be detected.

Indene was practically completely changed, and the reaction mixture slowly gave the reaction for a peroxide. A relatively large amount of resinous matter was produced which was partly soluble in ether, the soluble portion being separable by boiling water into a colourless substance, crystallising in leaflets, m. p. 72°, and a yellow, amorphous substance, m. p. 123° (approx.). The acidic portion of the reaction product contained formic and phthalic acids, together with a third substance, m. p. 174°, probably homophthalic acid.

Naphthalene proved quite resistant to autoxidation, but tetrahydronaphthalene (Bamberger and Kitschelt, A., 1890, 1146) is readily oxidised, giving much resinous matter and a little phthalic acid.

D. F. T.

**Influence of Substituents in Benzene on the Binary Systems. Substituted Benzene-Antimony Trihaloids.** Boris N. MENSCHUTKIN (*J. Chim. phys.*, 1912, 10, 598—611. Compare A., 1912, i, 98, 99, 100, 177).—The compounds of benzene with antimony trichloride and tribromide are of the type  $2\text{SbCl}_3\text{C}_6\text{H}_6$ , but some substituted benzenes give in addition compounds of the type  $\text{SbCl}_3\text{PhR}$ . Methyl-, ethyl-, propyl- and *isoamyl*-benzenes exhibit a decreasing stability in the compounds  $2\text{SbCl}_3\text{PhR}$ , whereas the stability of the compounds  $\text{SbCl}_3\text{PhR}$  attains a maximum in ethylbenzene.

Antimony tribromide has less affinity for the phenyl nucleus than the chloride. Toluene gives compounds of both types, but ethyl-, propyl- and *isoamyl*-benzenes of the type  $\text{SbBr}_3\text{PhR}$  only, the ethyl compound again having the maximum stability.

Diphenyl forms the compounds  $2\text{SbCl}_3\text{PhPh}$  (stable) and  $2\text{SbBr}_3\text{PhPh}$  (unstable), and diphenylmethane gives two stable compounds of the same types. Triphenylmethane, however, does not combine with antimony tribromide, and with the chloride gives only an unstable compound of the formula  $\text{SbCl}_3\text{CHPh}_3$ .

The xylenes form with antimony trichloride compounds of both types, which are intermediate in stability between those of toluene and ethylbenzene. *p*-Xylene gives the most, and *m*-xylene the least, stable. With antimony tribromide, *p*-xylene gives only the compound  $2\text{SbBr}_3\text{C}_6\text{H}_4\text{Me}_2$ , which is intermediate in stability between those of benzene and toluene, whilst *m*- and *o*-xylene give also compounds,  $\text{SbBr}_3\text{C}_6\text{H}_4\text{Me}_2$ , which are less stable than that of toluene.

The compounds of antimony trichloride and tribromide with cymene are analogous in composition and inferior in stability to those of *p*-xylene. The unfavourable influence of the *isopropyl* group is thus manifest in presence of the methyl group.

Mesitylene and  $\psi$ -cumene form compounds of both types with antimony trihaloids, those of  $\psi$ -cumene being less and those of mesitylene more stable than the toluene compounds. Apparently the three methyl groups in mesitylene neutralise each other's effects on the phenyl nucleus.

R. J. C.

**Influence of Substituents in Benzene on the Properties of the Binary Systems Formed by Substituted Benzenes and Antimony Trichloride or Tribromide.** BORIS N. MENSCHUTKIN (*J. Chim. phys.*, 1912, **10**, 612–623. Compare A., 1912, i, 193).—The compounds of monosubstituted benzenes with antimony trichloride are all of the two types  $2\text{SbCl}_3\text{PhR}$  and  $\text{SbCl}_3\text{PhR}$ . When R is H, OH, Me, OMe, Et, Pr<sup>a</sup> or  $\text{C}_5\text{H}_{11}^{\text{s}}$ , both compounds are formed. When R is OEt, Bz, Ph, COH, COMe, COPh, CN, compounds of the second type only are produced. When R is NO<sub>2</sub>, F, Cl, Br, I, CHPh<sub>2</sub>, compounds of the second type are also produced, which, however, decompose on melting, and when R is SO<sub>3</sub>H, CO<sub>2</sub>H, or COCl no combination occurs.

From the behaviour of phenol and anisole it is argued that oxygen has very little influence, although in phenetole the cumulative effect of the oxygen and the ethyl group prevents the formation of the compound  $2\text{SbCl}_3\text{PhOEt}$ . Neither anisole nor ethylbenzene forms compounds of this type with antimony tribromide. Nitro-, fluoro-, chloro-, bromo-, and iodo-benzene do not combine with the tribromide at all.

*m*-Dinitrobenzene gives an unstable compound,  $\text{SbCl}_3\text{C}_6\text{H}_4(\text{NO}_2)_2$ , which, like the compound  $\text{SbCl}_3\text{PhI}$ , does not invariably crystallise out, so that complete f.p. diagrams of these systems are obtainable showing only one eutectic point. The nitro-group diminishes the affinity of the phenyl nucleus for antimony less than the halogens. *p*-Dichloro- and *p*-dibromo-benzene do not combine with antimony trichloride.

*p*-Chlorotoluene gives no compounds, but *o*- and *m*-chlorotoluene give compounds,  $\text{SbCl}_3\text{C}_6\text{H}_4\text{MeCl}$ , which decompose on melting. No corresponding compounds of antimony tribromide exist.

The three nitrotoluenes form compounds of the formula



the most stable being given by *o*-nitrotoluene, which also combines with antimony tribromide.

Benzene has more affinity for antimony haloids than any of its derivatives, but cyclohexane does not combine at all. The degree of saturation of the phenyl nucleus varies with the nature of the substituting atoms or groups. This variation is not expressible by ordinary structural formulæ, but such formulæ as have been proposed recently by Kaufmann and by Stark are capable of giving some explanation of it.

The compounds of aniline containing 1, 2, 3, 4, and 6 molecules of aniline per molecule of antimony trichloride are in a class by themselves, and are to be attributed to the residual affinity of the amino-group.

R. J. C.

**The Catalytic Action of Mercury in Nitrations.** RICHARD WOLFFENSTEIN and OSKAR BÖTERS (*Ber.*, 1913, **46**, 586—589).—Mercury has no catalytic action on the nitration of benzene when concentrated nitric acid or a nitric acid-sulphuric acid mixture is used, nitrobenzene being formed as usual (compare Holdermann, A., 1906, i, 439). When, however, a more dilute nitric acid ( $D=1\cdot31$ ) is used, nitro-phenols are produced. The reaction is first one of oxidation to phenol, and then nitration, since when nitrobenzene is used instead of benzene, no trace of a nitrophenol is produced. Similar reactions take place with toluene, and ethyl- and propyl-benzenes.

To prepare dinitro- or trinitro-phenol, a mixture of benzene (100 grams), nitric acid (800 grams;  $D=1\cdot31$ ), and mercuric nitrate (15 grams) is heated on the water-bath under reflux, stirring vigorously meanwhile. At the end of the reaction, the flask contains a mass of crystals of 2:4-dinitrophenol and of picric acid. Additive mercury compounds are formed as intermediate products.

Instead of using nitric acid, nitrous acid, nitrogen dioxide or tetroxide, and nitrogen pentoxide may be used. For example, a mixture of 120 grams of benzene, 20 grams of mercuric nitrate, and 270 grams of nitrogen tetroxide is kept at the ordinary temperature for a few days, after which a crystalline mass of almost pure 2:4-dinitrophenol is obtained.

T. S. P.

**Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen. II. Dihydronaphthalene.** RICHARD WILLSTÄTTER and VICTOR L. KING (*Ber.*, 1913, **46**, 527—535). Compare Willstätter and Hatt, A., 1912, i, 545).—Dihydronaphthalene has not previously been prepared free from contamination with naphthalene or tetrahydronaphthalene. It may be obtained pure by distilling the quaternary hydroxide of tetrahydro- $\beta$ -naphthylamine in a vacuum, or more conveniently by reducing naphthalene dibromide by means of zinc powder and alcohol at  $60^\circ$ . Pure dihydronaphthalene is a colourless oil with a sweet odour, b. p.  $84\cdot5^\circ/16$  mm.,  $D_4^{20} 0\cdot9974$ ; it crystallises in large plates, m. p.  $-9^\circ$ .

When hydrogenated by means of platinum and hydrogen, the first stage is the formation of tetrahydronaphthalene, the one nucleus only being saturated. The further reduction to a completely saturated perhydronaphthalene takes place very slowly.

Naphthalene under similar conditions yields no tetrahydronaphthalene at any stage of the process, but a mixture of naphthalene and perhydronaphthalene,  $C_{10}H_{16}$ , is always obtained. This behaviour is not in accord with an aromatic-olefinic structure for naphthalene, such as proposed by Willstätter and Waser (A., 1912, i, 18). E. F. A.

**Derivatives of *p*-Xylene.** JAN J. BLANKSMA (*Chem. Weekblad*, 1913, **10**, 136—141. Compare A., 1910, i, 661).—The melting-point curve of mixtures of 2:3-dinitro-*p*-xylene and 2:6-dinitro-*p*-xylene has been plotted, and a number of derivatives of *p*-xylene have been prepared. The curve indicates the formation of an additive product containing equimolecular proportions of the two substances.

Reduction of 2:5-dinitro-*p*-xylene with ammonium sulphide yields

5-nitro-*p*-2-xylidine, m. p. 142°, converted by Sandmeyer's reaction into 2-bromo-5-nitro-*p*-xylene, colourless crystals, m. p. 70°, which is reduced by iron powder and sulphuric acid to 5-bromo-*p*-2-xylidine, colourless crystals, m. p. 96°. Acetic anhydride converts this substance into 5-bromo-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 180°, also formed by the action of a solution of bromine in glacial acetic acid on 2-aceto-*p*-2-xylidide. On saponification it yields 5-bromo-*p*-2-xylidine, already mentioned. On substituting bromine for the amino-group by Sandmeyer's reaction, there is formed 2:5-dibromo-*p*-xylene, m. p. 75°, also produced by bromination of *p*-xylene.

Bromine dissolved in glacial acetic acid transforms 5-nitro-*p*-2-xylidine into 3-bromo-5-nitro-*p*-2-xylidine, pale yellow crystals, m. p. 125°, converted by acetic anhydride and a trace of concentrated sulphuric acid into 3-bromo-5-nitro-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 208°. Replacement of the amino-group in 3-bromo-5-nitro-*p*-2-xylidine produces 2:3-dibromo-5-nitro-*p*-xylene, colourless crystals, m. p. 99°.

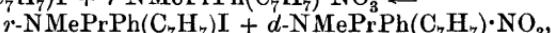
Bromine in glacial acetic acid reacts with *p*-2-xylidine, forming 3:5-dibromo-*p*-2-xylidine, m. p. 65°, converted by diazotisation and the action of boiling alcohol into 2:6-dibromo-*p*-xylene, colourless plates of mother-of-pearl lustre, m. p. 32°, also obtained in an impure liquid form by the bromination of *p*-xylene. Nitration in presence of sulphuric acid converts 2:6-dibromo-*p*-xylene into 2:6-dibromo-3:5-dinitro-*p*-xylene, colourless crystals, m. p. 190°.

3:5-Dibromo-*p*-2-xylidine is converted by acetic anhydride and concentrated sulphuric acid into 3:5-dibromo-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 192° (not 165°, as stated in *Rec. trav. chim.*, 1906, 25, 362). This substance is transformed by nitric and sulphuric acid into 3:5-dibromo-6-nitro-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 256°, which is hydrolysed to 3:5-dibromo-6-nitro-*p*-2-xylidine, yellow crystals, m. p. 176°, also formed by bromination of 6-nitro-*p*-2-xylidine. By diazotisation and the action of boiling alcohol, this substance yields 3:5-dibromo-2-nitro-*p*-xylene, colourless crystals, m. p. 83°, which is converted by nitric and sulphuric acid into 3:5-dibromo-2:6-dinitro-*p*-xylene, already mentioned.

Replacement of the amino-group in 6-nitro-*p*-2-xylidine by bromine by the Sandmeyer reaction produces 2-bromo-6-nitro-*p*-xylene, pale yellow crystals, m. p. 38°.

A. J. W.

**Kinetics of Ammonium Salts.** EDGAR WEDEKIND and F. PASCHKE (*Zeitsch. physikal. Chem.*, 1913, 82, 314—324).—Polemical. an answer to von Halbau (A., 1911, i, 852; compare also A., 1909, ii, 722; 1908, i, 723; 1911, i, 628). Several new preliminary experiments are given. It is shown that the addition of an inactive non-decomposable salt to a chloroform solution of an active iodide does not decrease the dissociation of the active iodide, but brings about a double decomposition, thus:



and of these four substances the iodides alone can dissociate, so that the decrease in the rate of dissociation, which is determined polaris-

metrically, is explained. The remaining and unchangeable activity is due to the active nitrate which exists together with inactive nitrate in the solution. The latter can be precipitated by ether, and the amount of active nitrate determined, which is always found to be equal in concentration to that of the inactive nitrate added. Preliminary experiments are given on the rate of formation of phenylbenzylmethyl-propylammonium bromide in chloroform solution at various temperatures from methylpropylaniline and benzyl bromide. J. F. S.

**The Kinetics of Ammonium Salts.** HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, 82, 510—512).—Polemical, an answer to Wedekind and Paschke's criticism (preceding abstract) of Halban's paper (A., 1911, i, 852). J. F. S.

**Nitro-derivatives of Cresyl Oxides [Tolyl Ethers].** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], 13, 169—173).—Most of this work has been published already (this vol., i, 173, 261). *p*-Tolyl ether on nitration yields only a *tetranitro*-derivative, m. p. 84°, crystallising in yellow needles, and furnishing on boiling with a dilute solution of potassium hydroxide an amorphous, red powder which does not melt at 300°. T. A. H.

**Nitro-derivatives of Cresylene Oxides [Tolylene Oxides].** ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], 13, 173—176. Compare this vol., i, 261).—Part of this work has been published already (*loc. cit.*). *p*-Tolylene oxide, m. p. 166°, on nitration in acetic acid solution at 80° yields a mixture of the *mono*- and *dinitro*-derivatives. The former has m. p. 197°, and is sparingly soluble in boiling alcohol. The *dinitro*-derivative has m. p. 136°, and is readily soluble in boiling alcohol; it alone is formed when the nitration is effected in sulphuric acid solution in the cold. No higher nitro-derivative of the para-ether could be obtained, whence the author considers that the union of the two nuclei is in the ortho-position to the ether linking, whilst in *o*-tolylene oxide (*loc. cit.*) it is in the meta-position. T. A. H.

**Preparation of Halogenated Aminonaphtholsulphonic Acids.** FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.P. 254715).—Substituted aminonaphtholsulphonic acids can be readily prepared by the halogenation of the *ON*-diacyl derivatives of 2-amino-naphtholsulphonic acids with subsequent elimination of the acyl groups. *5-Chloro-6-amino-1-naphthol-3-sulphonic acid* crystallises from water as a colourless powder. *5-Bromo-di-p-tolylsulphonyl-6-amino-1-naphthol-3-sulphonic acid* is a yellow, crystalline powder. The preparation of *8-bromo-6-amino-1-naphthol-3-sulphonic acid* is also described.

F. M. G. M.

**3-Aminophenyl Mercaptan.** THEODOR ZINCKE and JOH. MÜLLER (*Ber.*, 1913, 46, 775—786).—The preparation of *3-aminophenyl mercaptan* and of *3-aminophenyl methyl sulphide* is described. A number of derivatives of the latter have been investigated.

*Acetylaniline-m-sulphonyl chloride*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$ , is formed by

the action of phosphorus pentachloride on the corresponding sodium salt. It forms white needles, m. p. 88°, and is readily converted into the *amide*, m. p. 217°, and the *anilide*, m. p. 179°. Reduction of an alcoholic solution of the chloride by means of zinc dust transforms it into *3 : 3'-diacetylaminodiphenyl disulphide*,  $S_2(C_6H_4 \cdot NHAc)_2$ , m. p. 210°, from which *3 : 3'-diaminodiphenyl disulphide*, colourless needles, m. p. 52°, is obtained by hydrolysis. The corresponding *hydrochloride* dissolves freely in water, whilst the *nitrate* and *sulphate* are sparingly soluble. When an alcoholic solution of the hydrochloride is boiled with sodium sulphide in the presence of a small quantity of sodium hydroxide, 3-aminophenyl mercaptan, b. p. 180—190°/16 mm., is formed as a pale yellow oil, which, when pure, is fairly stable towards air, but is readily oxidised when impure. Ferric chloride converts it into the disulphide. The *hydrochloride* and *sulphate* were examined. It forms a *diacetyl* derivative, m. p. 97°. With alcoholic benzaldehyde, it yields a *benzylidene* derivative,  $CHPh(S \cdot C_6H_4 \cdot N \cdot CHPh)_2$ , yellow powder, m. p. 59° (compare A., 1912, i, 257).

*3-Acetylaminophenyl methyl sulphide*,  $NHAc \cdot C_6H_4 \cdot SMe$ , needles, m. p. 75°, is obtained by reducing *3 : 3'-diacetylaminodiphenyl disulphide* in alcoholic solution by means of sodium sulphide in the presence of sodium hydroxide and treatment of the product so obtained with methyl sulphate. Bromine converts it into a *perbromide*, which is readily transformed into a dibromo-substitution product. When a solution of it in chloroform is cooled in ice and saturated with chlorine, a pentachloro-compound, needles, m. p. 160°, probably having annexed formula, is obtained, which, when heated with aniline, yields triphenylguanidine and *dichloro-3-acetylaminophenyl mercaptan*, m. p. 152°. Hydrolysis of *3-acetylaminophenyl methyl sulphide* by means of hydrochloric acid in aqueous alcoholic solution yields the *hydrochloride* of *3-aminophenyl methyl sulphide*, from which the free base, pale yellow oil, b. p. 163—165°/16 mm., is obtained by means of ammonia. The *sulphate* was examined.

*3-Methylthiophenyltrimethylammonium iodide*,  $SMe \cdot C_6H_4 \cdot NMe_3I$ , m. p. 183—185° (decomp.), is obtained by the action of excess of methyl iodide on a methyl-alcoholic solution of *3-acetylaminophenyl methyl sulphide*. It forms a di-iodo- and a tetra-iodo-additive product. The free base is obtained by evaporation of its solution in a vacuum as yellowish-white, hygroscopic crystals.

*3-Methylthiophenyltrimethylammonium chloride*, obtained from the corresponding iodide and silver chloride, forms white, hygroscopic needles. It yields a pale yellow, stable *platinichloride*, and an orange-yellow *dichromate*.

*3-Dimethylaminophenyl methyl sulphide*, pale yellow oil, b. p. 165—167°/16 mm., is obtained when the above iodide is heated above its m. p. under diminished pressure. It forms a readily soluble *hydrochloride* and *sulphate*.

*3-Acetylaminophenyl methyl sulphide* is oxidised by hydrogen peroxide in glacial acetic acid solution to the corresponding *sulphoxide*,  $NHAc \cdot C_6H_4 \cdot SO \cdot CH_3$ , needles, m. p. 112°; this is converted by

hydrogen bromide into a *perbromide*, which readily passes into a mono-bromo-substitution product. When heated with aqueous alcoholic potassium hydroxide the above acetyl derivative is transformed into *3-aminophenylmethylsulphoxide*, colourless, rhombic leaflets, m. p. 115°. The *hydrochloride*, white needles, is readily soluble in water.

*3-Acetylaminophenylmethylsulphone*,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Me}$ , obtained by the action of a larger quantity of hydrogen peroxide on a solution of 3-acetylaminophenyl methyl sulphide in glacial acetic acid (compare above), forms small, white needles, m. p. 137°, and is converted by aqueous alcoholic hydrogen chloride into *3-aminophenylmethylsulphone*, m. p. 72°.

*3-Methylthiolbenzenediazonium chloride*,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ , is obtained in moderately stable, yellow leaflets by the addition of amyl nitrite to an alcoholic solution of the hydrochloride of 3-aminophenyl methyl sulphide in the presence of alcoholic hydrogen chloride. It couples with dimethylaniline and with  $\beta$ -naphthol, yielding dyes which crystallise in red needles. It decomposes when heated with water, but a phenol could not be isolated from the product of the reaction. It was transformed by the usual methods into *3-methylthiolbenzonitrile*, white needles, m. p. 40° (*3-methylthiolbenzoic* acid, leaflets, has m. p. 129°), and *3-methylthiolphenyl iodide*, almost colourless oil, b. p. 157°/16 mm.

*3 : 3'-Diacetylaminodiphenyl disulphide* is converted into the corresponding ammonium *iodide*,  $\text{S}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_2$ , m. p. 185—186° (decomp.), when heated with methyl alcohol and methyl iodide; this substance, when heated under diminished pressure, yields *3 : 3'-dimethylaminodiphenyl disulphide*,  $\text{S}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , colourless oil, b. p. 162—166°/16 mm. A solution of the latter in formic acid is converted by amyl nitrite in the presence of a little hydrochloric acid into *6 : 6'-dinitroso-3 : 3'-dimethylaminodiphenyl disulphide*,



dark green needles, m. p. 130°, which is reduced by hydrogen sulphide in ammoniacal solution to *6-amino-2-dimethylaminophenyl mercaptan*. The *hydrochloride* of the latter, white needles, m. p. 235° (decomp.), was investigated. It forms a colourless double salt with mercuric chloride. With potassium ferricyanide, it yields a dark green *precipitate*, the colour of which deepens on addition of alkali. Ferric chloride converts it into a dark red oxidation *product*, which yields a dark violet double salt with mercuric chloride. Hydrogen sulphide decomposes the latter, the original mercaptan being regenerated.

H. W.

**Basic Properties of Sulphoxides and their Position Among the Organo-metallic Bases.** EMIL FROMM (*Annalen*, 1913, 396, 75—103).—The similarities in behaviour between bases of the type  $\text{R}_{n+1}\text{Md}\cdot\text{OH}$  (where Md represents a metalloid element such as N, P, As, Sb, O, S, Se, Te, or I, and n the number of atoms of hydrogen with which it can unite, and R an organic radicle) have frequently been emphasised. Compounds of the type  $\text{MdR}_n$  may be regarded as the anhydrides of  $\text{R}_{n+1}\text{Md}\cdot\text{OH}$ . All these bases are monoacidic.

The anhydrides,  $R_n\text{MdO}$ , of a second series of bases of the type  $R_n\text{Md(OH)}_2$  are known. In the anhydrides, Md may be any one of the elements given above, but in the hydroxides hitherto Md has been only N, P, As, Sb, or Te. All these bases and their anhydrides are diacidic, and the anhydrides or their salts are characterised by the three equilibrium reactions : (i)  $\text{R}_n\text{MdO} \rightleftharpoons \text{R}_n\text{Md} + \text{O}$ ; (ii)  $\text{R}_n\text{MdX}_2 \rightleftharpoons \text{R}_n\text{Md} + \text{X}_2$  (where X is halogen); (iii)  $\text{R}_n\text{MdCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}_n\text{MdCl}\cdot\text{OH} + \text{HCl} \rightleftharpoons \text{R}_n\text{MdO} + 2\text{HCl}$ .

In the present communication the author deals with substances in which Md is sulphur, and, therefore,  $n=2$ . Sulphoxides can be prepared by reaction (i), the oxygen being supplied by nitric acid, hydrogen peroxide, or chromic acid, and also by reactions (ii) and (iii). The dichlorides of diaryl sulphides have been prepared by Fries and Vogt (A., 1911, i. 538), and are converted into sulphoxides by water; di-iodides of dialkyl sulphides, which have long been known, are, it is now shown, converted into sulphoxides by silver acetate.

It is also shown that sulphoxides can combine with one equivalent of hydrogen chloride to form hydrogen salts,  $\text{OH}\cdot\text{SR}_2\text{Cl}$ , and with two equivalents of hydrogen bromide or iodide to form normal salts,  $\text{R}_2\text{SX}_2$ , which are identical with the dibromides or di-iodides produced by reaction (ii). The hydrogen salts and the normal salts are both hydrolysed more or less rapidly by water, reproducing the sulphoxide. In addition to hydrolysis, the normal salts can also dissociate according to reaction (i), and it depends on the relative velocities of dissociation and of hydrolysis whether a normal salt yields the sulphoxide or the sulphide by treatment with aqueous alkali hydroxide or silver acetate. The parent substance,  $\text{H}_2\text{SO}$ , of the sulphoxides, and its tautomeric form,  $\text{HS}\cdot\text{OH}$ , are unknown; anthraquinone derivatives of both have been described by Fries (A., 1912, i, 1005).

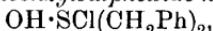
The relations between disulphides and disulphoxides and the basic properties of the latter can be represented by equations similar to (i), (ii), and (iii).

[With FRITZ SCHÄFER, AQUILA FORSTER, and BORIS VON SCHERSCHEWITZKI.]—*o*-Nitrophenyl benzyl sulphide and the para-isomeride, 2:4-dinitrophenyl benzyl sulphide, dinitrophenyl methyl sulphide, and *s*-di-*o*-nitrophenylthioethane, resemble di-*p*-tolyl sulphide (Fromm and Raiziss, A., 1910, i, 554) in not forming additive compounds with bromine; 2:4-dinitrophenyl benzyl sulphide in cold chloroform yields *bromodinitrophenyl benzyl sulphide*,  $\text{C}_6\text{H}_2\text{Br}(\text{NO}_2)_2\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ , m. p. 104°, yellow needles. Also the dibromides cannot be obtained from the sulphoxides and hydrogen bromide. Both reactions proceed, however, when the nitro-groups are reduced to amino-groups and the latter acetylated; thus di-*o*-acetylaminophenylthioethane and bromine in cold chloroform yield the *tetrabromide*,  $\text{C}_2\text{H}_4(\text{SBr}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc})_2$ , m. p. 60–61°, unstable, orange crystals, which is converted by water into *di-*o*-acetylaminophenylsulphoxyethane*,  $\text{C}_2\text{H}_4(\text{SO}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc})_2$ , m. p. 214°, colourless needles; the latter and hydrogen bromide in chloroform regenerate the tetrabromide.

Dibenzyl sulphide and chlorine in petroleum at 0° yield the very unstable *dichloride*,  $\text{SCl}_2(\text{CH}_2\text{Ph})_2$ , which is converted into the sulphoxide by water. The dibromide is more stable (Fromm and

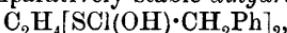
Raiziss, *loc. cit.*). The *di-iodide*,  $\text{SI}_2(\text{CH}_2\text{Ph})_2$ , m. p.  $64-65^\circ$ , violet crystals, prepared from the sulphide and iodine in glacial acetic acid on the water-bath, is extremely stable. It is decomposed, without hydrolysis, by dilute sodium hydroxide, dibenzyl sulphide being regenerated; the hydrolysis is effected by silver acetate in dilute acetic acid, whereby dibenzylsulphoxide is produced.

Dibenzylsulphoxide and hydrogen iodide in chloroform at  $0^\circ$  yield the preceding dibenzyl sulphide di-iodide. The sulphoxide and hydrogen chloride in benzene form *dibenzylsulphoxide hydrochloride*,



m. p.  $90^\circ$ , colourless crystals, which does not further react with hydrogen chloride, and is decomposed into the sulphoxide by water or in a vacuum.

*s*-Dibenzylthielethane reacts with chlorine in cold petroleum to form the unstable *tetrachloride*,  $\text{C}_2\text{H}_4(\text{SCl}_2\cdot\text{CH}_2\text{Ph})_2$ , white crystals, with bromine in cold chloroform to form the moderately stable *tetrabromide*, m. p.  $84^\circ$ , orange-red crystals, and with iodine in boiling glacial acetic acid to form the *tetraiodide*, m. p.  $94^\circ$ , red needles. The tetrachloride and the tetrabromide are very rapidly converted into the disulphoxide by water. On the contrary, the disulphoxide suspended in cold petroleum or chloroform is converted into the tetrabromide by hydrogen bromide, and into a comparatively stable *dihydrochloride*,



by hydrogen chloride.

*p-Tolyl benzyl sulphide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{S}\cdot\text{CH}_2\text{Ph}$ , m. p.  $44^\circ$ , prepared from *p-tolyl mercaptan* and benzyl chloride, yields the *sulphoxide*, m. p.  $136-137^\circ$ , by oxidation with 30% hydrogen peroxide in glacial acetic acid or with nitric acid, and reacts with chlorine or bromine in cold petroleum to form respectively the very unstable *dichloride*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SCl}_2\cdot\text{CH}_2\text{Ph}$ , and comparatively unstable *dibromide*, and with iodine in hot glacial acetic acid to form the stable *di-iodide*, m. p.  $72^\circ$ , dark blue plates. The dichloride and the dibromide by treatment with water, and the di-iodide by treatment with silver acetate, are converted into *p-tolylbenzylsulphoxide*; the di-iodide and aqueous sodium hydroxide yield *p-tolyl benzyl sulphide*. The dibromide and the di-iodide are obtained from the sulphoxide and hydrogen bromide or iodide in chloroform. *p-Tolyl methyl sulphide di-iodide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{SMeI}_2$ , m. p.  $40^\circ$ , prepared from its components in petroleum, crystallises in dark blue needles.

Formaldehyde-*p-tolylmercaptal* (this vol., i, 176) forms a *tetraiodide*,  $\text{CH}_2(\text{SI}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$ , m. p.  $68-70^\circ$ , which can also be obtained from the disulphoxide and hydrogen iodide in chloroform, and is not converted into the disulphoxide by silver acetate. Formaldehydebenzyl-mercaptal also forms a *tetraiodide*,  $\text{CH}_2(\text{SI}_2\cdot\text{CH}_2\text{Ph})_2$ , decomp.  $110-140^\circ$ , which is converted by silver acetate, not into the sulphoxide as usual, but into formaldehydebenzylmercaptal.

In boiling glacial acetic acid, benzyl disulphide and iodine form the *tetraiodide*,  $\text{S}_2(\text{CH}_2\text{Ph})_2\text{I}_4$ , decomp.  $113-120^\circ$ , green crystals, which is converted into the disulphoxide by silver acetate in hot glacial acetic acid; from the latter the tetraiodide is regenerated by hydrogen iodide at  $-5^\circ$  in carbon tetrachloride. *Benzyl disulphide tetrachloride* is

extremely unstable, and the *tetrabromide* has m. p. 2° (decomp.); the latter and silver acetate yield the disulphoxide. C. S.

**Substituted Aryl Sulphonamides.** OTTO N. WITT and D. UERMÉNYI (*Ber.*, 1913, **46**, 296—308).—Hinsberg's method for the preparation of secondary bases (A., 1891, 49) has not yet received general application, owing to the difficulty which has been experienced in hydrolysing the sulphonamides. For this purpose Schroeter and Eisleb (A., 1909, i, 575) dissolved the substances in cold concentrated sulphuric acid, but obtained in the case of benzenesulphonanilide, not aniline but sulphanilic acid. It is now shown that good results may be obtained with 80% sulphuric acid. The toluene-*p*-sulphonamide is suspended in this acid and heated to 135—150°, when solution and hydrolysis take place. On cooling, *p*-toluenesulphonic acid separates, and is removed by filtration, whilst the base is liberated from the diluted filtrate and distilled in steam. The yields are somewhat impoverished by the formation of non-volatile by-products, which occur to a preponderating extent in the case of ethyl-*p*-toluidine, and consist of a sulphone, being due to the displacement of the *p*-toluenesulphonic acid residue into the ring.

Toluene-*p*-sulphon-*p*-toluidide and also its *acetyl* derivative, m. p. 133.5°, give *p*-toluidine-*m*-sulphonic acid with concentrated sulphuric acid, but sulphonation of the base does not occur with 80% acid at 150°. Crude methyl- and ethyl-aniline and also methyl-*o*-toluidine (*toluene-p-sulphon-methyl-o-toluidide*,  $C_{15}H_{17}O_2NS$ , has m. p. 119—120°) may be conveniently purified by this process. *Toluene-p-sulphonethyl-o-toluidide*,  $C_{16}H_{19}O_2NS$ , forms long needles, m. p. 75°, but the ethyl-*o*-toluidine is accompanied by a small quantity of the rearranged sulphone, white needles, m. p. 134°. The hydrolysis of *toluene-p-sulphonethyl-p-toluidide*, colourless needles, m. p. 71—72°, gives less than a 50% yield of ethyl-*p*-toluidine, the chief product being precipitated on adding water, in colourless needles, m. p. 113°. It is formed in still greater quantity when concentrated acid is used, and is a secondary base, since it gives an *acetyl* compound,  $C_{16}H_{18}O_2NS \cdot C_2H_3O$ , in silky, white needles, m. p. 143—144°. When the base is heated at 275° in a current of hydrogen chloride, ethyl chloride is removed and the resulting primary *aminoditolylsulphone*,  $C_{14}H_{15}O_2NS$ , colourless crystals, m. p. 169°, may be diazotised and deprived of the amino-group. The resulting compound forms colourless needles, m. p. 116°, and can be synthesised by condensing the chloride of *m*-toluenesulphonic acid with toluene by means of aluminium chloride. It is, therefore, mp-*ditolylsulphone*, and the rearrangement of the sulphonamide into a sulphone is to be represented thus :



The sulphone may be nitrated in the cold, and the mononitro-derivative, intensely yellow needles, m. p. 161°, forms an *acetyl* compound,  $NO_2 \cdot C_{16}H_{17}O_2NS \cdot C_2H_3O$ , in colourless crystals, m. p. 159—160°.

J. C. W.

**Preparation of *p*-Alkyloxyphenylaminoalkyl Sulphites.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 255305).—When acetaldehyde (or its higher homologues) is condensed with *p*-alkyloxyaminobenzenes in the presence of an alkali (or ammonium) hydrogen sulphite it furnishes salts of therapeutic value, and having the general formula  $\text{OR}^1\text{C}_6\text{H}_4\text{NH}\cdot\text{CHR}\cdot\text{O}\cdot\text{SO}_2\text{M}$ , where M is an alkali metal or ammonium, R = methyl or ethyl, and R<sup>1</sup> an alkyl group.

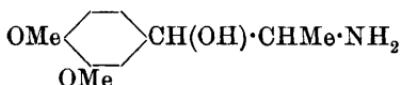
*Sodium p-phenetidinoethyl sulphite*, needles, is obtained when a cooled aqueous solution of 40% sodium hydrogen sulphite (110 parts) is treated with acetaldehyde (20 parts) and *p*-phenetidine (55 parts), and subsequently gently heated until a clear solution is obtained; on cooling, the solution sets to a crystalline mass.

The *p*-phenetidine can be replaced by *p*-anisidine, and the acetaldehyde by propaldehyde.

F. M. G. M.

**Preparation of Aromatic Amino-alcohols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254438).—The reduction of aromatic ketones to the corresponding alcohols has previously been described, and is now found to proceed quantitatively if hydrogen is

employed in the presence of colloidal metals of the platinum group.



*3 : 4-Dimethoxyphenyl- $\alpha$ -propanol-amine* (annexed formula), hard, colourless crystals, m. p. 138°, is

obtained when 100 parts of *a*-aminopropionylveratrole (A., 1910, i, 313) in 300 parts of water with palladous chloride (5 parts), gum arabic (10 parts), and hydrazine hydrate are submitted to the action of hydrogen during two days at 20° and under a pressure of 1.5 atmospheres;

the *hydrochloride*, colourless leaflets, has m. p. 212°; whilst

the reduction in a similar manner of *4-a-aminopropionylcatechol* (A., 1910, i, 313) gives rise to a 95% yield of

*3 : 4-dihydroxyphenyl- $\alpha$ -propanolamine* (annexed formula), m. p. 188°; the *hydrochloride*, a colourless powder, has m. p. 95°. F. M. G. M.

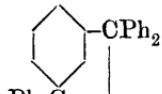
**Preparation of Esters of Nitroanthraquinonylanthranilic Acid.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254475).—When nitroaminoanthraquinones are treated with the esters of *o*-halogenated benzoic acids in the presence of copper (or a salt of copper), they give rise to nitroanthraquinonylanthranilic acid esters.

*Methyl 4-nitro-1-anthraquinonylanthranilate*, reddish-brown needles, m. p. 234—240°, is thus obtained from 1-nitro-4-aminoanthraquinone and methyl *o*-chlorobenzoate. On hydrolysis and subsequent reduction, these compounds furnish the corresponding aminoanthraquinonylanthranilic acids, which are of technical value.

F. M. G. M.

**Metaquinonoids.** OTTO STARK and O. GARBN (Ber., 1913, 46, 659—666).—The method by which Thiele and Balhorn obtained yellow

tetraphenyl-*p*-xylylene from methyl terephthalate (A., 1904, i, 491) has been applied to methyl *isophthalate*, and a yellow tetraphenyl-*m*-xylylene of the annexed formula has been prepared.



*Tetraphenyl-m-xylylene glycol*,  $C_{32}H_{26}O_2$ , is obtained by the action of magnesium phenyl bromide on methyl *isophthalate* in a boiling mixture of benzene and anisole. It crystallises from glacial acetic acid with one molecule of the solvent in light yellow prisms, m. p.  $88^\circ$ , and from light petroleum in the free state, m. p.  $112-113^\circ$ . Hydrogen chloride precipitates from an acetic acid solution the *dichloride*,  $C_{32}H_{24}Cl_2$ , which crystallises from petroleum in white needles, m. p.  $137^\circ$ , and like the *dibromide*, m. p.  $167-168^\circ$ , can be titrated with alkali in alcoholic solution. When heated with zinc dust and Devarda's alloy in benzene (compare Schmidlin, A., 1908, i, 150), a golden-yellow solution with red fluorescence is obtained, from which petroleum precipitates *tetraphenyl-m-xylylene*, in yellow needles, m. p.  $210-220^\circ$  (decomp.). It gives the above dichloride with chlorine, but is stable towards oxygen.

When hydrogen chloride is passed into the acetic acid mother liquors of the glycol, a *dichloride* is obtained, which is insoluble in hot petroleum, and has m. p.  $236-238^\circ$ . It may be hydrolysed and converted into a *dimethyl ether*,  $C_{34}H_{30}O_2$ , m. p.  $187-188^\circ$ , from which the *dibromide*, m. p.  $242^\circ$ , is obtained. It is supposed that the  $-C(OH)Ph_2$  group has wandered into the *para*-position and that the compounds are isomeric, according to Schmidlin's isomerism (A., 1912, i, 32), with tetraphenyl-*p*-xylylene glycol dimethyl ether, m. p.  $181-182.5^\circ$ , and tetraphenyl-*p*-xylylene dibromide, m. p.  $270-272^\circ$  (Thiele and Balhorn, *loc. cit.*). J. C. W.

**Direct Hydrogenation of the Phenylacetic Esters. Preparation of cycloHexylacetic Acid.** PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 424-427. Compare A., 1912, i, 353).—The esters of phenylacetic acid are readily hydrogenated by excess of hydrogen in the presence of very active nickel at  $180^\circ$ . By this means the following esters have been prepared.

*Methyl cyclohexylacetate*, b. p.  $200-202^\circ$  (corr.),  $D_0^0 0.9961$ ,  $D_0^{14} 0.9896$ ,  $n_D^{14} 1.459$ . *Ethyl cyclohexylacetate*, b. p.  $211-212^\circ$  (corr.),  $D_0^0 0.9626$ ,  $D_0^{14} 0.9537$ ,  $n_D^{14} 1.451$  (compare Freundler, A., 1905, i, 890). *Propyl cyclohexylacetate*, b. p.  $228-229^\circ$  (corr.),  $D_0^0 0.9560$ ,  $D_0^{15} 0.9431$ ,  $n_D^{15} 1.450$ . *isoButyl cyclohexylacetate*, b. p.  $240-241^\circ$  (corr.),  $D_0^0 0.9445$ ,  $D_0^{14} 0.9307$ ,  $n_D^{14} 1.452$ . *isoAmyl cyclohexylacetate*, b. p.  $250-251^\circ$  (corr.),  $D_0^0 0.9388$ ,  $D_0^{16} 0.9267$ ,  $n_D^{16} 1.454$ .

The refractive indices are practically constant throughout, but the density diminishes regularly with increase in molecular weight. All these esters are readily saponified by alcoholic potassium hydroxide, giving the free acid, m. p.  $32^\circ$ .

The phenylpropionic esters undergo similar hydrogenation.

It is of interest to note that benzyl acetate, the isomeride of methyl phenylacetate, submitted to similar hydrogenation is decomposed, giving

toluene and acetic acid, at the same time destroying the activity of the nickel.  
W. G.

**Esters of Cellulose with Benzoic Acid and its Derivatives.**  
 OTTO HAUSER and H. MUSCHNER (*Zeitsch. angew. Chem.*, 1913, **26**, 137—139).—In the preparation of the esters the authors used hydrocellulose, which was made according to the method of Girard. The hydrocellulose is treated, under cooling, with a large excess of benzoyl chloride and sodium hydroxide, and the resulting product washed with hot water to remove alkali, and finally with alcohol and ether. The results show that the product obtained is always cellulose monobenzoate; no dibenzoate is formed, whatever may be the concentration of the sodium hydroxide (compare Cross and Bevan, A., 1901, i, 452). The only effect of the concentration of the sodium hydroxide is on the time of reaction, the stronger the alkali the shorter the time. The best concentration is 20%, and the temperature should be kept at 20° by appropriate cooling.

*Cellulose mono-p-chlorobenzoate*,  $C_{19}H_{23}O_{11}Cl$ , was prepared similarly from hydrocellulose and *p*-chlorobenzoyl chloride. It is an amorphous, white powder, insoluble in all solvents, non-hygroscopic and non-fusible. Esters could not be obtained from *m*-nitrobenzoyl chloride and *p*-bromobenzoyl chloride, owing to the fact that the high temperature necessary to melt the chloride resulted in its saponification by the sodium hydroxide before the cellulose entered into reaction. *p*-Toluoyl chloride gave a product corresponding with the formula  $C_{18}H_{26}O_{11}$ , instead of the expected formula  $C_{20}H_{26}O_{11}$ .  
T. S. P.

**An Interesting Case of Dimorphism.** ALEXIS DUFFOUR (*Compt. rend.*, 1913, **156**, 473—475).—Vanillyl benzoate is obtained in two distinct crystalline forms, monoclinic or triclinic, accordingly as it is prepared by the hydrogenation of vanillin benzoate in the cold in the presence of platinum black (compare Vavon, A., 1912, i, 260), or by the condensation of benzoyl chloride and sodium vanillyloxide. These two forms are both stable at the ordinary temperature, having been kept for a year unaltered. The triclinic crystals

[ $a:b:c = 0.8697:1:0.5283$ ;  $\alpha = 90^\circ 20'$ ;  $\beta = 72^\circ 22'$ ;  $\gamma = 72^\circ 44'$ ]  
 have m. p. 99°, whilst the monoclinic

[ $a:b:c = 0.7814:1:1.3460$ ;  $\beta = 111^\circ 9'$ ].

observed under a microscope, begin to melt at 90°, and in the liquid obtained, triclinic crystals begin to form, transforming the whole into a friable mass only melting at 99°. This transformation of the monoclinic into the triclinic form when the two are in contact is retarded by diminution in temperature and becomes inappreciable at 30°.

W. G.

**Nitration of Benzoic Acid in the Presence of Mercury**  
 RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, **46**, 589—599).—When benzoic acid (50 grams) is nitrated with nitric acid (300 grams;  $D = 1.35$ ) in the presence of mercuric nitrate, 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid is obtained. The mixture is heated on the brine-bath at

105° for twenty hours, after which it is filtered from unchanged benzoic acid, the filtrate made alkaline to remove the mercury, acidified, and then extracted with ether to dissolve out any *m*-nitrobenzoic acid formed. The aqueous solution is then concentrated in order to obtain crystals of the readily soluble 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid. Various trinitrohydroxybenzoic acids have been described in the literature, and in order to compare them with the above acid they have been again prepared by the authors. Shadinger (A., 1876, 584) obtained an acid by the nitration of anthraflavone. Since anthraflavone is a mixture of the two isomerides, anthraflavic acid and 1 : 7-dihydroxy-anthraquinone, the authors have nitrated each of these substances. In each case a tetranitro-derivative is first obtained, which undergoes fission, on further action of nitric acid, with the formation of the above-mentioned 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid. The third isomeride of anthraflavic acid is anthrarufin, the tetranitro-derivative of which has been prepared by Liebermann (A., 1879, 537). This on boiling with nitric acid undergoes fission with the formation of the above acid. Tetranitroanthrarufin is therefore 3 : 4 : 6 : 8-tetranitro-1 : 5-dihydroxyanthraquinone. Beilstein and Geitner (*Annalen*, 1866, 139, 12) obtained a trinitrohydroxy-acid by the action of fuming nitric acid on *m*-aminobenzoic acid, and this the authors prove to be identical with their acid.

2 : 4 : 6-Trinitro-*m*-hydroxybenzoic acid,  $C_7H_3O_9N_3$ , crystallises with one molecule of water of crystallisation, in rhombic tablets ; m. p. 180°. It forms a series of salts, characterised by their water of crystallisation. The sodium, potassium, barium, and silver salts have  $2H_2O$ , and the copper salt,  $5H_2O$ . Its constitution was proved by its conversion into picric acid when heated in small quantities (0.2 gram) at a time at 195°. The simplest method of preparation is from *m*-hydroxybenzoic acid. Five grams of this acid are dissolved in 30 grams of fuming nitric acid ( $D = 1.52$ ), and the solution heated on the water-bath. The nitric acid is expelled on the water-bath, the residue again evaporated down with nitric acid, then with water, and finally extracted with benzene, leaving the pure acid.

T. S. P.

**2 : 4 : 6-Trinitro-*m*-hydroxybenzoic Acid.** RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, 46, 680—682. Compare preceding abstract).—E. F. Smith (*Proc. Amer. Phil. Soc.*, 25) described a compound, which he obtained by treating ethyl *m*-hydroxybenzoate with nitrous acid and then with an excess of potassium hydroxide, as a trinitro-*m*-hydroxybenzoic acid, basing his formula on an estimation of potassium in the monopotassium salt. It might be expected that the hydroxyl hydrogen should also have been replaced by potassium and that the acid might be identical with Wolffenstein and Paar's compound. These authors have repeated Smith's experiment, and find that the product is in reality an ester which cannot be hydrolysed by prolonged boiling with alcoholic or aqueous potash, and is therefore, according to Victor Meyer's rule that ortho-substituents protect a carboxyl or ester group, *ethyl 2 : 6-dinitro-*m*-hydroxybenzoate*. It has m. p. 117°.

J. C. W.

**Action of Hydrogen Cyanide on *p*-Nitrobenzaldehyde.** GUSTAV HELLER [with OTTO FRITSCH] (*Ber.*, 1913, **46**, 280—294).—When *p*-nitrobenzaldehyde is suspended in glacial acetic acid and shaken with a concentrated aqueous solution of potassium cyanide until dissolved, it is converted into *p*-nitromandelonitrile, which may be precipitated by water. The behaviour of this substance towards various reagents, its conversion into nitro- and amino-mandelic acid, and attempts to form anhydrides of the latter acid are described.

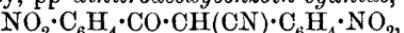
***p*-Nitromandelonitrile,**  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$ , crystallises from benzene in faintly yellow needles, m. p. 109—110°, which on hydrolysis with hydrochloric acid readily yield *p*-nitromandelic acid. Towards sodium hydroxide it is very sensitive, and from the product of the reaction, *p*-nitroso-, *p*-nitro-, and *p*-azoxo-benzoic acids have been isolated.

***a*-Benzoyloxy-*p*-nitrophenylacetic acid,**  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH(OBz)}\cdot\text{CO}_2\text{H}$ , is obtained by benzoylating the acid in pyridine solution, in yellowish-white prisms, m. p. 185—186°. It is easily hydrolysed, and all attempts to reduce it resulted in the production of benzoic acid. The reduction of *p*-nitromandelic acid itself follows different courses; with zinc and acetic acid it results in *p*-azoxymandelic acid,  $\text{C}_{18}\text{H}_{14}\text{O}_7\text{N}_2$ , in yellow needles, which darken at 190°; with stannous chloride the product is *p*-aminophenylacetic acid; ferrous sulphate and ammonia lead to *p*-aminomandelic acid,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , which forms faintly yellow needles from warm water, and a colourless *hydrochloride*. When warmed for a long time in water, it gradually deposits a yellow *anhydride*,  $(\text{C}_8\text{H}_7\text{O}_2\text{H})_x$ , m. p. 210° (decomp.), which is insoluble in organic solvents. *p*-Aminomandelic acid yields a normal *benzoyl* derivative in sodium carbonate solution as a crystalline powder, m. p. 218°, which does not lose water when heated with acetic anhydride, but

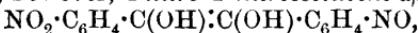
when benzoylated in pyridine in the cold, the product is *3-hydroxy-1-benzoylindole* (annexed formula).

This substance could only be obtained as a colourless, amorphous powder, which was not readily attacked by warm aqueous alkali, but was hydrolysed by cold alcoholic potash to *p*-benzoylamino-mandelic acid.

If the solution of *p*-nitrobenzaldehyde in concentrated potassium cyanide and acetic acid is not immediately precipitated by water, but is left for a day, *pp'*-*dinitrodeoxybenzoin cyanide*,



is deposited. This crystallises in pale yellow needles, m. p. 267—268°, cannot be acetylated, and gives no reaction with ferric chloride. On reduction it yields *p*-aminobenzoic acid, and when dissolved in hot sodium hydroxide it deposits *p*-azoxobenzoic acid. When the red solution in cold sodium hydroxide is at once filtered into hydrochloric acid, however, *4-nitro-4'-nitrosostilbene-aβ-diol*,



can be extracted by means of boiling water from the precipitate. It forms colourless leaflets, m. p. 225° (decomp.), which give an intense, dark red colour with ferric chloride, and form acetyl and benzoyl derivatives which could not be obtained pure.

J. C. W.

**Preparation of Carboxydiarylhydrols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254122).—*6-Hydroxy-2:4-dimethylbenzoic acid*, m. p.  $66^{\circ}$ , is prepared by the action of carbon dioxide on *s*-xyleneol; when it is slowly added to a cooled solution of *p*-diethylaminobenzaldehyde (1 mol.) in concentrated sulphuric acid, it gives rise to a *hydrol*, which can be further condensed with *o*-hydroxytoluic acid to yield *compounds*, which dye wool in violet shades.

Similar *compounds* are also described from *o*-chloro-*p*-diethylaminobenzaldehyde with *m*-hydroxytoluic acid, and its further condensation with *o*-hydroxytoluic acid; from *o*-chlorobenzaldehyde with *6-hydroxy-2:4-dimethylbenzoic acid*, followed by condensation with *o*-hydroxytoluic acid, whilst the tinctorial properties of other similar compounds are tabulated in the original.

F. M. G. M.

**Preparation of 2-Halogen-5-acylaminobenzoylbenzoic Acid.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 254091).—

3-Aminobenzoylbenzoic acid (annexed formula) and its homologues can be readily acetylated by ordinary methods, and on subsequent halogenation (in the same solution) yield 2-halogen-5-acetylaminobenzoylbenzoic acid.

The following compounds are described: *6-Bromo-3-acetylaminobenzoylbenzoic acid*, hard crystals, m. p.  $218^{\circ}$ ; *6-bromo-3-acetylamino-p-toluoylbenzoic acid* (prepared from 3-amino-*p*-toluoylbenzoic acid), colourless needles, m. p.  $226^{\circ}$ ; *2-bromo-5-acetylamino-4-carboxybenzoylbenzoic acid* (from 3-amino-4-carboxybenzoylbenzoic acid, m. p.  $265^{\circ}$ ), short, colourless, rod-like crystals, m. p.  $264-266^{\circ}$ , and *2-chloro-5-p-toluenesulphonyl-p-toluoylbenzoic acid*, colourless rods, m. p.  $135^{\circ}$ .

F. M. G. M.

**$\alpha$ -Hydroxy- $\gamma$ -phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate.** J. BOUGAULT (*Compt. rend.*, 1913, **156**, 555—556).—The acid amide,  $C_{20}H_{28}O_6N$ , obtained by the hydrolysis of  $\alpha$ -hydroxy- $\gamma$ -phenylcrotonamide (compare this vol., i, 269) on treatment

with potassium permanganate in dilute acid solution gives a *compound*,  $C_{20}H_{19}O_3N$ , m. p.  $120^{\circ}$ , to which the author assigns the annexed constitution. The presence of the imide group in the compound is shown (1) by its pseudo-acid properties; (2) by its transformation into an *acid amide*,  $C_{20}H_{21}O_4N$ , m. p.  $171^{\circ}$ , and finally to the dibasic *acid*,  $C_{20}H_{20}O_5$ , m. p.  $204^{\circ}$ , by the action of dilute alkali hydroxides; (3) by the formation of a *N-methyl* derivative, m. p.  $86^{\circ}$ , which liberates methylamine on treatment with alkali. The compound, unlike the acid amide from which it is prepared (*loc. cit.*), is not readily decomposed by alkalis to give benzylpyruvic acid. Its preparation by the elimination of two tertiary hydroxyl groups appears to be the reverse of Wagner's action.

W. G.

**Preparation of Esters of Acetylsalicylic [*o*-Acetoxybenzoic] Acid.** RICHARD WOLFFENSTEIN and JOSEF ZELTNER (*Ber.*, 1913, **46**, 582—586).—Attempts to prepare ethyl *o*-acetoxybenzoate by the action of *o*-acetoxybenzoyl chloride on ethyl alcohol led to the isolation of ethyl salicylate, ethyl acetate, salicylic acid, and salicylic anhydride, the primarily formed ethyl *o*-acetoxybenzoate being decomposed by the hydrogen chloride liberated during the reactions. Satisfactory results were, however, obtained when the reaction was carried out in the presence of a substance capable of absorbing hydrogen chloride, for example, quinoline.

*Trichloroisopropyl o-acetoxybenzoate* was obtained by heating a mixture of *o*-acetoxybenzoyl chloride, trichloroisopropyl alcohol, and dimethylaniline on the water-bath during two hours. It had m. p. about 65°, and could not be distilled without decomposition. Occasionally this ester was obtained in an oily form, which could not be caused to crystallise, but which, according to analysis, was pure.

*Trichloro-tert.-butyl o-acetoxybenzoate*, m. p. 55—57°, after previous softening, b. p. about 180°/16 mm. (slight decomp.), was obtained by heating *o*-acetoxybenzoyl chloride and *tert*.-trichlorobutyl alcohol at 140° in the presence of barium carbonate.

H. W.

**Preparation of Chloroanthraquinonecarboxylic Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P., 255121).—The method previously described (A., 1911, i, 466), in which anthraquinone was chlorinated in sulphuric acid solution in the presence of iodine, has now been extended to the anthraquinone- $\alpha$ - and  $\beta$ -carboxylic acids.

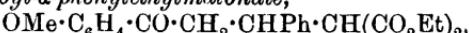
When anthraquinone- $\beta$ -carboxylic acid dissolved in fuming sulphuric acid (in the presence of iodine) is chlorinated at 125°, it gives rise to a *dichloroanthraquinonecarboxylic acid*, yellow crystals, m. p. above 300°, which when heated with *p*-toluidine furnishes an intensely green quinazarin-like derivative, thus indicating that the chlorine atoms are in the para-position with regard to each other.

The analogous compound from anthraquinone- $\alpha$ -carboxylic acid crystallises from acetic acid, and has m. p. 240—241°. The anthraquinonedicarboxylic acids can also be employed in this reaction.

F. M. G. M.

**Saturated  $\delta$ -Ketonic Esters and their Derivatives.** DOROTHY A. HAHN AND ANGIE G. ALLBEE (*Amer. Chem. J.*, 1913, **49**, 171—179).—Kohler (A., 1911, i, 384) has described a general method for the preparation of unsaturated  $\delta$ -ketonic esters; this method has now been applied to the production of the corresponding saturated compounds.

*Ethyl  $\beta$ -anisoyl- $\alpha$ -phenylethylmalonate*,



m. p. 78°, obtained by the condensation of ethyl malonate with anisoyl styryl ketone in presence of piperidine, crystallises in plates or stout needles. The corresponding *methyl* ester, m. p. 104°, forms plates or slender needles. When an alcoholic solution of the ethyl ester is treated with concentrated aqueous solution of potassium hydroxide, the *potassium* salt of  $\beta$ -anisoyl- $\alpha$ -phenylethylmalonic acid separates, which

is converted by acids into the *potassium hydrogen* salt and subsequently into the acid itself.  $\beta$ -*Anisoyl- $\alpha$ -phenylethylmalonic acid, m. p.  $165^\circ$  (decomp.), crystallises from water in slender needles containing water of crystallisation, which is eliminated below  $130^\circ$ . By the action of bromine on a solution of ethyl  $\beta$ -anisoyl- $\alpha$ -phenylethylmalonate in chloroform, the  $\beta$ -*bromo*-derivative,*

$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , m. p.  $97^\circ$ , is obtained, which forms large, six-sided prisms.

When  $\beta$ -anisoyl- $\alpha$ -phenylethylmalonic acid is heated at  $165-170^\circ$  until the evolution of carbon dioxide ceases,  $\gamma$ -*anisoyl- $\beta$ -phenylbutyric acid,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $152^\circ$ , is obtained, which crystallises in plates or prisms; its *methyl ester*, m. p.  $86^\circ$ , forms long plates or prisms, and is hydrolysed by potassium hydroxide with formation of the *potassium salt*, which crystallises with  $1\text{H}_2\text{O}$ . On the addition of bromine to a solution of  $\gamma$ -anisoyl- $\beta$ -phenylbutyric acid in chloroform, two isomeric  $\gamma$ -*bromo*-derivatives,*

$\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , are obtained with m. p.  $144^\circ$  (decomp.) and  $119^\circ$  respectively, which both behave in the same way when treated with sodium carbonate, yielding  $\gamma$ -*anisoyl- $\beta$ -phenyl- $\gamma$ -butyrolactone*,



m. p.  $109^\circ$ , which forms large, six-sided prisms. The methyl ester also yields two  $\gamma$ -*bromo*-derivatives, m. p.  $84^\circ$  and  $122^\circ$ .

E. G.

**A New Oxide of Carbon,  $\text{C}_{12}\text{O}_9$ .** HANS MEYER and KARL STEINER (*Ber.*, 1913, **46**, 813—815).—When mellitic acid is subjected to the action of dehydrating agents, either it remains unchanged or,

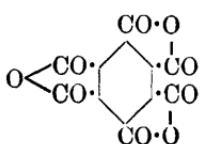
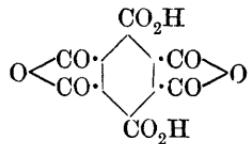
by more drastic treatment, it is converted into the anhydride of pyromellitic acid. As intermediate product, an anhydrocarboxylic acid (annexed formula) appears to be formed. This substance can be isolated in the pure state by prolonged boiling of mellitic acid with thionyl chloride or by heating these substances at  $160^\circ$

during several hours. It forms a white, crystalline powder, which unites with the calculated quantity of water to form mellitic acid, and which, when strongly heated, yields pyromellitic anhydride and carbonised products.

The *oxide [mellitic anhydride]* (annexed formula) is obtained when mellitic acid is boiled under reflux with much benzoyl chloride during six hours. It separates from boiling benzoyl

chloride in colourless crystals, which are perfectly stable and non-hygroscopic. It is practically insoluble in cold water, but unites with warm water to form mellitic acid. It gives characteristic colorations with various solvents of high b. p.; thus with naphthalene, retene, phenanthrene, and fluorene it yields rose-red to bluish-red solutions, and with nitrobenzene a bluish green solution. It darkens when heated above  $320^\circ$ .

H. W.



**Constituents of Essential Oils. [Degradation of the Diketone,  $C_{13}H_{20}O_2$ , Obtained from Selinene.]** FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, **46**, 599—603. Compare this vol., i, 66, 188).—The diketone,  $C_{13}H_{20}O_2$ , obtained by the oxidation of natural selinene and also the diketo-monocarboxylic acid, obtained by the action of ozone on ortho(*a*)selinene, have been further oxidised, whereby a tribasic acid,  $\begin{matrix} CH_2 & -CH_2 & -CH \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H \\ & & | \\ & & CHMe \cdot CH_2 \cdot CH \cdot CO_2H \end{matrix}$ , has been obtained.

The diketone was most advantageously oxidised by a cold solution of bromine in aqueous sodium hydroxide. The acid,  $C_{12}H_{18}O_6$ , so obtained was purified by solution in alcohol and addition of chloroform, when the precipitated product was found to contain chloroform (about one mol. of chloroform to two mols. of acid), which could only be completely removed by heating it in a vacuum at the temperature of boiling xylene. The pure acid had m. p. 188°. Its tribasic nature was shown by converting it into the methyl ester,  $C_{15}H_{24}O_6$ , b. p. 200—205°,  $D^{20} 1.140$ ,  $n_D 1.47948$ ,  $\alpha_D -27^{\circ}48'$ , by the action of methyl iodide on the silver salt. The acid could be recovered unchanged after saponification of the ester.

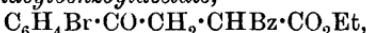
The same acid was obtained when the diketo-monocarboxylic acid,  $C_{14}H_{22}O_4$ , was oxidised by bromine in alkaline solution or by nitric acid.

H. W.

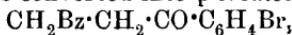
**Studies in the cycloPentadiene Series. III. Certain Derivatives of 5-Nitro-2:3-dibenzoyl- $\Delta^{1:3}$ -cyclopentadiene.** WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc.*, 1913, **35**, 262—272. Compare A., 1912, i, 566; this vol., i, 184).—In the earlier papers, it has been shown that the formation of a cyclopentadiene ring by the condensation of a 1:3-dialdehyde with diphenacyl proceeds more slowly than with acetylacetone. A study has now been made of the behaviour of *pp'*-dimethyl-, *pp'*-dibromo-, and *p*-bromo-diphenacyl. The results show that the effect of methyl groups in the phenyl rings of diphenacyl is to retard the activity of the methylene groups of this ketone, whilst the presence of bromine atoms increases their activity.

By the condensation of *pp'*-dimethyldiphenacyl (Limprecht, A., 1900, i, 600) with sodium nitromalonaldehyde, 5-nitro-2:3-di-p-toluoyl- $\Delta^{1:3}$ -cyclopentadiene,  $\text{NO}_2 \cdot \text{CH} \begin{matrix} < & \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me} \\ & | \\ & \text{CH} \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{Me} \end{matrix}$ , was obtained in a yield of about 75% of the theoretical; it crystallises in yellow prisms, and decomposes at 243—244°. The silver salt decomposes at about 200°, and the monoxime at 150—151°.

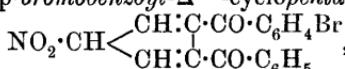
*Ethyl p-bromophenacylbenzoylacetate,*



m. p. 81°, obtained in 75% of the calculated yield by the condensation of *p*-bromophenacyl bromide with the sodium derivative of ethyl benzoylacetate, forms colourless needles, and when boiled with dilute potassium hydroxide, is converted into *p*-bromodiphenacyl,

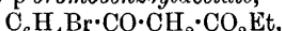


m. p. 116°, which crystallises in white plates with a pearly lustre. The yield of the latter compound amounted to 45% of the theoretical. *5-Nitro-3-benzoyl-2-p-bromobenzoyl- $\Delta^{1:3}$ -cyclopentadiene,*

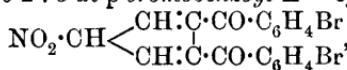


was obtained in a yield of about 75% of the calculated by the condensation of *p*-bromodiphenacyl with nitromalonaldehyde; it forms small, yellow prisms and decomposes at 240—241°.

The sodium derivative of *ethyl p-bromobenzoylacetate* was prepared by Claisen's method. When the ester itself is warmed with aqueous ammonia, *ethyl p-bromobenzoylacetate*,

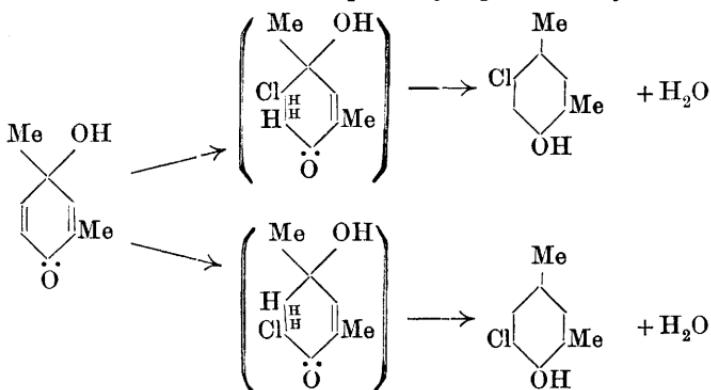


is obtained as a pale yellow, oily liquid which cannot be distilled without decomposition even under 5 mm. pressure. Its sodium derivative condenses with *p*-bromophenacyl bromide to form *ethyl p-bromobenzoyl-p-bromophenacylacetate*,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{C}_6\text{H}_4\text{Br})\cdot\text{CO}_2\text{Et}$ , m. p. 75°, which crystallises in small, colourless prisms; a 60% yield of the theoretical was obtained. When this ester is boiled with dilute potassium hydroxide, it gives 30% of the calculated yield of *pp'*-dibromo-diphenacyl,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Br}$ , m. p. 182°, which forms lustrous, colourless plates, and condenses with nitromalonaldehyde with production of *5-nitro-2 : 3-di-p-bromobenzoyl- $\Delta^{1:3}$ -cyclopentadiene*,



which forms yellow crystals and decomposes at 230—232°. E. G.

**Action of Hydrochloric and Hydrobromic Acids on 2 : 4-Dimethylquinol [2 : 4-Dimethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-1-one].** EUGEN BAMBERGER and EMIL REBER (*Ber.*, 1913, **46**, 787—813).—It has been previously shown (Bamberger and Brady, A., 1901, i, 142) that aqueous sulphuric acid converts 2 : 4-dimethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-1-one into *p*-xyloquinol. Hydrochloric acid, in aqueous solution, transforms it mainly into *5-chloro-m-4-xyleneol* and *6-chloro-m-4-xyleneol*, whilst, in anhydrous glacial acetic acid solution, the latter isomeride is alone obtained. The actions are probably represented by the scheme:



Under similar conditions, hydrobromic acid forms mainly 5-bromo-

*m*-4-xlenol and 6-bromo-*m*-4-xlenol. The identity of the products was also synthetically established. In the light of the present work, a modified interpretation is given to the observation of Bamberger, Büsdorf, and Szolayski (A., 1899, i, 341) that *p*-nitrosotoluene is converted by hydrochloric and hydrobromic acids into 3-chloro-*p*-cresol, in that hemiquinols are now assumed to be formed as intermediate products.

An improved method for the preparation of 1:3-dimethylphenylhydroxylamine is described (compare Bamberger and Brady, *loc. cit.*).

2:4-Dimethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-1-one was heated during one hour at 100° with fuming hydrochloric acid, the mixture diluted with water, and extracted with ether. After drying the ethereal extract, the ether was removed, the residue was allowed to solidify as completely as possible, the solid portions filtered off, and the liquid part submitted to fractional distillation with steam. The following substances were obtained: 5-chloro-*m*-4-xlenol, b. p. 86.5—87°/9 mm. (*phenylurethane*, m. p. 129—130°; *p*-nitrobenzoate, white needles, m. p. 94—95°); 6-chloro-*m*-4-xlenol, white, silky needles, m. p. 90—91° (*benzoate*, glassy prisms, m. p. 84.5—85.5°); a substance, m. p. 169—170°, possibly chlorodixylenol; a substance, m. p. 190°, reddish-yellow needles, possibly chloro-*p*-xyloquinol; traces of *p*-xyloquinol and resin. In a second experiment, dixylenol was obtained in addition to *p*-xyloquinol and *p*-xyloquinone.

5-Chloro-*m*-4-xlenol was prepared by pouring a diazotised solution of 5-amino-*m*-4-xlenol into boiling cuprous chloride solution, and had b. p. 100—101°/17 mm. The phenylurethane and *p*-nitrobenzoate obtained from it were identical with those obtained above.

The synthesis of 6-chloro-*m*-4-xlenol was effected in the following manner: 6-nitro-*m*-4-xylidine was diazotised and treated with cuprous chloride solution, whereby 4-chloro-6-nitro-*m*-xylene, m. p. 42°, was obtained (compare Ahrens, *Annalen*, 1892, 271, 17). The latter was reduced by tin and hydrochloric acid to 6-chloro-*m*-4-xylidine, leaflets, m. p. 98.5—99°, which, according to Bamberger and Cadgène (*Dissert.*, 1903), is also formed by the action of concentrated hydrochloric acid on *as-m*-xylylhydroxylamine. The hydrochloride, sulphate, and oxalate were also prepared. The acetyl derivative forms silky needles, m. p. 158.5°. *Phenyl-4-chloro-m-xylylcarbamide*,  $C_6H_2Me_2Cl \cdot NH \cdot CO \cdot NHPb$ , white, silky needles, has m. p. 217—218° after previous softening. It immediately re-solidifies, melting again at 255° (decomp.). The corresponding thiocarbamide has m. p. 140—140.5° when rapidly heated. When slowly heated it melts at a lower temperature. Diazotisation and subsequent boiling of the aqueous solution converts 6-chloro-*m*-4-xylidine into 6-chloro-*m*-4-xlenol, which is identical with the substance described above.

The action of hydrogen chloride dissolved in glacial acetic acid on 2:4-dimethylcyclohexadienolone gave 6-chloro-*m*-4-xlenol, chloro-*p*-xyloquinol, traces of an oily chloroxylenol, resin, and, possibly, *p*-xyloquinol.

2:4-Dimethylcyclohexadienolone, when heated on the water-bath with aqueous hydrobromic acid, b. p. 122—123°, yielded 5-bromo-*m*-4-xlenol (which possibly contained small quantities of 6-bromo-*m*-4-

xylenol, *as-m*-xylenol, and *p*-xyloquinone), dixylenol, *p*-xyloquinol (or *p*-xyloquinone), and an amorphous acid.

To determine the constitution of the above bromoxylenol, it was treated with bromine in glacial acetic acid solution. The *product* obtained, long, white needles, m. p. 179·5–180°, had the same m. p. as 2 : 3 : 6-tribromo-*p*-5-xylene (obtained by bromination of *p*-xylenol) and 2 : 5 : 6-tribromo-*m* : 4-xylene (obtained by brominating *m*-xylenol), whilst mixtures of any of the three compounds showed no noticeable depression of m. p. When acted on by benzoyl chloride, however, the *benzoates*, m. p. 151–152°, obtained from 2 : 5 : 6-tribromo-*m* : 4-xylene, and from the product of the successive action of hydrobromic acid and bromine on 2 : 4-dimethylcyclohexadienolone, proved to be identical, whereas 2 : 3 : 6-tribromo-*p*-xylenyl-5-benzoate had m. p. 128–129°; hence, the above monobromoxylene is probably 5-bromo-*m*-4-xylene. The *benzoate* and *phenylurethane* of the latter were prepared.

The direct synthesis of 5-bromo-*m*-4-xylene (compare Stoermer and Göhl, A., 1903, i, 848; Orton, Coates, and Burdett, T., 1907, 91, 53) was effected by the action of cuprous bromide solution on a diazotised solution of 5-amino-*m*-4-xylene hydrobromide. It had b. p. 121·5–122·5°/37 mm., and yielded a benzoate, m. p. 49–50·5°, and a phenylurethane, m. p. 136·5–137°, after previous softening, which proved to be identical with the above-mentioned products.

2 : 4-Dimethylcyclohexadienolone, when treated with hydrogen bromide in anhydrous glacial acetic acid solution, gave 6-bromo-*m*-4-xylene, m. p. 76–76·5°, 5-bromo-*m*-4-xylene, probably *p*-xyloquinone, possibly crude monobromo-*p*-xyloquinol and resin. The constitution of the solid bromoxylenol follows from its identity with the product obtained from 6-nitro-*m*-4-xylylene by conversion of the latter into 4-bromo-6-nitro-*m*-xylene, reduction of this substance by iron filings and acetic acid to 6-bromo-*m*-4-xylylene and diazotisation of the latter substance (compare Noelting, Braun, and Thesmar, A., 1901, i, 589).

H. W.

**Preparation of Derivatives of *p*-Benzoquinone.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253091).—When the dinaphthylamino-*p*-benzoquinones (and their derivatives), obtained by the action of *p*-benzoquinone on  $\alpha$ - and  $\beta$ -naphthylamines, are heated with reagents having a high boiling point, they furnish highly coloured compounds, which after sulphonation are of technical importance.

Di-2-naphthylaminodichloro-*p*-benzoquinone,  $C_6O_2Cl_2(NH \cdot C_{10}H_7)_2$  (obtained from tetrachloro-*p*-benzoquinone and  $\beta$ -naphthylamine), when boiled during three hours with nitrobenzene furnishes the *compound*,  $C_{26}H_{15}O_2NCl$ , glistening, green crystals, m. p. above 300°, whilst the isomeric *compound* from  $\alpha$ -naphthylamine has similar properties.

The *compound*,  $C_{52}H_{29}O_4N_4Cl$ , is obtained from di-2-naphthylamino-chloro-*p*-benzoquinone, whilst that from di-2-naphthylamino-*p*-benzoquinone,  $C_6H_2O_2(NH \cdot C_{10}H_7)_2$ , forms a brownish-yellow powder.

F. M. G. M.

**Preparation of Chloroanthraquinones.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 254450). Compare A., 1908, i, 994, and this vol., i, 49, 61).—The preparation of  $\alpha$ -chloroanthraquinones by the replacement of a nitro-group by chlorine has been described (*loc. cit.*), and the reaction has now been extended to the  $\beta$ -nitroanthraquinones.

When a suspension of 2-nitro-3-methylanthraquinone in trichlorobenzene is treated with chlorine at 150—180°, it gives rise to a yellow precipitate consisting of a mixture of  $\omega$ -2-tetrachloro- and  $\omega$ -2-trichloro-3-methylanthraquinones, which by the action of hot concentrated sulphuric acid, followed by treatment with sodium carbonate, furnishes a readily separable mixture of 2-chloroanthraquinone-3-carboxylic acid, m. p. 280°, and of 2-chloroanthraquinone-3-aldehyde, m. p. 229°, whilst the technical mixture of 1:6- and 1:7-dinitroanthraquinones give rise on similar treatment to 1:6-dichloroanthraquinone,  $C_{14}H_6O_2Cl_2$ , m. p. 202—204°.

F. M. G. M.

**Preparation of 1-Halogen-2-aminoanthraquinones.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253683). Compare A., 1904, i, 256).—When 2-aminoanthraquinone-3-sulphonic acid is treated with a halogen (1 mol.) it readily yields a 1-halogen-2-aminoanthraquinone-3-sulphonic acid, which by heating with 80% sulphuric acid is converted into the corresponding 1-halogen-2-aminoanthraquinone.

Sodium 1-chloro-2-aminoanthraquinone-3-sulphonate forms orange-red crystals; 1-chloro-2-aminoanthraquinone, yellow needles, m. p. 228—229°; sodium 1-bromo-2-aminoanthraquinone-3-sulphonate, orange-red leaflets, and 1-bromo-2-aminoanthraquinone, glistening, brownish-red leaflets, m. p. 305°, which on further bromination yields 1:3-dibromo-2-aminoanthraquinone.

F. M. G. M.

**Preparation of Nitro-p-acyldiaminoanthraquinone.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D. R.-P. 254185).—Nitro-p-acyldiaminoanthraquinones are readily obtained by the action of nitric acid (D 1·5) at temperatures not exceeding 25° on diacyl-1:4-diaminoanthraquinones, the nitro-group entering the ortho-position with respect to an amino-group.

2-Nitro-1:4-diacyldiaminoanthraquinone forms yellowish-brown needles, m. p. 237° (decomp.), and on hydrolysis furnishes 2-nitro-1:4-diaminoanthraquinone as a blue, crystalline powder.

2-Nitro-1:4-diaminoanthraquinonourethane, orange-red needles, m. p. 230—232°, is obtained in a similar manner from 1:4-diaminoanthraquinonourethane.

F. M. G. M.

**Preparation of Dianthraquinonylthio-ethers.** FARBFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254561).—Dianthraquinonyl thio-ethers are readily prepared by heating anthraquinone mercaptans.

$\beta\beta$ -Dianthraquinonyl thio-ether, yellow needles, is thus obtained from anthraquinone  $\beta$ -mercaptan; the isomeric  $\alpha\alpha$ -dianthraquinonyl thio-ether is a reddish-brown, crystalline powder, whilst  $\alpha\beta$ -dianthraquinonyl thio-ether is prepared by heating together molecular proportions of  $\alpha$ - and  $\beta$ -anthraquinone mercaptans.

6-Chloro-1-benzoylaminoanthraquinone when treated with sodium

sulphide furnishes 1-benzoylaminoanthraquinone 6-mercaptan ; this, when heated, gives rise to 1 : 1'-dibenzoyldiamino-6 : 6'-dianthraquinonyl thio-ether, which crystallises from nitrobenzene in yellow needles.

F. M. G. M.

**Anthraflavone-G.** EDUARD HEPP, RUDOLF UHLENHUTH, and FRITZ RÖMER (*Ber.*, 1913, **46**, 709—712).—To the above dye (D.R.-P. 199756) has been attributed the structure 1 : 2 : 5 : 6-diphthaloylanthracene (Bohn, A., 1910, i, 405). In its preparation by the action of calcium hydroxide on  $\omega$ -dichloromethylanthraquinone, the occurrence of large quantities of anthraquinone-2-carboxylic acid as by-product suggests that the first product of the reaction is anthraquinone-2-aldehyde, which then undergoes change into the corresponding acid and alcohol, the latter of which then condenses to anthraflavone. According to this view the dye must be diphthaloylstilbene, and its formation by the action of lead oxide on 2-methylanthraquinone and its derivatives would be analogous to the well-known formation of stilbene from toluene. A convincing proof of the untenability of the older view with regard to the structure is given by the preparation of the dye in better yields than hitherto, from  $\omega$ -dibromo-2-methylanthraquinone by the action of copper powder or sodium iodide on solutions in nitrobenzene and acetone respectively.

The last method of preparation can be extended to substituted anthraflavones. 1-Chloro-2-methylanthraquinone, yellow needles, m. p. 171°, obtained from 2-methylanthraquinone-1-sulphonic acid by heating with potassium chlorate and hydrochloric acid, when treated with bromine in nitrobenzene solution is converted into 1-chloro- $\omega$ -dibromo-methylanthraquinone, yellow leaflets, m. p. 176° ; the action of sodium iodide on the acetone solution of this substance produces 1 : 1'-dichloro-anthraflavone (2 : 2'-dichloro-3 : 4 : 3' : 4'-diphthaloylstilbene), a yellow, crystalline powder.

The new formula for this class of dye also gives a satisfactory explanation of other properties, such as the quantitative conversion into the corresponding anthraquinonecarboxylic acids.

D. F. T.

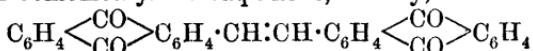
**2-Methylanthraquinone.** FRITZ ULLMANN AND KARL LUDWIG KLINGENBERG (*Ber.*, 1913, **46**, 712—725).—The authors have found that for the preparation of anthraquinone-2-aldehyde in larger quantities, the best method is by the intermediate formation of  $\omega$ -dibromomethylanthraquinone. The stilbene structure for anthraflavone (see Hepp, Uhlenhuth, and Römer, preceding abstract) is confirmed.

*Anthraquinone-2-aldehyde* can be obtained by the gradual addition of a mixture of chromic acid and acetic acid to a suspension of 2-methylanthraquinone in acetic anhydride containing a little sulphuric acid, and also by heating  $\omega$ -dibromomethylanthraquinone (prepared by the action of bromine on the methylanthraquinone in nitrobenzene solution at 150—160°) with concentrated sulphuric acid at 125—130°. The aldehyde forms pale yellow leaflets or needles, m. p. 188—189° (corr.) ; *phenylhydrazone*, reddish-violet needles, m. p. 242° (corr.) ; *oxime*, straw-yellow needles, m. p. 238—239° ; *semicarbazone*, yellow needles, m. p.

397° (corr.); *azine*, yellow needles, m. p. 410°: *sodium disulphite compound*, colourless crystals.

When a suspension of anthraquinone-2-aldehyde in dimethylaniline with zinc chloride is heated on a water-bath, condensation occurs; the same substance, *2-anthraquinonyltetramethylidiaminodiphenylmethane*, is obtained when  $\omega$ -dibromomethylanthraquinone is warmed with dimethyl-aniline and zinc chloride; it crystallises in red needles, m. p. 240—241° (corr), and can be oxidised to a green colouring matter.

The reaction between  $\omega$ -dibromomethylanthraquinone and dimethyl-amine or diethylamine follows a different course at the b. p. of the mixture, the product being the same as that from the action of copper powder on dibromomethylanthraquinone, namely, anthraflavone,

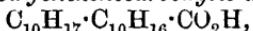


(diphthaloylstilbene, dianthaquinonylethylene), identical with the known dye; it is oxidised by sodium dichromate and nitric acid to anthraquinone-2-carboxylic acid, m. p. 285°, and when boiled with bromine in nitrobenzene solution yields the *dibromide*, m. p. above 400°; this on boiling with diethylaniline regenerates the anthraflavone.

If  $\omega$ -dibromomethylanthraquinone is heated at 240—250°, hydrogen bromide is eliminated and *2:2'-dianthaquinonylacetylene dibromide*, yellow needles, m. p. 360°, is obtained; when heated with diethylaniline or alkali phenoxide, the last substance is converted into *2:2'-dianthaquinonylacetylene (diphthaloyltolane)*, yellow leaflets, m. p. 350—353°, which unites with bromine to yield the dibromide, and is oxidised by chromic acid in the presence of nitric acid to anthraquinone-2-carboxylic acid; it can also be reduced by hyposulphite to a red vat, which dyes cotton yellow.

D. F. T.

**Action of Carbon Dioxide on the Magnesium Compound of Fenchyl Chloride.** GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1913, **46**, 645—648).—Fenchyl chloride reacts with magnesium in the course of a week, and when carbon dioxide is passed through the product, the reaction leads to as complicated a mixture as Houben experienced in the case of pinene hydrochloride (*A.*, 1893, i, 42). When the ethereal extract is shaken with sodium carbonate it gives, starting from inactive fenchyl chloride, a clear aqueous solution containing hydrodifenchencarboxylic acid and an emulsion from which a small quantity of *hydrodifenchencarboxylic acid*,



may be isolated in the form of long, glistening needles, m. p. 106°, whilst the predominating, neutral portion, on fractionation, yields an almost inactive *hydrodifenchene*,  $\text{C}_{20}\text{H}_{34}$ , as a glycerol-like liquid, b. p. 155—157°/10 mm.,  $D_4^{27} 0.9564$ ,  $n_D 1.50928$ , and also inactive fenchene, and probably some fenchyl alcohol.

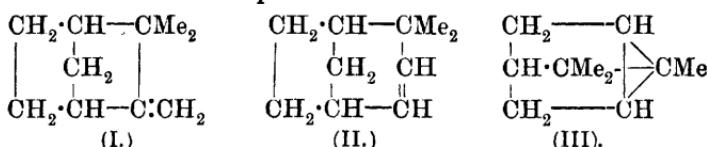
Active fenchyl chloride,  $a_D^{18} - 6^{\circ}0'$ , however, gives a better yield of *hydrodifenchencarboxylic acid*,  $\text{C}_{10}\text{H}_{17} \cdot \text{CO}_2\text{H}$ , in the form of a white, very soluble, inactive mass, b. p. 140—142°/20 mm., m. p. 52—53°, which yields an *amide*, m. p. 107°, and an *anilide*, m. p. 105—106°. On the other hand, no hydrodifenchencarboxylic acid is obtained, and less neutral substances are formed, from which active *hydrodifenchene*,

b. p. 155—156°/10 mm.,  $D_4^{17}$  0.9652,  $n_D$  1.51299,  $a_D^{18} + 5^{\circ}30'$ , and an active fenchene,  $a_D^{20} + 4^{\circ}17'$ , have been isolated. J. C. W.

**Preparation of Esters of Dibromo- $\beta$ -phenylpropionic Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254666. Compare this vol., i, 63).—*Fenchyl dibromo- $\beta$ -phenylpropionate*, colourless, tasteless prisms, m. p. 105°, and of therapeutic value, is readily prepared by heating together fenchyl alcohol and dibromo- $\beta$ -phenylpropionyl chloride in benzene solution. F. M. G. M.

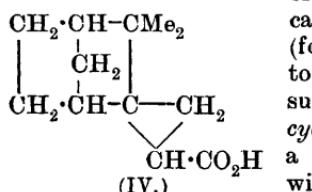
**Preparation of a Fenchyl Ester.** CHEMISCHE FABRIK VON KERESZTY, WOLF & CIE (D.R.-P. 253756).—*Fenchyl salicylate*, m. p. 51°, is of therapeutic value, and can be prepared by known methods from fenchyl alcohol and salicylic acid (or methyl salicylate). F. M. G. M.

**The Constitution of Camphene.** EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, **46**, 759—768).—Of the three suggested formulae for camphene:



the first (Wagner's formula) has been received with most favour (compare Semmler, A., 1909, i, 170; Harries and Palmén, A., 1910, i, 497; Komppa, A., 1911, i, 388), and has received additional support from molecular refractivity considerations (von Auwers, A., 1912, ii, 214). A final decision on purely chemical grounds appears to be possible by the application of ethyl diazoacetate.

It has already been shown that benzene and ethyl diazoacetate couple with loss of nitrogen to form ethyl norcaradienecarboxylate,  $\text{CH}:\text{CH}\cdot\text{CH}>\text{CH}\cdot\text{CO}_2\text{H}$ , which after hydrolysis can be oxidised to cyclopropane-*trans*-1:2:3-tricarboxylic acid (Braren and Buchner, A., 1901, i, 385). If this reaction could be applied generally, a substance of formula I should yield 2:2-dimethylnorcamphane-3-*spiro*cyclopropanecarboxylic acid (formula IV annexed), which might be oxidised to cyclopropane-1:1:2-tricarboxylic acid; a substance of formula II would give finally cyclopropane-1:2:3-tricarboxylic acid, whilst a substance of formula III would not react with ethyl diazoacetate. Experiment gives results in entire accord with the first of these possibilities, thus providing apparently final evidence in favour of formula I.



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It is interesting to note that the condensation product of ethyl diazoacetate and camphene is a *spirane* molecule with three-ring systems, this view being supported by determinations of the molecular refraction and dispersion.

The camphene used was mainly prepared from bornyl chloride by the action of aniline (Ullmann and Schmid, A., 1911, i, 70); the same condensation product was always obtained. For the condensation, a mixture of 5 grams of camphene with 5 grams of methyl diazoacetate was gradually added to 30 grams of camphene (m. p. 44—45°; b. p. 156—157°/745 mm.;  $[\alpha]_D^{20} + 62.59^\circ$ ) containing 1 gram of copper powder as catalyst, at 160—165°. A practically theoretical volume of nitrogen is liberated, and *methyl 2 : 2-dimethylnorcamphane-3-spirocyclopropanecarboxylate* is obtained as a colourless oil, b. p. 126°/14 mm.,  $[\alpha]_D^{18.5} + 6.79^\circ$ ,  $D_4^{18.5} 1.0268$ ,  $n_D^{18.5} 1.48567$ , with an odour resembling camphene; in suspension in sodium carbonate solution it is stable towards potassium permanganate. The corresponding *ethyl ester*, obtained by the application of ethyl diazoacetate, has b. p. 128—136°/14 mm. The esters can be hydrolysed to the corresponding acid (formula IV) by alcoholic potassium hydroxide, and the product was purified by conversion into the acid *chloride*, which is changed by concentrated aqueous ammonia into the *amide*, colourless leaflets, m. p. 124°; *2 : 2-dimethylnorcamphane-3-spirocyclopropanecarboxylic acid*, obtained by hydrolysis of this, forms colourless needles, m. p. 108°; the *calcium*, *barium*, *lead*, and *silver* salts were obtained by precipitation from an aqueous solution of the *ammonium salt*. When an intimate mixture of the amide with sodium hypobromite solution is warmed on a water-bath, *2 : 2-dimethylnorcamphane-3-spiroaminocyclopropane* is produced as an unpleasant smelling oil; *hydrochloride*, colourless leaflets, m. p. 253° (decomp.); *yellow aurichloride*, m. p. 160° (decomp.); *platinichloride*, golden prisms decomposing at 237°; *yellow picrate*, m. p. 201°.

If the methyl ester obtained by the condensation of camphene and methyl diazoacetate is treated in alcoholic solution with sodium, it becomes reduced to *2 : 2-dimethylnorcamphane-3-spirocyclopropane-methylol*,  $C_{11}H_{17}\cdot CH_2\cdot OH$ , a colourless, viscous liquid, b. p. 129°/12 mm.,  $a_D^{20} + 26.79^\circ$ ,  $D_4^{19} 0.9972$ ,  $n_D^{19} 1.50205$ , with an odour resembling that of camphene; *phenylurethane*, needles, m. p. 234°.

The oxidation of *2 : 2-dimethylnorcamphane-3-spirocyclopropanecarboxylic acid* was effected in dilute sulphuric acid by potassium permanganate, the last substance is added as required, and the process occupies many hours; the oxidation tends to proceed too far, and only a relatively small quantity of *cyclopropane-1 : 1 : 2-tricarboxylic acid* was obtained, which on heating lost carbon dioxide with formation of a mixture of *cyclopropane-1 : 2-cisdicarboxylic acid* and the corresponding anhydride; acetyl chloride dehydrated this to the pure anhydride, which was definitely recognisable.

D. F. T.

**The Constituents of Ethereal Oils. High-boiling Camphor Oil.** FRIEDRICH W. SEMMLER and IRENE ROSENBERG (*Ber.*, 1913, **46**, 768—774).—A more careful investigation of the constituents of the blue-coloured, high-boiling camphor oil (compare Schimmel & Co., A., 1909, i, 816).

The oil was separated by distillation into three fractions, b. p. 130—150°/10 mm., 150—170°/10 mm., and 170—190°/10 mm.

The first fraction contained limene and a little cadinene, which were

identified by their hydrogen chloride additive compounds; limene trihydrochloride, m. p. 79°, has before solidification the following properties, b. p. 177—189°/8 mm., D<sup>20</sup> 1·0370, n<sub>D</sub> 1·50152, [α]<sub>D</sub> ± 0°. The presence of three ethylenic linkings in limene was proved by reduction in acetic acid with hydrogen and platinum black to *hexahydrolimene*, an optically inactive liquid, b. p. 123—125°, D<sup>20</sup> 0·8244, n<sub>D</sub> 1·45423. This fraction also contained a sesquiterpene, C<sub>15</sub>H<sub>24</sub>, b. p. 129—133°, D<sup>20</sup> 0·9015, n<sub>D</sub> 1·50058, [α]<sub>D</sub> + 3°, for which the name *sesquicamphene* is suggested; although the data suggest a bicyclic diolefinic substance, no solid hydrogen chloride additive compound was obtainable.

The second fraction had as almost sole constituent a sesquiterpene alcohol, C<sub>15</sub>H<sub>26</sub>O, b. p. 159—162°, D 0·95413, for which the name *sesquicamphenol* is suggested; it was purified by conversion into the sodium alcoholate and regeneration by treatment with water; by heating with potassium hydrogen sulphate at 180° for two hours a molecule of water is eliminated with formation of a *hydrocarbon*, b. p. 125—130°, D<sup>20</sup> 0·9138, n<sub>D</sub> 1·50895, [α]<sub>D</sub> + 50°, which is probably a reduced naphthalene derivative; no solid hydrochloride was obtainable.

The least volatile fraction consisted chiefly of hydrocarbons, from which small quantities of oxygen compounds were removed by heating with sodium; the purified product, b. p. 180—190°/11 mm., D<sup>20</sup> 0·9276, n<sub>D</sub> 1·51986, [α]<sub>D</sub> + 1°, is a diterpene, C<sub>20</sub>H<sub>32</sub>, a class of substance generally absent from ethereal oils. If this crude product is treated in ethereal solution with hydrogen chloride, a *tetrahydrochloride*, thin tablets, m. p. 129—131°, is obtained, from which the hydrocarbon can be regenerated in a purer condition by treating successively with a mixture of sodium acetate and acetic acid and then alcoholic potassium hydroxide; it then has b. p. 177—178°/6 mm., D<sup>20</sup> 0·8870, n<sub>D</sub> 1·50339, [α]<sub>D</sub> ± 0°. This monocyclic hydrocarbon, for which the name *α-camphorene* is proposed, is reduced by hydrogen and platinum black to *octahydro-α-camphorene*, C<sub>20</sub>H<sub>40</sub>, b. p. 174—176°/9 mm., D<sup>20</sup> 0·8526, n<sub>D</sub> 1·46470, [α]<sub>D</sub> ± 0°. From the oily residue obtained in the preparation of the tetrahydrochloride, could be regenerated by alcoholic potassium hydroxide a bicyclic isomeride, *β-camphorene*, C<sub>20</sub>H<sub>32</sub>, b. p. 170—180°/10 mm., D<sup>20</sup> 0·930, n<sub>D</sub> 1·518°, [α]<sub>D</sub> ± 0°, which gives no solid additive compound with hydrogen chloride.

The blue colour of all high-boiling fractions of camphor oils is due to such small traces of a coloured substance that no particulars of its composition could be determined.

D. F. T.

**Caoutchouc and Guttapercha Resins.** G. H. HILLEN (*Arch. Pharm.*, 1913, **251**, 94—121).—Proximate analyses have been made of the resinous portions of various kinds of caoutchouc and allied products.

The resinous portion of "pontianac," "bresk" or "dead Borneo," an inferior "rubber" obtained from the latex of *Dyera costulata*, Hook, was found to contain lupeol acetate, α-amyrin acetate, β-amyrin acetate, and a resen (compare Sack and Tollens, A., 1904, i, 1011; Cohen, A., 1907, i, 211, 230). The formula C<sub>26</sub>H<sub>42</sub>O is suggested for lupeol.

The caoutchouc (Ceara rubber) of *Manihot glaziovii*, prepared by the

Lewa process in German East Africa, contains 7% of resin, composed of *isoocholesterol acetate*, a soft resin, and a green, amorphous substance.

Guayule caoutchouc contains 16% of resin, composed of soft resinous material, probably formed by the oxidation of the essential oil contained in the plant, which contains no substances giving the phytosterol reactions (compare Alexander, A., 1911, i, 897).

"Malabuwai guttapercha" from *Alstonia grandifolia*, Miq., contains  $\alpha$ -amyrin acetate,  $\beta$ -amyrin acetate, an oily substance, and traces of a yellow resen.

The resin of *Palaquium Gutta* from German New Guinea contains lupeol cinnamate, an oily substance, and a small quantity of a resen.

A table giving the percentages of resin, the appearance of the resins under the microscope, and their reactions with the usual phytosterol reagents for a number of commercial caoutchoucs is provided.

The colour reactions of most of the substances referred to in the paper with phytosterol reagents are tabulated. T. A. H.

**The Viscous Transformation of Caoutchouc.** A. von Rossem (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 78—83).—According to Gorter (*Mededeelingen over Rubber*, 1911) the transformation of ordinary caoutchouc into the viscous, glue-like modification under the influence of heat, light, and certain chemical reagents is due to depolymerisation. It is suggested that normal polymerised caoutchouc is under ordinary conditions metastable, and that the formation of the viscous variety simply corresponds with the transition from the metastable to the stable form. In support of this view, Gorter describes experiments which show that if a benzene solution of caoutchouc, prepared and kept in the dark, is mixed with a caoutchouc solution which has been exposed to sunlight for some time, the viscosity of the mixed solution gradually diminishes when the solution is protected from the light by means of red glass. In exactly similar circumstances, the viscosity of the original solution was found to remain constant, and the difference in behaviour is supposed to be due to the "inoculation" of the original solution with the stable modification when this solution is mixed with the insolated solution.

To test this theory, measurements of the viscosity of 1% solutions of caoutchouc have been made, with special reference to the influence of light. After exposure to the light from an arc lamp for some hours, the viscosity is found to have diminished, but the subsequent fall is very slow if the solution is kept in the dark, and does not differ from that exhibited by a portion of the original solution which has not been exposed to the arc light. If diffused daylight is allowed access to the solution, the subsequent fall in the viscosity is very much more rapid.

Similar experiments were made with solutions exposed to the light from a Uviol lamp. The results obtained in both series show that there is no after-effect of the light in so far as the viscosity of the solutions is concerned. In some of these experiments the caoutchouc solutions were exposed to the Uviol lamp in glass vessels, whilst in others, quartz vessels were employed. After six and three-quarter

hours' exposure, the time of out-flow of a certain volume of solution was found in a particular case to have fallen from 560 to 412 seconds with the glass apparatus, whilst the time required by the solution after exposure in the quartz tube was only 56 seconds. These results indicate that the active rays are the short-waved rays which are absorbed by glass.

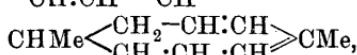
H. M. D.

The Hydrohaloids of Artificial and Natural Caoutchoucs, and the Caoutchouc-like Substances Regenerated from Them. CARL D. HARRIES (*Ber.*, 1913, **46**, 733—743).—Contrary to the statement of Weber (*A.*, 1900, i, 353), caoutchouc forms additive compounds with hydrogen bromide and hydrogen iodide, as well as with hydrogen chloride. The method followed was to saturate the chloroform solution of the caoutchouc with the gas, and then after several hours to precipitate by alcohol.

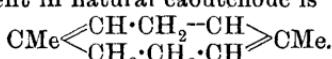
Natural caoutchouc unites with two molecules of each acid, forming substances :  $C_{10}H_{18}Cl_2$ ,  $C_{10}H_{18}Br_2$ ,  $C_{10}H_{18}I_2$ ; guttapercha, caoutchouc obtained by the polymerisation of isoprene under the influence of heat and of sodium, and also caoutchouc obtained from dimethylbutadiene, behave in a similar manner, except that the additive compounds of the two former synthetic caoutchoucs with hydrogen iodide, after precipitation, contain only one molecule of hydrogen iodide.

The halogen hydride is only partly removed by treatment with organic bases, but pyridine and piperidine at 125—145° act on the compounds, if necessary in benzene solution, with elimination of the two molecules of hydracid. The products are not identical with natural caoutchouc, but resemble more the synthetic substance obtained by the action of sodium (Harries, *A.*, 1911, i, 798). The elimination of halogen hydride by heating with sodium hydroxide or sodium amide gives a halogen-free caoutchouc, which, however, is apparently different from the natural product and from that obtained by polymerisation with sodium. The dihydrochloride of guttapercha, when treated for the elimination of two molecules of hydracid, yields a compound resembling caoutchouc, possibly indicating a conversion of guttapercha into caoutchouc.

From a consideration of the difficulty with which the above new forms of caoutchouc undergo ozonisation, it is tentatively suggested that their molecules include a conjugated pair of ethylenic linkings, for example,  $CHMe < \begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \\ CH:CH - CH \end{matrix} > CMe$  and



whilst the arrangement in natural caoutchouc is



[With EWALD FONROBERT.]—From natural caoutchouc were prepared the dihydrochloride, dihydrobromide, and dihydriodide; from caoutchouc, obtained by polymerisation on warming, were prepared a dihydrochloride, dihydrobromide, and a hydriodide; "sodium polymerised" caoutchouc yielded a dihydrochloride, a hydrobromide, and a hydriodide; "dimethylbutadiene" caoutchouc yielded a dihydrochloride, dihydro-

*bromide*, and a *dihydriodide*; guttapercha yielded a *dihydrochloride*, *dihydrobromide*, and a *dihydriodide*. Although affected by hydrofluoric acid no hydrofluoride was obtainable from any of the preceding hydrocarbon substances. The above hydrohaloids are amorphous, sometimes viscous, substances, which undergo decomposition at temperatures between 100° and 200°.

The caoutchouc regenerated from the dihydrochlorides by treatment with pyridine or piperidine at 125—135° resembles “sodium isoprene” caoutchouc in solubility and slow absorption of ozone to produce a diozonide, but yields a relatively stable *dihydrobromide* and *dihydriodide*.

D. F. T.

**Theory of Vulcanisation.** DAVID SPENCE (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 84—85).—Polemical against Kindscher and Hinrichsen (A., 1912, i, 1007) and Ostwald (A., 1912, i, 706).

H. M. D.

**$\alpha$ - and  $\beta$ -Antiarin and on Crystallised Albumin from Antiaris Latex.** HEINRICH KILIANI (*Ber.*, 1913, 46, 667—680. Compare A., 1897, i, 91, and A., 1911, i, 138).—Crystallised rhamnose, m. p. 93—94°, and antiarigenin, m. p. 188°, have been obtained from  $\beta$ -antiarin by means of dilute hydrochloric acid. The  $\alpha$ - and  $\beta$ -antiarins only differ in their sugars, and careful analyses lead to the formulæ  $C_{27}H_{40}O_{10}, 4H_2O$  and  $C_{27}H_{40}O_{10}, 3H_2O$  respectively, whilst antiarigenin receives the formula  $C_{21}H_{28}O_5$ . The hydrolysis of these glucosides by means of dilute acids is accompanied by the extensive formation of resinous matter, which seems to indicate the presence of a labile aldehyde or ketone group in antiarigenin. The action of the common moulds is quite unavailing, although the glucosides soon disappear from unpreserved antiaris latex, which may, therefore, contain a specific enzyme.

Antiarose could not be obtained crystalline, but the lactone of antiaronic acid, well-defined monoclinic crystals of the epidote type, has been converted into the following derivatives, which differ from those of the known metameric acids: *phenylhydrazone*, long needles, m. p. 143—145°; *quinine salt*, very slender needles, m. p. 180—181°, more soluble in cold water than the *quinine salt* of rhamnonic acid, which forms nodules of silky needles, m. p. 180—182°; *brucine salt*, small, pointed needles with  $2H_2O$ , m. p. 118—119°; *brucine salt* of rhamnonic acid, large crystals with  $7H_2O$ , m. p. 120—126°.

$\alpha$ -Antiarin is considerably attacked by sodium amalgam, and forms an *oxime*,  $C_{27}H_{41}O_{10}N, 2H_2O$ , m. p. 239—240°, which, however, like the parent substance, is unaffected by aluminium amalgam in the cold. Antiarigenin yields a *semicarbazone*,  $C_{22}H_{31}O_5N_3$ , which begins to sinter at 225°.

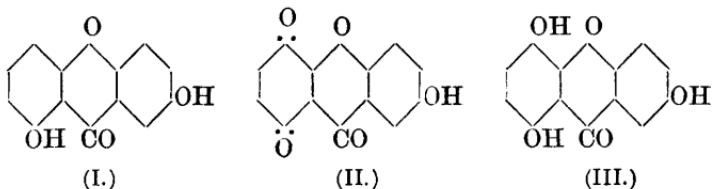
Attempts to oxidise the glucosides with silver oxide or hydrogen peroxide were without result, but the action of chromic acid, nitric acid, or permanganate promises to throw light on their constitution.

“Antiaris residue,” the portion of the latex which is insoluble in alcohol, contains a protein which may be extracted to the extent of 6·3% by means of 0·8% acetic acid (compare Kotake and Knoop,

A., 1912, ii, 81). It may be recrystallised from hot 10% acetic acid in the form of white, hygroscopic crystals, which darken at 250°,  $[a]_D - 15.2^\circ$ . The substance may be titrated, using phenolphthalein, but it could not be shown that the magnesium which accompanies the crude protein is combined as a salt.

J. C. W.

**Anthocyanin. III. An Anthocyanin-like Oxidation Product of Euxanthone.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1913, **46**, 649—650. Compare A., 1912, i, 42, 292).—When euxanthone (2:8-hydroxyxanthone) (I), which is obtained by treating Indian-yellow with hydrochloric acid and ammonia, is oxidised by chromic acid in glacial acetic acid, 2-hydroxy-5:8-quinoxanthone (II) is formed in small, sparkling, deep red needles, which give a blue solution in alkalis and a red in concentrated sulphuric acid. On reduction with zinc dust in acetic anhydride suspension, an amorphous product is obtained, which, on hydrolysis, yields 2:5:8-trihydroxy-xanthone (III) in small, light yellow, silky needles with  $2H_2O$ , m. p. 328—330°. This compound, like its isomeride, gentisein, gives a blood-red colour with sodium amalgam, and its alcoholic solution dyes mordanted cotton. It forms a triacetyl derivative,  $C_{19}H_{14}O_8$ , in faintly yellow needles, m. p. 226—230°, and with diazomethane a trimethoxyxanthone,  $C_{16}H_{14}O_5$ , in pale yellow needles, m. p. 194—195°.



J. C. W.

**Action of Sodium Methoxide on Bilirubin, Bilirubin, and Hemibilirubin.** HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1913, **46**, 439—442).—Bilirubin and hemibilirubin resemble the earlier examined pyrrole derivatives (this vol., i, 71, Fischer and Bartholomäus, this vol., i, 209) in their behaviour towards sodium methoxide at elevated temperatures. When heated with sodium methoxide in alcoholic solution at 220—230°, each gives rise to 2:4:5-trimethyl-pyrrole-3-propionic acid (identified by the picrate; compare Fischer and Bartholomäus, *loc. cit.*), together with a little xanthobilirubin acid (see below).

Bilirubin under similar treatment gives in good yield an acid substance, yellow prisms, m. p. 274°, for which the name *xanthobilirubin acid* (or *xanthopyrrolecarboxylic acid*) is proposed; sodium salt sparingly soluble. It is possible that the acid is the pure form of the dehydrobilic acid of Piloty and Thannhauser (A., 1912, i, 925). On reduction by a mixture of hydriodic and acetic acids it is reconverted into bilirubin acid.

The above results must be regarded as a proof of the presence of a third pyrrole ring in bilirubin and hemibilirubin.

D. F. T.

**The Identity of Baphinitone with Homopteroocarpin.** HUGH RYAN and R. FITZGERALD (*Proc. Roy. Irish Acad.*, 1913, **30**, 106—108).—Baphinitone,  $C_{17}H_{16}O_4$ , obtained from barwood, forms colourless, acicular crystals, m. p.  $84^\circ$  (Anderson, T., 1876, ii, 582, gives m. p. about  $88^\circ$ , and formula  $C_{26}H_{26}O_6$ ). In 4% solution in chloroform it has  $[\alpha]_D^{20} - 211.7^\circ$ . Similarly, homopteroocarpin, obtained from santalin by the method of Cazeneuve and Hugounenq (A., 1887, 971; 1889, 160), was found to melt at  $84^\circ$  (Brooks, A., 1911, i, 154, gives  $86^\circ$ ), and to have  $[\alpha]_D^{20} - 211^\circ$  in 4% solution in chloroform. In appearance, solubility and m. p., homopteroocarpin is identical with baphinitone, and a mixture of the two substances melts at the same temperature as each of its constituents.

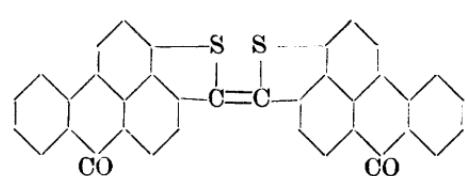
A solution of homopteroocarpin in chloroform reacts readily with bromine in bright sunlight with the formation of a substance,  $C_{17}H_{14}Br_2O_4$ , colourless needles, m. p.  $200^\circ$ , and of a yellow, amorphous solid. Contrary to Cazeneuve's statement, homopteroocarpin does not yield methyl iodide when treated with hydriodic acid, and thus contains no methoxy-group; nevertheless, a phenolic substance is obtained by the action of hydriodic acid on it.

H. W.

**Optical Activity of Tannin.** EMANUEL NAVASSART (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 97—99).—The rotatory power of tannin solutions has been examined with reference to the influence of concentration. In the case of aqueous solutions, the rotatory power varies very considerably with the concentration, the value of  $[\alpha]_D^{20}$  increasing from  $49.8^\circ$  to  $89.7^\circ$  when the concentration falls from 20% to 0.08%. When dissolved in ethyl alcohol, acetone, and acetic acid, the rotatory power of tannin is much smaller, and varies less with the concentration. For concentrations between 1% and 20%, the observed values of  $[\alpha]_D^{20}$  vary from  $12.7^\circ$  to  $16.9^\circ$  in alcohol, from  $12.9^\circ$  to  $15.1^\circ$  in acetone, and from  $9.4^\circ$  to  $14.5^\circ$  in acetic acid. These results seem to show that the rotatory power of the tannin increases as the degree of dispersity of the substance in the various solvents diminishes.

H. M. D.

[**Preparation of Derivatives of Benzanthrone Containing Sulphur.**] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE (D.R.-P. 254098).—The action of chlorine (or chlorinating reagents) on 2-methylbenzanthrone (m. p.  $199^\circ$ ) gives rise to *chloromethylbenzanthrone*, m. p.  $175^\circ$ ; this, when heated with sulphur or polysulphides during two hours at  $200—240^\circ$ , yields the compound (annexed formula), glistening, coppery needles.



The preparation of *bromomethylbenzanthrone*, *dichloro-2-methylbenzanthrone*, and of *nitro-* and *amino-benzanthrone* with their sulphur derivatives is also described.

F. M. G. M.

**Preparation of Homologues of Hydroquinine.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 254712. Compare A., 1892, 1253).—The alkylation of hydrocupreine has furnished the following derivatives : *Ethylhydrocupreine*,  $C_{21}H_{28}O_2N_2$ , is amorphous, but its sulphate forms colourless needles, whilst *propylhydrocupreine*,  $C_{22}H_{30}O_2N_2$ , colourless crystals, has m. p.  $142^\circ$ . F. M. G. M.

**Alkaloids of Javanese Coca** [*Erythroxylon novogranatense*]. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, **30**, 204—210; 1912, **31**, 249—259. Compare A., 1906, ii, 315).—The method of analysis previously described has been slightly modified, since it is found that the insoluble barium salts, obtained by heating the alkaloids with barium hydroxide, contain small quantities of barium cinnamate in addition to barium  $\beta$ -truxillate. The cinnamic acid is recovered by agitating the mixed acids with chloroform. The mixed acids obtained from the soluble barium salts are also treated with chloroform, when  $\alpha$ -truxillic acid, possibly containing also the  $\beta$ -isomeride, remains. The acids obtained from the chloroform solution were found to contain about 50·3% cinnamic acid and 37·9% benzoic acid.

A second specimen of mixed acids was obtained by decomposing the alkaloids by means of hot hydrochloric acid and solution of the product in ether, which left a small residue of impurities. The ethereal solution was shaken with potassium hydroxide, the latter acidified with hydrochloric acid, and again treated with ether, whereby a small quantity of  $\alpha$ -truxillic acid remained undissolved. The ethereal solution was evaporated to dryness, and the residue extracted with chloroform, which left a small residue consisting of a mixture of  $\alpha$ - and  $\beta$ -truxillic acids. The acids obtained from the chloroform solution contained 52·1% cinnamic acid, and 34% benzoic acid mixed with acids of higher molecular weight or with neutral substances.

In the second paper the author has worked out a process for the separation of the acids obtained by the decomposition of the alkaloids of Javanese coca, and has ascertained the presence of the following substances in a specimen of these acids : cinnamic, benzoic, *allo*-cinnamic,  $\alpha$ -truxillic,  $\beta$ -truxillic and  $\delta$ -truxillic acids, resinous acids, and neutral substances, together with an acid, m. p. about  $150^\circ$  (probably identical with protococaine acid obtained by Hesse, A., 1903, i, 192), and an acid, m. p. about  $190^\circ$ , possibly identical with  $\beta$ -cocaine acid.

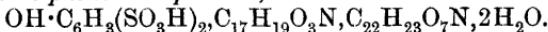
The properties of the truxillic acids and their salts have been investigated. The former are insoluble in light petroleum, but are dissolved in the presence of benzoic or cinnamic acids, the solubility of the  $\alpha$ - and  $\gamma$ -acids being, however, only slightly affected.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Truxillic acids are only sparingly soluble in chloroform at the ordinary temperature. Hot chloroform dissolves the  $\beta$ -acid, particularly in the presence of benzoic and cinnamic acids. The  $\delta$ -acid is soluble in chloroform. The  $\alpha$ - and  $\gamma$ -acids are insoluble in benzene, whereas the  $\beta$ - and  $\delta$ -acids are more soluble in the hot than in the cold solvent. The latter acids may be crystallised from boiling water, in which the  $\alpha$ - and  $\gamma$ -acids are but slightly soluble.

One hundred c.c. of an aqueous solution of barium  $\beta$ -truxillate, saturated at  $26^\circ$ , contain 0.028 gram of the salt.

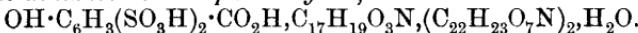
The following salts are sparingly soluble in water: the zinc, cadmium, iron, lead, copper, mercury, and silver salts of the  $\alpha$ -acid; the calcium, barium, strontium, zinc, cadmium, manganese, iron, cobalt, nickel, lead, copper, mercury, and silver salts of the  $\beta$ -acid; the lead, copper, mercury, and silver salts of the  $\gamma$ -acid; the same salts of the  $\delta$ -as of the  $\beta$ -acid, and in addition the magnesium salt. The magnesium salt of the  $\beta$ -acid is soluble in water.

H. W.

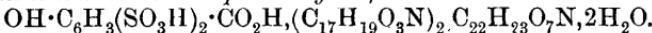
**Preparation of Therapeutically Valuable Double Salts from Morphine and Narcotine.** C. F. BOEHRINGER & SOEHNE (D.R.-P. 254502).—The following therapeutically valuable double salts are readily obtained by treating a hot alcoholic solution of the acid with the requisite amount of the other components. *Morphine narcotine meconate*,  $C_7H_4O_7 \cdot C_{17}H_{19}O_3N \cdot C_{92}H_{23}O_7N \cdot 4H_2O$ . *Morphine dinarcotine benzenetrisulphonate*,  $C_6H_8(SO_3H)_3 \cdot C_{17}H_{19}O_3N \cdot (C_{22}H_{23}O_7N)_2 \cdot 2H_2O$ . *Morphine narcotine phenoldisulphonate*,



*Morphine dinarcotine disulphosalicylate*,



*Dimorphine narcotine disulphosalicylate*,



*Morphine narcotine sulphate*,  $H_2SO_4 \cdot C_{17}H_{19}O_3N \cdot C_{22}H_{23}O_7N \cdot 4\frac{1}{2}H_2O$ . They form colourless crystals, sparingly soluble in cold, readily in hot water, and somewhat insoluble in the ordinary organic media.

F. M. G. M.

**Preparation of Morphine Esters of Alkyl- and Aryloxy-fatty Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 254094).—*Diethoxyacetyl morphine*, an oil, is prepared by heating morphine (10 parts) with ethoxyacetic anhydride (37 parts) during several hours at  $40-45^\circ$ ; the *hydrochloride*, glistening leaflets, decomposes at about  $142^\circ$ .

*Ethoxyacetyl morphine*, m. p.  $155^\circ$  (about), is obtained accompanied by the foregoing compound when the proportions of the reacting components are varied, and the mixture heated at  $40-50^\circ$ ; the *hydrochloride*, needles, has m. p.  $183-186^\circ$ . *Diphenoxycetyl morphine*, m. p.  $125^\circ$  (decomp.), faintly-coloured crystals, is prepared in an analogous manner.

F. M. G. M.

**Alkaloids of Pareira Root.** MAX SCHOLTZ (*Arch. Pharm.*, 1913, **251**, 136—151. Compare A., 1913, i, 87, and Faltis, 1912, i, 796).—As the result of further analyses, the author now reverts to the formula  $C_{18}H_{21}O_3N$ , which he used originally for the bebeerines. Bebeerine, *iso-bebeerine*, and  $\beta$ -bebeerine can all be represented by the extended formula  $OH \cdot C_{16}H_{14}O(OMe) \cdot NMe$ . The first and third isomerides yield with acetic anhydride the same optically inactive hydroxytriacyetylbebeerine. The latter appears to be formed by the opening of a ring containing nitrogen, the attachment of an acetyl group to the N-atom, and of the residue  $CH_3 \cdot CO \cdot O$  to the carbon atom formerly linked to the N-atom.

*iso*Bebeleine yields two hydroxytriacetyl*iso*bebeleines, one dextro-rotatory and the other inactive.

*iso*Bebeleine,  $C_{18}H_{21}O_3N$ , m. p. 297° (decomp.), is the chief constituent of "crystallised bebeleine sulphate" (Merck); the *hydriodide*, m. p. 300° (approx. decomp.), forms prisms from water; the *hydrochloride* is precipitated as colourless needles on adding hydrochloric acid to a solution of the sulphate; the *methiodide*,  $B_2MeI$ , m. p. 275° (decomp.), forms large, prismatic crystals containing water of crystallisation. On heating with acetic anhydride, *iso*bebeleine yields (1)  $\alpha$ -*hydroxytriacetyliso*bebeleine, m. p. 130—140°,  $[\alpha]_D^{20} + 68.1^\circ$  in pyridine, which is colourless and amorphous, and  $\beta$ -*hydroxytriacetyliso*bebeleine, m. p. 291° (approx.),  $[\alpha]_D = 0^\circ$ , which crystallises in colourless needles and is only soluble in pyridine. On hydrolysis by sodium hydroxide in alcohol, each triacetyl derivative yields a corresponding *hydroxymonoacetyliso*bebeleine; the  $\alpha$ -compound, m. p. 280° (approx.), crystallises in colourless, slender needles, and the  $\beta$ -isomeride, m. p. 332° (approx.), forms microscopic needles. Both are insoluble, except in solutions of the alkali hydroxides. *Benzoylisobebeleine*, m. p. 215° (approx.), obtained by the action of benzoic anhydride on *iso*bebeleine, crystallises from alcohol in glancing, yellow leaflets.

$\beta$ -Bebeleine,  $C_{18}H_{21}O_3N$ , is amorphous, but yields a crystalline *methiodide*,  $B_2MeI$ , m. p. 80° (hydrated) or 258—259° (dry, decomp.). Both bebeleine and  $\beta$ -bebeleine on heating with acetic anhydride yield the same *hydroxytriacetylbebeleine*,  $C_{21}H_{29}O_7N$ , m. p. 125—135°, which is amorphous, and loses two acetyl groups on treatment with potassium hydroxide in alcohol.

T. A. H.

Zygadenine, the Crystalline Alkaloid of *Zygadenus intermedium*. FREDERICK W. HEYL, F. E. HEPNER, and SYLVESTER K. LOY (*J. Amer. Chem. Soc.*, 1913, 35, 258—262).—It has been shown already (A., 1911, ii, 325) that the leaves of *Zygadenus intermedium* yield 0.3—0.4% of a mixture of alkaloids. Further work on this subject has resulted in the isolation of a pure alkaloid, *zygadenine*,  $C_{39}H_{62}O_{10}N$ , m. p. 200—201°,  $[\alpha]_D - 48.2^\circ$ , which crystallises from benzene in clusters of lustrous needles, and from alcohol in orthorhombic prisms containing 2Et·OH; the *aurichloride* forms long, dense prisms. The alkaloid gives a yellowish-orange coloration with concentrated sulphuric acid, changing to a brilliant cherry-red. Its physiological action resembles that of veratrine.

E. G.

Electrochemical Reductions. III. Reduction of Nitrosoamines. HILMAR JOHANNES BACKER (*Rec. trav. chim.*, 1913, 32, 39—47. Compare A., 1912, i, 339, 730).—Nitrosopiperidine suspended in sulphuric acid (10%) was electrolysed at a cathode of tinned copper when an 81% yield of the corresponding hydrazine (estimated by oxidation to the tetrazone) was obtained (compare Knorr, A., 1884, 467; Ahrens, A., 1897, i, 369). At a platinum electrode, the hydrogen was incompletely utilised, and the yield of hydrazine sank to 32%. An excess of hydrogen was found to be practically without effect on the hydrazine.

Diaminopiperazine was obtained in 55% yield by the action of zinc

dust and acetic acid on dinitrosopiperazine (compare Schmidt and Wichmann, A., 1892, 210). Electrolytic reduction at a tinned copper cathode of a suspension of the latter in a mixture of acetic and sulphuric acids gave a 38% yield of diaminopiperazine, which, however, increased to 72% when the mixture of acids was replaced by an aqueous solution of sodium sulphate to which a few drops of sulphuric acid had been added. An attempt to convert dinitrosopiperazine into dinitropiperazine by the action of nitric acid was unsuccessful.

Phenylmethylhydrazine (compare Fischer, A., 1878, 312; 1887, 138) was formed by electrolytic reduction of phenylmethylnitroso-amine suspended in dilute acetic acid at a tinned copper cathode. The yield was 79% of the theoretical.

*α*-Nitroso-*α*-methylcarbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{NO}$ , was readily reduced in sulphuric acid suspension at a tin cathode with the formation of methylsemicarbazide (compare Brüning, A., 1890, 23; Young and Oates, T., 1901, 79, 662), which was identified by conversion into benzylidenemethylsemicarbazone, white needles, m. p. 163°. Young and Oates (*loc. cit.*) give 159—160° as m. p. of this substance, whilst Michaelis and Hadanck (A., 1908, i, 1020) found 162°. H. W.

**Indole.** RUDOLF WEISSGERBER (*Ber.*, 1913, 46, 651—659).—The difficulty experienced in preparing derivatives of indole is chiefly due to the lability of the imino-hydrogen atom. If this atom is replaced by a group which can be subsequently removed, it is found possible to obtain halogen derivatives by direct substitution and to disrupt the indole ring so that anthranilic acid results.

[With ARNO KLEMM.]—Halogens react violently with indole, and only by working in very dilute solutions could Pauly and Gundermann obtain iodoindole (A., 1909, i, 71). When 1-benzoylindole (A., 1911, i, 155), however, is treated in the cold with bromine in carbon disulphide, *bromo-1-benzoylindole*,  $\text{C}_{15}\text{H}_{10}\text{ONBr}$ , is obtained in thick plates, m. p. 97—98°, which may be hydrolysed by dilute ammonia or, more conveniently, by means of sodium ethoxide in alcoholic solution, when water precipitates *bromoindole*,  $\text{C}_8\text{H}_6\text{NBr}$ , in silvery leaflets which have a strong faecal odour and undergo vigorous decomposition at 67°. The compound is not very stable, but the bromine atom resists the action of alkalis.

1-Benzoylindole also combines with chlorine, and the *chloro-1-benzoyl-indole*, colourless prisms, m.p. 97—99°, may be hydrolysed to the chloroindole which Mazzara and Borgo obtained by the action of sulphuryl chloride on indole (A., 1906, i, 304). Since the benzoyl derivatives may be oxidised to benzoylanthranilic acid, the halogen is present in the pyrrole ring, and, from their similarity to Pauly's 3-iodo-indole, the constitution of which was satisfactorily determined, the conclusion is drawn that the bromo- and chloro-derivatives are also substituted in position 3, although all three compounds give 2-oxindole when treated with dilute acids.

[With O. HERZ.]—The oxidation of indole itself results in the formation of amorphous masses, but the benzoyl compound is readily converted by permanganate in acetone solution into benzoylanthranilic acid, and this, by hydrolysis, into anthranilic acid itself.

[With F. KRAFT.]—The conversion of an indole derivative into indigotin has been accomplished by passing ozone through a strongly alkaline solution of 3-indolecarboxylic acid (A., 1911, i, 155). The reaction commences quickly, but the yield is only about 38%, anthranilic acid being isolated from the by-products. Other oxidising agents do not yield indigotin, neither does 2-indolecarboxylic acid give rise to that dye.  
J. C. W.

**Preparation of Substituted Indoles by the Catalytic Decomposition of Hydrazones.** ALEXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 70—74).—When heated with cuprous chloride or bromide, or platinous or zinc chloride, hydrazones of aldehydes and ketones undergo catalytic decompositions in directions depending on their structures and on the magnitudes of the radicles present. In the cases already investigated, the principal products are substituted indole derivatives.

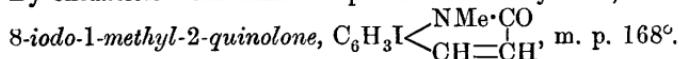
Methyl-ethyl-ketone-phenylhydrazone (50 grams), when heated at 180—230° in presence of cuprous chloride (0·1 gram), yields 2:3-dimethylindole, the yield being about 60%.

Similarly, propaldehyde-phenylhydrazone gives skatole in 73—74% yield, whilst propaldehydetolylhydrazone gives 3:5-dimethylindole,  $C_{10}H_{11}N$ , which crystallises in feathery masses of colourless, silky needles, m. p. 74—74·5°.  
T. H. P.

**5-, 6-, and 8-Iodoquinolines and Their Derivatives.** JOHANN HOWITZ, HEDWIG FRAENKEL, and ELSE SCHROEDER (*Annalen*, 1913, **396**, 53—75).—8-Aminoquinoline is obtained by the reduction of 8-nitroquinoline best by iron and acetic acid. When tin or stannous chloride and hydrochloric acid are used, the resulting 8-aminoquinoline is contaminated with 5-chloro-8-aminoquinoline. 8-*Iodoquinoline*,  $C_9NH_6I$ , m. p. 36°, colourless needles, prepared from diazotised 8-aminoquinoline in the usual manner, forms a *platinichloride*,

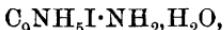


m. p. 251°, orange needles, and *methiodide*, m. p. 200°, yellow needles. By oxidation with alkaline potassium ferricyanide, the latter yields



The 8-iodoquinoline, m. p. 136°, described by Claus and Grau in 1893, is 5-chloro-8-iodoquinoline, produced from the impure 8-aminoquinoline mentioned above.

8-Iodoquinoline is readily nitrated by concentrated sulphuric acid and nitric acid (D 1·5) in the cold, yielding 8-*iodo-5-nitroquinoline*, m. p. 192°, pale yellow needles. 8-*Iodo-5-aminoquinoline*,



m. p. 148° (anhydrous, 155°), brown prisms (*benzoyl* derivative,

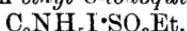


m. p. 218°, leaflets), yields 5:8-*di-iodoquinoline*, m. p. 162°, and 5-*chloro-8-iodoquinoline*, m. p. 138°, by the usual methods.

By the Sandmeyer process, 5-aminoquinoline yields 5-chloroquinoline, m. p. 44—45° (Claus and Junghanns give 31°), the nitration of which

produces 5-chloro-8-nitroquinoline, m. p. 136° (184°, Claus and Junghanns). 5-Chloro-8-aminoquinoline, m. p. 75° (69°, Claus and Junghanns), forms an *acetyl* derivative, m. p. 140°, and is converted into 5-chloro-8-iodoquinoline by the usual method.

8-Iodoquinoline is readily attacked by 40% fuming sulphuric acid in the cold, yielding 8-*iodoquinoline-5-sulphonic acid*,  $C_9NH_5I \cdot SO_3H$ , silver-grey leaflets, of which the sodium and barium salts are described. The *silver* salt,  $C_9NH_5I \cdot SO_3Ag \cdot H_2O$ , when dehydrated, reacts with methyl iodide at 120—130° to form chiefly the *betaine*, m. p. 292° (decomp.), of 8-*ido-1-methylquinoline-5-sulphonic acid*, and with ethyl iodide at 130—140° to form *ethyl 8-iodoquinoline-5-sulphonate*,



m. p. 156°, colourless leaflets, and the *betaine*, m. p. about 340° (decomp.), of 8-*ido-1-ethylquinoline-5-sulphonic acid*. Sodium 8-*idoquinoline-5-sulphonate* and phosphorus pentachloride at 125—130° yield 8-*idoquinoline-5-sulphonyl chloride*, m. p. 116°, yellow needles or prisms, from an ethereal solution of which and dry ammonia the *sulphonamide*,  $C_9NH_5I \cdot SO_2 \cdot NH_2$ , m. p. 212°, is obtained. The position of the sulpho-group in 8-*idoquinoline-5-sulphonic acid* is proved by nitration, whereby the sulpho- is replaced by the nitro-group, and 8-*ido-5-nitroquinoline*, m. p. 192°, is obtained.

5-Iodoquinoline methiodide is oxidised to 5-*ido-1-methyl-2-quinolone*, m. p. 172°, yellow leaflets, by alkaline potassium ferricyanide. 5-*Iodo-8-nitroquinoline*, m. p. 160°, yellow needles, obtained by the nitration of 5-*idoquinoline* on the water-bath, yields by reduction 5-*ido-8-aminoquinoline*, m. p. 122°, brown needles (*benzoyl* derivative, m. p. 161°), from which 5:8-di-*idoquinoline*, m. p. 161°, and 8-*chloro-5-idoquinoline*, m. p. 118°, are prepared by the usual methods; the formation of the di-*ido*-compound determines the orientation of the nitro-group in nitrated 5-*idoquinoline*.

The following derivatives of 6-*idoquinoline* have been prepared: 6-*Iodo-1-methyl-2-quinolone*,  $C_{10}H_8ONI$ , m. p. 129°, yellow needles or leaflets; 6-*ido-5-aminoquinoline*, m. p. 176° (*acetyl* derivative,

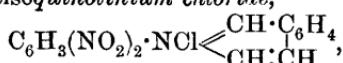


m. p. 197°); 5:6-*di-idoquinoline*, m. p. 125°, and 5-*chloro-6-idoquinoline*, m. p. 141°.

C. S.

**2-*op*-Dinitrophenylisoquinolinium Chloride and its Products of Transformation.** THEODOR ZINCKE and G. WEISSPFENNING (*Annalen*, 1913, 396, 103—131).—The authors' experiments have not realised their expectations that the action of arylamines or of cyanogen bromide on 2-*op*-dinitrophenylisoquinolinium chloride would yield the glutacondialdehyde derivative,  $CHO \cdot C_6H_4 \cdot CH_2 \cdot CHO$ , or colour bases,  $NAr \cdot CH \cdot C_6H_4 \cdot CH \cdot CH \cdot NHAr$ , analogous to those obtained in the pyridine series (A., 1904, i, 448, 921; 1905, i, 467, 923; 1907, i, 625).

2-*op*-*Dinitrophenylisoquinolinium chloride*,



decomp. 130°, stout, rhombic crystals, is obtained by keeping an ethereal solution of isoquinoline and 1-chloro-2:4-dinitrobenzene for

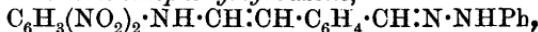
several weeks or months at the ordinary temperature. It forms a *platinichloride*, m. p. 222°, and *periodide*,  $C_{15}H_{10}O_4N_3I_3$ , dark brown needles, and is readily hydrolysed by hot aqueous sodium nitrite, yielding *isoquinoline*, hydrogen chloride, and 2:4-dinitrophenol (in the form of the dinitrophenylisoquinolinium and *isoquinoline* salts; the latter has m. p. 127°). Hydrogen sulphide decomposes the chloride, 2:4-dinitrophenyl mercaptan being produced in the aqueous solution and 2:4-dinitrophenyl sulphide in alcoholic solution.

Dinitrophenylisoquinolinium chloride is converted by aqueous ammonia or sodium carbonate or by an aqueous solution of methylamine or aniline, less satisfactorily by aqueous sodium hydroxide, into the  $\psi$  base,  $C_6H_8(NO_2)_2 \cdot N < \begin{matrix} CH(OH) \cdot C_6H_4 \\ CH = CH \end{matrix}$ , orange-red needles, m. p. 141—142°, darkening at about 90°, which is reconverted into dinitrophenylisoquinolinium chloride by dilute hydrochloric acid, and yields ethers,  $C_6H_8(NO_2)_2 \cdot N < \begin{matrix} CH(OR) \cdot C_6H_4 \\ CH = CH \end{matrix}$ , by warming with alcohols; the *methyl ether*, m. p. 149°, dark red crystals, *ethyl ether*, m. p. 135°, pale red prisms, and *isobutyl ether*, m. p. 122°, orange-red crystals, have been prepared. These ethers, which are also produced directly from dinitrophenylisoquinolinium chloride and ammonia dissolved in the alcohol, are converted one into another by warming with the necessary alcohol.

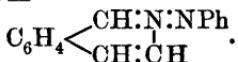
By heating with water at 90—95° for some hours, or with acetone at 100°, or with boiling acetic anhydride, the freshly precipitated  $\psi$ -base is converted into an *isomeride*, m. p. 151°, dark red crystals with a violet shimmer. The isomeride is only slowly attacked by warm dilute hydrochloric acid, does not form ethers by boiling with alcohols, and is slowly converted into dinitrophenylisoquinolinium chloride by hot concentrated hydrochloric acid. It does not react with phenylhydrazine, and is, therefore, not the aldehydo-base,  $CHO \cdot C_6H_4 \cdot CH:CH \cdot NH \cdot C_6H_8(NO_2)_2$ ; probably it has the constitution  $NHR \cdot CH:CH \cdot C_6H_4 \cdot CH(OH) \cdot O \cdot CH < \begin{matrix} NR-CH \\ C_6H_4-CH \end{matrix}$  [where R is  $C_6H_8(NO_2)_2$ ], and is formed by the union of the  $\psi$ -base and the aldehydo-base.

When boiled in alcoholic solution with aniline or *p*-toluidine, dinitrophenylisoquinolinium chloride or, better, the  $\psi$ -base or the violet isomeride is decomposed into 2:4-dinitroaniline and the 2-arylisooquinolinium chloride. 2-*Phenylisoquinolinium chloride*,  $C_{15}H_{12}NCl, 2H_2O$ , long needles, forms a *platinichloride*, m. p. 228—229°, orange needles, and *mercurichloride*, m. p. 183—184°; the *dichromate*, decomp. about 195°, and *picrate*, m. p. 136—137°, yellow needles, are described. 2-*p-Tolylisoquinolinium chloride*,  $C_{16}H_{14}NCl, 2H_2O$ , colourless needles, forms a *platinichloride*, m. p. 216—217°, orange-yellow needles.

Dinitrophenylisoquinolinium chloride is converted into the  $\psi$ -base by hydrazine hydrate, but reacts with phenylhydrazine in boiling alcohol just as does dinitrophenylpyridinium chloride (A., 1904, i, 448), yielding the *dinitroanilinophenylhydrazone*,



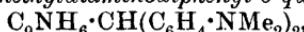
m. p. 183—184°, black needles. In a similar manner the *dinitro-anilino-p-tolylhydrazone*,  $C_{22}H_{19}O_4N_5$ , m. p. 185—186°, black leaflets with a red shimmer, and the *dinitroanilino-phenylmethylhydrazone*,  $C_{22}H_{19}O_4N_5$ , m. p. 181—182°, reddish-brown leaflets, have been obtained. These three substances are decomposed by boiling alcohol and hydrochloric acid, D 1·19, into 2:4-dinitroaniline and 2-*anilinoisoquinolinium chloride*,  $C_9H_7N(NHPh)Cl$ , m. p. 198—200°, faintly yellow, monoclinic prisms (*platinichloride*, m. p. 190° [decomp.]), 2-*p-toluidinoisoquinolinium chloride*, rhombic plates, and 2-*methylanilinoisoquinolinium chloride*, faintly yellow needles (*picrate*, m. p. 170°; *platinichloride*, m. p. 185°; *mercurichloride*, m. p. 174°), respectively. 2-Anilinoisoquinolinium chloride yields isoquinoline (aniline could not be detected) by reduction with zinc dust and dilute hydrochloric acid, and by treatment with aqueous sodium hydroxide, sodium carbonate, or ammonia yields a red precipitate which is apparently a mixture of the  $\psi$ -base,  $C_6H_4\begin{array}{c} CH(OH)\cdot N\cdot NHPh \\ | \\ CH=CH \end{array}$ , and the azo-compound,



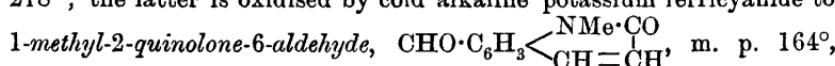
C. S.

**Bromination of 6-Methylquinoline and 6-Quinolinealdehyde.** JOHANN HOWITZ and J. PHILIPP (*Annalen*, 1913, 396, 23—37).—The dibromide of 6-methylquinoline hydrobromide is obtained as a brick-red, crystalline powder by saturating a cold chloroform solution of 6-methylquinoline with hydrogen bromide and subsequently adding bromine (1 mol.). By carefully heating it at 170—180° for two hours, cooling to 140°, and adding more bromine (1 mol.), and heating again at 170—180° for two hours, the substance is converted into 6-*dibromo-methylquinoline*,  $C_9NH_6\cdot CHBr_2$ , m. p. 159—160°, white needles (*platinichloride*,  $2C_{10}H_7NBr_2\cdot H_2PtCl_6$ , m. p. 235°, orange crystals), and 3-bromo-6-*dibromomethylquinoline*,  $C_{10}H_6NBr_3$ , m. p. 141°, yellowish-white needles, each of which loses two atoms of bromine by hydrolysis with alcoholic potassium hydroxide.

By boiling with water for ten to fifteen minutes and basifying, 6-dibromo-methylquinoline is converted into 6-*quinolinealdehyde*,  $C_{10}H_7ON$ , glistening needles containing  $H_2O$ , m. p. 55° (anhydrous, 75—76°), which exhibits the usual reducing and additive properties of an aldehyde. It yields quinoline-6-carboxylic acid by oxidation, forms a *platinichloride*,  $2C_{10}H_7ON\cdot H_2PtCl_6$ , m. p. 244°, reddish-yellow needles, *aldazine*,  $N_2(CH\cdot C_9NH_6)_2$ , m. p. 261°, yellow needles, *semicarbazone*, m. p. 239°, *oxime*, m. p. 191°, *phenylhydrazone*, m. p. 185°, yellow crystals containing  $H_2O$ , *anil*,  $NPh\cdot CH\cdot C_9NH_6$ , m. p. 99°, and *o-tolil*, m. p. 97°, and condenses with dimethylaniline in the presence of zinc chloride to form *tetramethyldiaminodiphenyl-6-quinolylmethane*,



m. p. 160°, almost colourless needles, which yields a green dye by oxidation with lead peroxide. When heated with methyl iodide at 100°, 8-quinolinealdehyde yields a *methiodide*,  $CHO\cdot C_9H_6NMeI$ , m. p. 218°; the latter is oxidised by cold alkaline potassium ferricyanide to

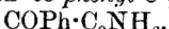


colourless needles, or the corresponding acid,  $C_{11}H_9O_3N$ , m. p. above  $300^\circ$ , according to the duration of the reaction.

3-Bromo-6-dibromomethylquinoline is hydrolysed by an excess of potassium carbonate and a little water at  $115-120^\circ$ , yielding 3-bromo-quinoline-6-aldehyde, m. p.  $139^\circ$ , white needles (*aldazine*, m. p.  $194^\circ$ , pale yellow needles; *oxime*, m. p.  $217^\circ$ ; *phenylhydrazone*, m. p.  $195^\circ$ ; *anil*, m. p.  $124^\circ$ ), in which the position of the halogen is determined by its oxidation to 3-bromopyridine-5:6-dicarboxylic acid by hot alkaline potassium permanganate. By oxidation with chromic and sulphuric acids, the aldehyde yields 3-bromoquinoline-6-carboxylic acid, m. p.  $245^\circ$ , long white needles.

C. S.

**8-Quinolyl Ketones and their Derivatives.** JOHANN HOWITZ and O. KÖPKE (*Annalen*, 1913, 396, 38—52).—Hitherto, only quinolyl ketones have been known containing the carbonyl group attached to the pyridine nucleus. Bromoquinolines and 8-bromomethylquinoline do not react with magnesium in ether. The interaction of 8-quinolin-aldehyde (Howitz and Schwenk, A., 1905, i, 471) and magnesium phenyl bromide in ether at  $0^\circ$ , leads to the formation of *phenyl-8-quinolylcarbinol*,  $OH \cdot CHPh \cdot C_9NH_6$ , m. p.  $104^\circ$ , large colourless plates, in about 60% yield. The carbinol forms a *platinichloride*, m. p.  $198^\circ$  (decomp.), and a *benzoate*, m. p.  $146^\circ$ , and is oxidised by chromic and acetic acids on the water-bath to *phenyl 8-quinolyl ketone*,



m. p.  $94^\circ$ , colourless plates (*platinichloride*, m. p.  $213^\circ$  [decomp.]). By treatment with hydroxylamine hydrochloride and potassium hydroxide in boiling alcohol, the ketone yields an *oxime*,  $C_{16}H_{12}ON_2H_2O$ , m. p.  $121^\circ$ , which is converted into an *isomeride*,  $C_{16}H_{12}ON_2H_2O$ , m. p.  $165^\circ$ , by heating at  $120^\circ$ , and then crystallising from alcohol. By treating a cold ethereal solution of the oxime, m. p.  $121^\circ$ , with phosphorus pentachloride, and decomposing the precipitated imino-chloride with water at  $0^\circ$ , *8-benzoylaminoquinoline*,  $C_9NH_6 \cdot NHBz$ , m. p.  $93^\circ$ , is obtained, the identity of which is established by its formation by the benzoylation of 8-aminoquinoline and by its decomposition into 8-aminoquinoline and benzoic acid by concentrated hydrochloric acid at  $160^\circ$ . The oxime, m. p.  $121^\circ$ , is therefore anti-phenyl 8-quinolyl ketoxime,  $C_9NH_6 \cdot CPh \begin{smallmatrix} || \\ N \\ HO \end{smallmatrix}$ . In a similar manner, the oxime, m. p.

$165^\circ$ , is proved to be syn-phenyl 8-quinolyl ketoxime,  $C_9NH_6 \cdot CPh \begin{smallmatrix} || \\ N \\ HO \end{smallmatrix}$ , by its conversion by the Beckmann transformation into the anilide of quinoline-8-carboxylic acid; unfortunately, neither the anilide nor the quinolincarboxylic acid produced by its hydrolysis has been isolated, but only the aniline resulting in the latter operation.

Phenyl 8-quinolyl ketone forms a *phenylhydrazone*, m. p.  $190^\circ$ , *semicarbazone*, m. p.  $188^\circ$ , and *azine*,  $C_{32}H_{22}N_4$ , m. p.  $287^\circ$ .

8-Quinolylmethylcarbinol,  $OH \cdot CHMe \cdot C_9NH_6$ , m. p.  $65^\circ$  (*platinichloride*, m. p.  $197^\circ$  [decomp.], orange-yellow crystals; *benzoate*, m. p.  $100^\circ$ ), obtained ultimately from magnesium methyl iodide and 8-quinolin-aldehyde in ether, is oxidised to 8-quinolyl methyl ketone,  $C_9NH_6 \cdot COMe$ , m. p.  $45^\circ$ , b. p. about  $295^\circ$ , by potassium dichromate

and very dilute sulphuric acid on the water-bath. The ketone forms a *semicarbazone*, m. p. 223°, and an *oxime*, m. p. 137°; the latter has only been obtained in one modification, which is *syn*-8-quinolyl methyl ketoxime, since it yields 8-acetylaminooquinoline by the Beckmann transformation.

*8-Quinolylethylcarbinol (platinichloride*, m. p. 210° [decomp.]; *benzoate*, m. p. 82°) and *8-quinolyl ethyl ketone*, b. p. about 290° (*semicarbazone*, m. p. 203°), have been prepared by methods similar to the preceding.

C. S.

**Preparation of 9-Methylcarbazole.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 255304).—The technically valuable 9-methylcarbazole can be prepared in about 70% yield by the following method.

Dry potassium carbazole is heated with freshly distilled ethyl chloroacetate during about three hours, yielding *ethyl carbazole-9-acetate*, m. p. 97°; this when hydrolysed with an alkaline hydroxide gives rise to *carbazole-9-acetic acid*, glistening, colourless leaflets, m. p. 215°, which, when carefully heated at 250—270°, evolves carbon dioxide and furnishes pure 9-methylcarbazole, m. p. 87°. F. M. G. M.

**Kehrmann's Interpretation of Chromo-Isomeric Acridonium Salts as "Quinhydrone Salts" which Contain Hydroacridine.** ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 682—684. Compare this vol., i, 298).—Kehrmann's view that the dark green iodide obtained from methylphenazonium salts is a quinhydrone salt composed of one molecule of azonium tri-iodide and two molecules of methyldihydrophenazine, is combated.

According to Kehrmann, the salt should be decomposed by water into phenylmethylacridonium iodide, phenylmethylhydroacridine, and hydrogen iodide, but in reality it gives a clear, neutral solution, and behaves as a normal binary electrolyte. J. C. W.

**"Halochromism" of the Derivatives of Phenylisooxazolone and of the Indogenides.** ANDRÉ MEYER (*Compt. rend.*, 1913, **156**, 714—717. Compare Baeyer and Villiger, A., 1901, i, 658; 1902, i, 380, 769; Meyer, A., 1912, i, 1019).—The indogenides and in particular the *isooxazole-indogenides* give coloured compounds with acids and metallic salts, comparable to the oxonium salts, and the author has prepared a number of such compounds.

On passing dry hydrogen chloride into a suspension of piperonylidene-*isooxazolone* in benzene at —10°, a deep red additive compound is formed and crystallises out.

Condensation products are also formed from the *isooxazolones* and stannic chloride, ferric chloride, or aluminium chloride, and a number of such stannichlorides, prepared by the addition of anhydrous stannic chloride to benzene solutions of the *isooxazolones*, are described.

*Phenylbenzylideneisooxazolone stannichloride*,  $C_{16}H_{11}O_2N,SnCl_4$ , a yellow, microcrystalline powder, decomposes at 200°.

*Phenylpiperonylideneisooxazolone stannichloride*,  $C_{17}H_{11}O_4N,SnCl_4$ , deep red leaflets, decomposes at 160°.

*Phenylanisylideneisooxazolone stannichloride*,  $C_{17}H_{13}O_3N, SnCl_4$ , a deep yellow powder, decomposes at  $155^\circ$ .

*Phenyl-o-methoxybenzylideneisooxazolone stannichloride*,



an orange powder, decomposes at  $130^\circ$ .

*Phenylvanillylideneisooxazolone stannichloride*,  $C_{17}H_{13}O_3N, SnCl_4$ , a brownish-red, microcrystalline powder, decomposes at  $150^\circ$ .

*Phenyldimethylaminobenzylideneisooxazolone stannichloride*,



a bright red powder, decomposes above  $250^\circ$ .

The indogenides furnish similar compounds, such as *piperonylidene-hydroxythionaphthen stannichloride*,  $C_{15}H_{10}O_3S, SnCl_4$ , a violet-black, microcrystalline powder, decomposing at  $230^\circ$ .

All these substances are hydrolysed by water and are practically insoluble in organic solvents, their colours being deeper than those of the parent substances.

The mixed azo-derivatives of phenylisooxazolone are also "halochromes" and give coloured stannichlorides, the one described being *3-zenzeneazophenylisooxazolone stannichloride*,  $C_{15}H_{11}O_2N_3, SnCl_4$ , an orange-yellow powder, decomposing at  $130^\circ$ .

W. G.

**Some Derivatives of the Methoxyphenylisooxazolones.**  
 ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. chim.*, 1913, [iv], 13, 236—240. Compare Wahl and Meyer, A., 1908, i, 368; Wahl, *ibid.*, 1909, i, 260).—The authors have condensed *o*-, *m*-, and *p*-methoxyphenylisooxazolone with a number of aldehydes, and have thus prepared the following substances : 3-*o*-methoxyphenyl-4-benzylideneisooxazolone, yellow leaflets, m. p.  $150^\circ$ ; 3-*m*-methoxyphenyl-4-benzylideneisooxazolone, yellow needles, m. p.  $110^\circ$ ; 3-*p*-methoxyphenyl-4-benzylideneisooxazolone, yellow leaflets, m. p.  $170^\circ$ ; 3-*o*-methoxyphenyl-4-anisylideneisooxazolone, pale yellow, m. p.  $154^\circ$ ; 3-*m*-methoxyphenyl-4-anisylideneisooxazolone, yellow crystals, m. p.  $164^\circ$ ; 3-*p*-methoxyphenyl-4-anisylideneisooxazolone, pale yellow leaflets, m. p.  $165^\circ$ ; 3-*o*-methoxyphenyl-4-cinnamylideneisooxazolone, orange-yellow, m. p.  $163^\circ$ ; 3-*m*-methoxyphenyl-4-cinnamylideneisooxazolone, orange-yellow, m. p.  $146$ — $147^\circ$ ; 3-*p*-methoxyphenyl-4-cinnamylideneisooxazolone, orange needles, m. p.  $163^\circ$ ; 3-*o*-methoxyphenyl-4-furfurylideneisooxazolone, yellow crystals, m. p.  $171$ — $172^\circ$ ; 3-*p*-methoxyphenyl-4-furfurylideneisooxazolone, yellow needles, m. p.  $141$ — $142^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-dimethylaminobenzylideneisooxazolone, red needles, m. p.  $190^\circ$ ; 3-*m*-methoxyphenyl-4-*p*-dimethylaminobenzylideneisooxazolene, red needles, m. p.  $140^\circ$ ; 3-*p*-methoxyphenyl-4-*p*-dimethylaminobenzylideneisooxazolone, red leaflets, m. p.  $192^\circ$ ; 3-*p*-methoxyphenyl-4-*o*-hydroxybenzylideneisooxazolone, yellow leaflets, m. p.  $195^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-hydroxybenzylideneisooxazolone, orange-yellow, m. p.  $218^\circ$ ; 3-*m*-methoxyphenyl-4-*p*-hydroxybenzylideneisooxazolone, yellow leaflets, m. p.  $215^\circ$ ; 3-*p*-methoxyphenyl-4-*p*-hydroxybenzylideneisooxazolone, golden-yellow needles, m. p.  $204$ — $205^\circ$ ; 3-*o*-methoxyphenyl-4-*p*-hydroxybenzylideneisooxazolone, yellow crystals, m. p.  $168^\circ$ ; 3-*m*-methoxyphenyl-4-*p*-hydroxy-*m*-methoxybenzylideneisooxazolone, orange-yellow crystals, m. p.  $203^\circ$ ; 3-*p*-methoxyphenyl-4-*p*-hydroxy-*m*-methoxybenzylideneisooxazolone, yellow crystals, m. p.  $199^\circ$ ; 3-*o*-methoxyphenyl-

*4-mp-dihydroxybenzylideneisooxazolone*, orange crystals, m. p. 209°; *3-methoxyphenyl-4-mp-dihydroxybenzylideneisooxazolone*, orange-red needles, m. p. 184°; *3-p-methoxyphenyl-4-mp-dihydroxybenzylideneisooxazolone*, orange crystals, m. p. 193°; with *o*-vanillin, the *3-o*- and *p*-methoxyphenylisooxazolones form yellow leaflets, m. p. 195°, and orange-yellow leaflets, m. p. 208°, respectively, whilst with resorcylic aldehyde, *3-o*, *m*- and *p*-methoxyphenylisooxazolones yield orange-yellow crystals, m. p. 235°, orange-yellow crystals, m. p. 240°, and yellow crystals, m. p. 209°, respectively. The phenolic derivatives dissolve in alkali, forming solutions in which the colour varies from yellow to reddish-violet. Presence of excess of alkali rapidly discharges these colorations, yielding colourless solutions from which acids re-precipitate the original substance. The action of excess of alkali probably causes a rupture of the lactonic grouping according to the scheme : O<  
 $\text{CO} \cdot \text{C}(\text{CH} \cdot \text{R}) \xrightarrow{\text{NaOH}} \text{CO}_2\text{Na} \cdot \text{C}(\text{CH} \cdot \text{R})$   
 $\text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3 \xleftarrow{\text{HCl}} \text{HO} \cdot \text{N}=\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3$ .

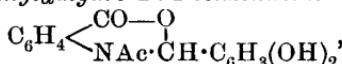
The three methoxyphenylisooxazolones have been condensed with 5-bromoisoatnin chloride, yielding the three *3-methoxyphenylisooxazolone-5-bromo-2-indoles*,

$\text{N}:\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3 > \text{C}:\text{C} < \text{NH}$   
 $\text{O} \text{---} \text{CO} \text{---} \text{C}_6\text{H}_3\text{Br}$ , the properties of which are similar to those of the previously described indigoid dyes derived from the three methoxyphenylisooxazolones and isatin chloride. If, however, sodium hyposulphite is added to their solution in alkali, the yellow colour of the latter persists. Addition of acid causes the formation of a flocculent, yellow precipitate. The latter dissolves in alcohol, forming a red solution, the colour of which deepens on addition of an oxidising agent, the initial dye being ultimately formed. The yellow precipitate appears to be the leuco-derivative of the dye. It presents no marked affinity for the textile fibres.

H. W.

**Action of Acetic Anhydride on some Benzylideneanthranilic Acids. II.** JOHN B. EKELEY AND STILES CLINTON (*J. Amer. Chem. Soc.*, 1913, 35, 282—284).—Ekeley and Dean (A., 1912, i, 211) have shown that a series of oxazines can be obtained by the action of acetic anhydride on benzylideneanthranilic acids. The reaction seems to be of general application, and further compounds are now described.

*Protocatechylideneanthranilic acid*, m. p. 204°, obtained by the condensation of protocatechualdehyde with anthranilic acid, forms orange-red crystals, and is converted by acetic anhydride into *4-acetyl-3-(3':4')dihydroxyphenyldihydro-2:4-benzoxazine-1-one*,



m. p. 121°. *Bromosalicylideneanthranilic acid*, m. p. 198°, crystallises in yellow needles, and furnishes *4-acetyl-3-(4':2')bromohydroxyphenyldihydro-2:4-benzoxazine-1-one*, m. p. 170°. *o-Nitrobenzylideneanthranilic acid*, m. p. 67°, forms straw-coloured needles, and yields *4-acetyl-3-o-nitrophenyldihydro-2:4-benzoxazine-1-one*, m. p. 167.5°. *o-Methoxybenzylideneanthranilic acid*, m. p. 122°, gives *4-acetyl-3-o-methoxyphenyldihydro-2:4-benzoxazine-1-one*, m. p. 165°. *Resorcylideneanthranilic acid* begins to

decompose at about  $150^{\circ}$ ; *4-acetyl-3-(1:3)-dihydroxyphenyldihydro-2:4-benzoxazine-1-one* has m. p.  $192^{\circ}$ . *p-Dimethylaminobenzylidene-anthraniic acid*, m. p.  $176^{\circ}$ , yields *4-acetyl-3-p-dimethylaminophenyl-dihydro-2:4-benzoxazine-1-one*, m. p.  $162^{\circ}$ .

E. G

**A Gelatinous Mercury Salt of an Organic Sulphonic Acid.**  
W. DÖHLE and BERTHOLD RASSOW (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 71–74).—By the action of fuming sulphuric acid on benzothiazole-methenesulphide, a monosulphonic acid of the composition :



is obtained. When aqueous solutions of the potassium salt and of mercuric chloride are mixed together, a yellow solution is obtained, which, sooner or later, depending on the concentration, solidifies to a jelly. The jelly-forming substance is the normal mercuric salt, and its activity is such, that even in *N*/100-solution it is capable of producing a jelly at the ordinary temperature. The mercury salt is unstable, and the jellies sooner or later become cloudy in consequence of the formation of the basic salt,  $\text{Hg}(\text{C}_8\text{H}_6\text{NS}_2 \cdot \text{SO}_3)_2 \cdot \text{HgO}$ , which separates out in the form of very small crystals. The stability of the jellies increases with the concentration of the mercury salt and those prepared from *N*/5-solutions of the potassium salt and mercuric chloride can be kept for some time before they begin to exhibit opalescence as a result of the initial precipitation of the basic salt.

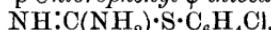
The colloidal mercury salt is coagulated by electrolytes and alcohol, the coagulum being converted into the crystalline basic salt on contact with water.

From the examination of freshly prepared solutions of the mercury salt, it has been found that the viscosity increases with time, the rate of increase varying very considerably from one solution to another even when the conditions under which the solutions were prepared, were exactly the same. Most electrolytes increase the viscosity, but potassium iodide increases it to a remarkable extent. H. M. D.

**Aromatic  $\psi$ -Thiocarbamides and Orthothiocarbonic Esters.**  
FRITZ ARNDT (*Annalen*, 1913, 396, 1–22. Compare A., 1911, i, 918).—*Phenyl- $\psi$ -thiocarbamide*,  $\text{NH:C}(\text{NH}_2)\cdot\text{SPh}$ , m. p.  $96-97^{\circ}$  (decomp.), glistening needles, prepared from phenyl mercaptan and cyanamide, forms a sparingly soluble *nitrate-sulphate*,



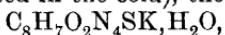
m. p.  $206^{\circ}$  (decomp.), which, however, is distinctly more soluble than the nitrate-sulphate of *p-tolyl- $\psi$ -thiocarbamide* (*loc. cit.*); in fact, the salts of phenyl- $\psi$ -thiocarbamide are much more soluble than those of the *p-tolyl* homologue. *p-Chlorophenyl- $\psi$ -thiocarbamide*,



forms a *nitrate-sulphate*,  $3\text{C}_7\text{H}_7\text{N}_2\text{SCl}, \text{H}_2\text{SO}_4, \text{HNO}_3$ , m. p.  $222^{\circ}$  (decomp.).

The substance previously described as *nitroso-p-tolyl- $\psi$ -thiocarbamide* (*loc. cit.*) is now shown to be the *p-tolyl- $\psi$ -carbamide* salt of *dinitroso-p-tolyl- $\psi$ -thiocarbamide*,  $\text{OH}\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{SC}_7\text{H}_7)\cdot\text{N}\cdot\text{NO}$ . The salt is decomposed by cold glacial acetic acid into nitrogen and *p-tolyl thiocyanate*, and by cold concentrated hydrochloric acid into nitrous acid and *p-tolyl- $\psi$ -thiocarbamide*. The yellow substance obtained by

its decomposition by boiling methyl alcohol receives the constitution  $C_7H_7S\cdot CO\cdot N\cdot NOH$ , since it yields *p*-tolylthiocyanate and mercaptan by treatment with concentrated hydrochloric acid. By gradually adding the *p*-tolyl- $\psi$ -thiocarbamide salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide to a gently boiling methyl-alcoholic solution of potassium acetate (saturated in the cold), the potassium salt,



of the dinitroso-derivative is obtained. It crystallises in glistening needles, yields the *calcium*, *barium*, and *ferric* salts by double decomposition, and the *benzamidine* salt, white leaflets, by treatment with aqueous benzamidine hydrochloride, and by the action of dilute acetic acid yields the free dinitroso-compound, which, however, instantly decomposes into nitrous acid and *nitroso-p-tolyl- $\psi$ -thiocarbamide*,



decomp. 115—120°, golden-yellow leaflets. The latter yields nitrous acid and *p*-tolyl- $\psi$ -thiocarbamide by treatment with concentrated hydrochloric acid, and nitrogen and *p*-tolyl thiocyanate with warm glacial acetic acid. By treatment with sodium nitrite and hydrochloric acid, phenyl- $\psi$ -thiocarbamide and *p*-chlorophenyl- $\psi$ -thiocarbamide each yield  $\psi$ -thiocarbamide salts of the dinitroso- $\psi$ -thiocarbamide.

As mentioned previously (*loc. cit.*), *p*-tolyl *ortho*-thiocarbonate is obtained by treating a methyl-alcoholic solution of the *p*-tolyl- $\psi$ -thiocarbamide salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide with aqueous ammonia. This reaction could not be explained when the *p*-tolyl- $\psi$ -thiocarbamide salt was considered to be a nitroso-compound. Its course is now clear. The ammonia liberates *p*-tolyl- $\psi$ -thiocarbamide and converts it into *p*-tolyl mercaptan, which then reacts with the dinitroso-compound (or its ammonium salt) in accordance with the equation:  $C_7H_7S\cdot C(N\cdot NO)\cdot N\cdot N\cdot OH + 3C_7H_7\cdot SH = C(SC_7H_7)_4 + 2N_2 + 2H_2O$ . The orthothiocarbonate is also obtained by treating a methyl-alcoholic solution of the *p*-tolyl- $\psi$ -thiocarbamide salt or the potassium salt of dinitroso-*p*-tolyl- $\psi$ -thiocarbamide directly with *p*-tolyl mercaptan.

*Phenyl orthothiocarbonate*,  $C(SPh)_4$ , m. p. 159°, small leaflets, and *p*-chlorophenyl *orthothiocarbonate*,  $C(S\cdot C_6H_4Cl)_4$ , m. p. 212—213°, are prepared by methods similar to the preceding. *p-Chlorophenyl orthothioformate*,  $CH(S\cdot C_6H_4Cl)_3$ , m. p. 111—112°, almost colourless leaflets, is obtained by boiling *p*-chlorophenyl mercaptan in aqueous sodium hydroxide with an excess of chloroform. *Phenyl tri-p-chlorophenyl orthothiocarbonate*,  $SPh\cdot C(S\cdot C_6H_4Cl)_3$ , small, white leaflets, m. p. about 191°, obtained by warming potassium dinitrosophenyl- $\psi$ -thiocarbamide and the calculated amount of *p*-chlorophenyl mercaptan in methyl alcohol, is converted by crystallisation from acetic acid into a mixture of the tetraphenyl and the tetra-*p*-chlorophenyl esters of orthothiocarbonic acid; the latter has been isolated. *Tri-p-chlorophenyl-p-tolyl orthothiocarbonate*, m. p. about 193°, is prepared in a similar manner, and also tends to change to the unmixed esters. By reduction with boiling glacial acetic acid and zinc dust, it is converted into *di-p-chlorophenyl-p-tolyl orthothioformate*,  $C_7H_7S\cdot CH(S\cdot C_6H_4Cl)_2$ , m. p. 96—97°, white leaflets, which is not changed by crystallisation from glacial acetic acid.

C. S.

**Preparation of 6-Aminodiarylmino- and 7-Aminodiaryl-amino-1-naphthol-3-sulphonic Acids with their Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254510).—Numerous compounds obtained by the condensation of aromatic benzenoid amines with aminonaphthols in the presence of sodium hydrogen sulphite have been previously described (A., 1905, i, 585), and the reaction has now been extended to the diphenyl series.

*4'-Amino-7-diphenylamino-1-naphthol-3-sulphonic acid* (annexed formula) is obtained when 1:7-dihydroxynaphthalene-3-sulphonic acid (240 parts) is boiled during forty-eight hours with benzidine (184 parts) and an aqueous solution of sodium hydrogen sulphite (2400 parts); the sodium salt forms grey leaflets.

The following compounds are also described: 3'-sulpho-4'-amino-6-diphenylamino-1-naphthol-3-sulphonic acid; 3'-sulpho-4'-amino-7-diphenylamino-1-naphthol-3-sulphonic acid, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid; 4'-amino-6-diphenylamino-1-naphthol-3-sulphonic acid, from benzidine with 1:7-dihydroxynaphthalene-3-sulphonic acid; and the compound, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid and a mixture of ammonium and sodium hydrogen sulphites; the sodium salt forms glistening, grey leaflets.

F. M. G. M.

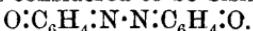
**Catalytic Decomposition of Phenylhydrazine by Cuprous Salts.** ALFAXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 69—70).—When heated with cuprous chloride, bromide or iodide, phenylhydrazine undergoes catalytic decomposition according to the equation:



(compare Struthers, P., 1905, 95). In all cases, an unstable intermediate compound is formed, that given by the iodide having the composition  $\text{CuI}, 2\text{NHPh}\cdot\text{NH}_2$ . Cuprous chloride is the most effective and the iodide the least so.

T. H. P.

**A Process for the Preparation of New Colouring Matters and its Application.** BRONISLAW PAWLEWSKI (*Bull. Soc. ind. Mulhouse*, 1912, **82**, 682—683).—When aniline in acid or alcoholic solution is oxidised at 50—60° with ammonium persulphate, a black dye is obtained, which is considered to be bisimino-*p*-benzoquinone,



By changing the conditions, other brown or black anilinoquinones are formed. Similar colouring matters containing oxygen have been prepared from *m*-phenylenediamine, *o*-dianisidine, and benzylaniline. They are easily fixed by cotton, linen or silk, with or without the aid of mordants.

J. C. W.

**Preparation of 1-p-Bromo-4-iodophenyl- and of 4-Bromo-1-p-iodophenyl-2:3-dimethyl-5-pyrazolone.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254487).—The introduction of bromine and iodine into the molecule of 1-phenyl-2:3-dimethyl-5-pyrazolone confers on it a markedly increased therapeutic activity.

**1-p-Bromo-4-iodophenyl-2:3-dimethyl-5-pyrazolone** (annexed formula), colourless crystals, m. p. 163°, is obtained when a benzene solution of *p*-bromophenyl-2:3-dimethyl-5-pyrazolone (A., 1900, i, 695) is treated with finely powdered iodine and heated at 50–60° during two hours, whilst **4-bromo-1-p-iodophenyl 2:3-dimethyl-5-pyrazolone**, pale yellow leaflets, m. p. 170°, is prepared by the bromination of 1-*p*-iodophenyl-2:3-dimethyl-5-pyrazolone (A., 1907, i, 84).

F. M. G. M.

**Hydantoins. XXI. Action of Ammonium and Potassium Thiocyanates on  $\alpha$ -Amino-acids.** TREAT B. JOHNSON and BEN H. NICOLET (*Amer. Chem. J.*, 1913, **49**, 197–204).—In an earlier paper (this vol., i, 203), it has been pointed out that ammonium and potassium thiocyanates behave somewhat differently towards  $\alpha$ -amino-acids. It has now been found that both salts combine with the acids to form the same thiohydantoins, but that the best yields are obtained by means of the ammonium salt.

When asparagine is treated with ammonium thiocyanate, 2-thio-3-acetylhydantoin-4-acetamide (Johnson and Guest, A., 1912, i, 807) is obtained in a yield amounting to 50% of the theoretical, whilst with the potassium salt a yield of only 6% is obtained.

Phenylalanine gives with ammonium thiocyanate a 94% yield of 2-thio-3-acetyl-4-benzylhydantoin, m. p. 170° (not 257° as stated by Johnson and O'Brien, A., 1912, i, 806); a somewhat smaller yield is obtained by the use of the potassium salt.

By the action of ammonium thiocyanate on tyrosine, a 94% yield is obtained of 2-thio-4-*p*-hydroxybenzylhydantoin,



m. p. 211°, which forms pale yellow needles; if potassium thiocyanate is employed, only a very small yield is obtained.

2-Thio-3-benzoylhydantoin (Johnson and Nicolet, A., 1912, i, 53) is obtained in 85–88% yield by the action of ammonium thiocyanate on hippuric acid, but in not more than 50% yield by the action of the potassium salt.

In the case of alanine, an excellent yield of 2-thiol-3-acetyl-4-methylhydantoin (Johnson, A., 1912, i, 390) is obtained with ammonium thiocyanate, but only about 34% with the potassium salt.

The thiohydantoin of pyrrolidonecarboxylic acid (Johnson and Guest, A., 1912, i, 317) is readily obtained in good yield by means of ammonium thiocyanate, but only in small amount by the action of the potassium salt.

E. G.

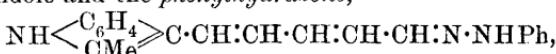
**The Reactivity of the  $\beta$ -Unsubstituted Pyrrole Ring. III. Action of Cyanogen Bromide and Pyridine on Indoles.** WALTER KÖNIG and R. SCHRECKENBACH (*J. pr. Chem.*, 1913, [ii], 87, 241—257). —In view of the parallelism, previously shown to exist (A., 1911, i, 808), in the reactivity of primary aromatic amines and phenols on the one hand, and of 3-unsubstituted indole derivatives on the other, the author has examined the behaviour of the latter compounds toward pyridine and cyanogen bromide, and finds that they yield dyes which have the general formula :



and are, therefore, closely related to the pyridine dyes derived from aromatic amines.

*a*-2-Methylindyl- $\epsilon$ -2-methylindolidene- $\Delta^{\alpha\gamma}$ -pentadiene hydrobromide,  $\text{NH} < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{CMe} \end{matrix} > \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} : \text{C} < \begin{matrix} \text{C}_6\text{H}_4 \\ \text{CMe} \end{matrix} > \text{NHBr}$ , is obtained in lustrous, golden leaflets by the action of hot acetone on its additive compound,  $\text{C}_{23}\text{H}_{21}\text{N}_2\text{Br}, \text{C}_5\text{H}_5\text{N}, \text{HBr}$ , with pyridine hydrobromide. The latter compound separates in green needles by the successive addition of pyridine and cyanogen bromide in ethereal solution to 2-methylindole, dissolved in methyl alcohol. The dihydrobromide, prepared by warming the monohydrobromide with acetone and hydrobromic acid, crystallises in lustrous, silky, bluish-green needles.

On treatment with aqueous sodium hydroxide and methyl alcohol, the hydrobromide yields the dye-base,  $\text{C}_{28}\text{H}_{20}\text{N}_2$ . This forms bluish-black needles, and is converted at  $220^\circ$  into a yellow substance, m. p.  $265^\circ$ , which probably has the same composition as the original dye-base, yields a phenylhydrazone (decomp.  $160$ — $170^\circ$ ), and when heated at  $160^\circ$  under diminished pressure decomposes, yielding 2-methylindole. The dye-base reacts with phenylhydrazine in alcoholic solution, yielding 2-methylindole and the phenylhydrazone,



which forms an amorphous, light yellow powder (decomp.  $170$ — $180^\circ$ ) containing alcohol (1 mol.).

On treatment with dry hydrogen chloride, the dye-base yields a hydrochloride,  $\text{C}_{23}\text{H}_{21}\text{N}_2\text{Cl}$ ; the perchlorate,  $\text{C}_{23}\text{H}_{21}\text{O}_4\text{N}_2\text{Cl}$ , forms small, compact, green crystals having a golden lustre, and crystallises with methyl alcohol in long, slender, bluish-green needles.

*a*-Indyl- $\epsilon$ -indolidene- $\Delta^{\alpha\gamma}$ -pentadiene hydrobromide,  $\text{C}_{21}\text{H}_{17}\text{N}_2\text{Br}$ , prepared from indole, cyanogen bromide, and pyridine in methyl alcoholic solution, forms a microcrystalline, dark blue powder, containing pyridine (1 mol.).

*a*-2:4-Dimethylindyl- $\epsilon$ -2:4-dimethylindolidene- $\Delta^{\alpha\gamma}$ -pentadiene hydrobromide, prepared from 2:4-dimethylindole, yields on treatment with aqueous sodium hydroxide and methyl alcohol the dye-base,  $\text{C}_{25}\text{H}_{24}\text{N}_2$ , which forms microcrystalline, bluish-black needles; a dihydrobromide and a perchlorate, crystallising in green leaflets of a golden lustre, are also described.

The action of cyanogen bromide and pyridine on phloroglucinol and

resorcinol gives rise to blue pyridine dyes, which, however, are too unstable to be isolated.

F. B.

[Preparation of 4-Chloro-5-bromoisoat.] KALLE & Co. (D.R.-P. 254468).—4-Chloroisatin, a yellow, crystalline powder, m. p. 254°, is prepared by treating a cooled acetic-chromic acid solution of 4 : 4'-dichloroindigotin with concentrated nitric acid; when warmed with bromine (in acetic acid solution) it gives rise to 4-chloro-5-bromoisoat, red needles, m. p. 255°, which on treatment with phosphorus pentachloride furnishes 4-chloro-5-bromoisoat chloride, brown needles, m. p. 278°; the corresponding anilide was also prepared.

F. M. G. M.

Preparation of 5 : 6 : 5' : 6'-Tetrachloroindigotin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254467).—4 : 5-Dichloro-2-nitrobenzaldehyde, yellow prisms, m. p. 73°, is prepared by the nitration of 4 : 5-dichlorobenzaldehyde; this when condensed with acetone in the presence of sodium hydrogen sulphite furnishes dichloronitrophenyl-lactyl ketone, m. p. 116°, which is readily converted by known methods into 5 : 6 : 5' : 6'-tetrachloroindigotin, a substance possessing valuable tinctorial properties.

F. M. G. M.

Preparation of Dinitro-1 : 1'-dianthrimide. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254186).—The nitration of dianthrimide (which has previously been described) takes place more smoothly and yields a definite characteristic product when carried out in the presence of boric acid.

1 : 1'-Dianthrimide (100 parts) and boric acid (65 parts) are dissolved in 1000 parts of concentrated sulphuric acid, treated at 5—10° with 27% nitric acid (122 parts), and left during two to three days at the ordinary temperature, when about 87% of the 4 : 4'-dinitro-1 : 1'-dianthrimide separates in glistening, coppery crystals. The m. p. is above 300°, and it is identical with the compound previously obtained by condensing 4-nitro-1-amino- with 4-chloro-1-amino-anthraquinone; on reduction it furnishes 4 : 4'-diamino-1 : 1'-dianthrimide.

F. M. G. M.

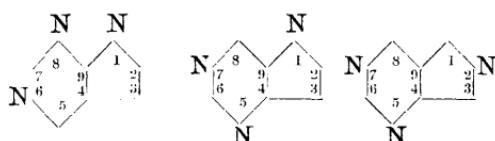
Preparation of  $\omega$ -Methylsulphites of Substituted Aminoarylpyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254711).—Compounds having valuable therapeutic properties are obtained when the substituted 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolones are heated with formaldehyde and sodium hydrogen sulphite; compounds obtained in this manner from the following pyrazolones have now been prepared. From 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, sintering and decomposing at 231—233°; from 4-amino-1-p-tolyl-2 : 3-dimethyl-5-pyrazolone, sintering at 120°, decomposing at 125°; from 1-p-aminophenyl-2 : 3-dimethyl-5-pyrazolone, isolated as its hygroscopic, crystalline sodium salt; from 1-p-aminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone, also isolated as a crystalline

sodium salt; from 4-amino-1-*p*-ethoxyphenyl-2:3-dimethyl-5-pyrazolone, m. p. 113—115°, decomp. at 133—135°. The foregoing 4-amino-*p*-ethoxyphenyl-2:3-dimethyl-5-pyrazolone, m. p. 132—133°, is obtained by the reduction of 4-nitroso-*p*-ethoxy-2:3-dimethyl-5-pyrazolone.

F. M. G. M.

**Pyrimidines. LIX. Barbituryl- and 2-Thiobarbituryl-5-acetic Acids.** TREAT B. JOHNSON and EDWARD F. KOHMANN (*Amer. Chem. J.*, 1913, **49**, 184—197).—An account is given of experiments

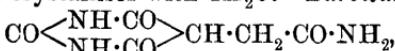
undertaken with a view to the preparation of compounds containing condensed pyrimidine and pyrrole nuclei, and corresponding with the indoles and pyridoles (Perkin



and Robinson, T., 1912, **101**, 1787). Compounds of this new class are termed 1:6:8-, 1:5:7-, and 2:5:7-pyrimazoles (annexed formulæ).

A 1:6:8-pyrimazole has already been obtained by heating ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate with alcoholic ammonia (A., 1911, i, 575); this compound, previously termed 2-ethylthiol-5:6-*a*-pyrrolidone-pyrimidine, is now designated 2-keto-7-ethylthiol-1:6:8-pyrimazole.

When ethyl ethane-*aaβ*-tricarboxylate is treated with carbamide in the presence of sodium ethoxide, the sodium salt of barbituryl-5-acetamide is obtained, which crystallises with 4H<sub>2</sub>O. *Barbituryl-5-acetamide*,

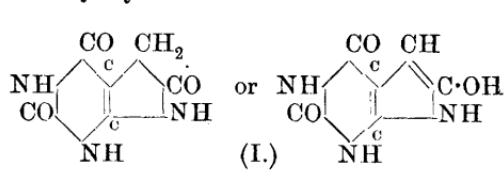


m. p. 258—261° (decomp.), crystallises in needles. *Barbituryl-5-acetic acid*, CO < NH · CO > CH · CH<sub>2</sub> · CO<sub>2</sub>H, obtained by the action of 20% hydrochloric acid on the sodium salt of the amide, separates in plates, becomes charred at 230°, and decomposes at 250°. An attempt to condense the amide to a 1:6:8-pyrimazole by the action of phosphoryl chloride on its sodium salt was not successful.

*Thiobarbituryl-5-acetamide*, CS < NH · CO > CH · CH<sub>2</sub> · CO · NH<sub>2</sub> · H<sub>2</sub>O,

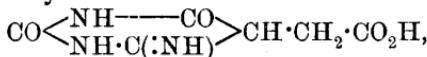
prepared by the condensation of thiocarbamide with ethyl ethane-*aaβ*-tricarboxylate, crystallises in needles and decomposes at 272°; the sodium salt forms long, colourless prisms. *Thiobarbituryl-5-acetic acid*, CS < NH · CO > CH · CH<sub>2</sub> · CO<sub>2</sub>H · 2H<sub>2</sub>O, crystallises in needles and decomposes above 230°.

Ethyl cyanosuccinate condenses with carbamide with formation of a



pyrimidine. The reaction does not take place smoothly, and only small yields of condensation products are obtained. In one experiment, barbituryl-5-acetic acid was pro-

produced, together with 2 : 5 : 7-triketo-1 : 6 : 8-pyrimazole (formula I), which forms a brown powder and does not melt below 320°. In another experiment, barbituryl-5-acetic acid and 4-ininobarbituryl-5-acetic acid,



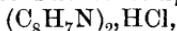
were isolated; the latter substance is a brown powder, and does not melt below 338°. E. G.

**Preparation of Azimino-[Triazole]-compounds in the Anthraquinone Series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254745).—The azimino-compounds having the general formula A  $\begin{array}{c} \text{NR} \\ \diagup \\ \text{N} \end{array} \Rightarrow \text{N}$ , where A is anthraquinone and R hydrogen, alkyl or aryl groups, and prepared by the action of nitrous acid on o-diaminoanthraquinones, are of technical value for the preparation of dyes. The preparation of the following compounds is described: From 1 : 2-diaminoanthraquinone, needles; from 2 : 3-diaminoanthraquinone, and from 1-p-tolylamino-2-amino-3-bromoanthraquinone, citron-yellow needles. The tinctorial properties of these compounds are enhanced by the introduction of halogens into the molecule.

F. M. G. M.

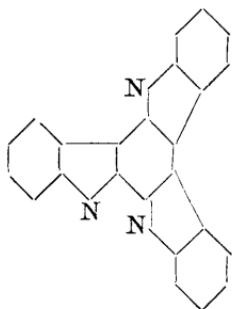
**Polymeric Indoles.** K. KELLER (*Ber.*, 1913, **46**, 726—733).—The high-boiling residue obtained in the distillation of practically pure indole consists of a trimeride, *tri-indole*, which after recrystallisation from benzene can be obtained in colourless crystals, m. p. 167°. The polymerisation can be better effected by heating indole with an aqueous solution of metaphosphoric acid. When distilled in a vacuum, tri-indole decomposes completely into indole; it gives a *monoacetyl* derivative, colourless crystals, m. p. 202°, and a *monobenzoyl* derivative, colourless, crystalline powder, m. p. 207°. These acyl compounds are remarkably resistant to alkalis. When benzoyltri-indole is heated in a vacuum, indole distils away, leaving a residue of *benzoyldi-indole*, colourless needles, m. p. 198°; this resisted all attempts at acetylation and hydrolysis. The easiest method for the preparation of benzoyl-tri-indole is by boiling together a benzene solution of indole with anhydrous sodium carbonate and benzoyl chloride, whilst a slow current of hydrogen chloride is passed through the mixture; the yield is then 90% of the indole taken.

The action of hydrogen chloride on a solution of indole in benzene yields a colourless salt of composition



presumably *di-indole hydrochloride*, but it was not found possible to isolate the corresponding base in a pure state.

From a consideration of the behaviour of the above tri-indole derivatives, the annexed structure is suggested for the base, the reactive indole nucleus being that on the left; this differs from the remaining two by being attached to the rest of the molecule at carbon atoms which are each adjacent to nitrogen atoms. D. F. T.



**Preparation of Formaldehyde Derivatives of Xanthine and its Substitution Products.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254488).—When xanthine, its derivatives, or the purine bases are gently heated in aqueous or hydrochloric acid solution with formaldehyde (or its generators), they furnish compounds of marked therapeutic value. The following are described: (1) From 1:3-dimethylxanthine and formaldehyde in aqueous solution, contains 14% formaldehyde, m. p. 265° when slowly heated, but if suddenly subjected to a temperature of 165—170°, violent decomposition occurs with regeneration of 1:3-dimethylxanthine.

(2) From 3:7-dimethylxanthine with paraformaldehyde in fuming hydrochloric acid solution, it forms characteristic needles, contains 14% formaldehyde, and does not melt below 300°.

(3) From xanthine and formaldehyde, contains 32% formaldehyde ; and (4) from 3-methylxanthine contains 16% of formaldehyde. These compounds readily decompose in the organism with elimination of formaldehyde.

F. M. G. M.

**The Anomalies in the Solubility of Uric Acid (Colloidal Uric Acid).** HEINRICH SCHADE and E. BODEN (*Zeitsch. physiol. Chem.*, 1913, **83**, 347—380).—If uric acid is suspended in boiling water, and alkali is then added very slowly until the mixture is just alkaline to phenolphthalein, the acid appears to pass into solution. This solution can be made by one of the following methods to set to a solid gel : (a) by the addition of concentrated sodium chloride solution ; (b) by addition of other salt solutions, such as ammonium sulphate, which are ordinarily employed for the precipitation of colloids ; (c) by addition of alcohol, and (d) by rapid cooling. The same phenomenon can be produced when the acid is neutralised by ammonia, lithium, sodium and potassium hydroxides, by the alkaline earths, and even ferric hydroxide. The appearance of the gel thus produced is described in great detail, and also the phenomena of its gradual transformation into the ordinary crystalline form. The colloid appears to be a supersaturated uric acid solution, in which the uric acid forms an adsorption compound with the alkali, which causes it to retain the colloidal form, and this adsorption compound appears to be a preliminary stage in the formation of the true chemical crystalline compound. The view here advanced can explain certain anomalies, to which Bechhold and Ziegler have called attention as regards the solubility of uric acid in serum.

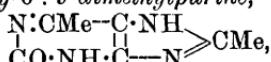
S. B. S.

**Purines. VIII. 2:8-Dihydroxy-1:9-dimethylpurine and 2-Hydroxy-6:9-dimethylpurine.** CARL O. JOHNS (*J. Biol. Chem.*, 1913, **14**, 1—7).—2:8-Dihydroxy-1:9-dimethylpurine is synthesised as follows : the potassium salt of 5-nitro-6-methylamino-2-hydroxy-pyrimidine (Johns, A., 1911, i, 506) when heated with methyl iodide gives 5-nitro-6-methylamino-2-hydroxy-3-methylpyrimidine, the constitution of which is established by heating the methylated product with sulphuric acid, when 5-nitro-2:6-dihydroxy-3-methylpyrimidine (Behrend and Thurm, A., 1902, i, 833) is obtained.

On reducing the methylated product with freshly precipitated

ferrous hydroxide, it is converted into *5-amino-6-methylamino-2-oxy-3-methylpyrimidine*,  $\text{N} \leqslant \begin{matrix} \text{C}(\text{NHMe}) \cdot \text{C} \cdot \text{NH}_2 \\ \text{CO} \cdot \text{NMe} \end{matrix} \text{---CH}$ . This is very soluble and purified only with difficulty. The crude base was accordingly heated with carbamide and converted into *2:8-dioxy-1:9-dimethylpurine*,  $\text{NMe} \cdot \text{CH} \cdot \text{C} \cdot \text{NH} \geqslant \text{CO} \cdot \text{NMe}$ .

By heating the potassium salt of acetyl-5 : 6-diamino-2-oxy-4-methylpyrimidine, *2-oxy-6 : 9-dimethylpurine*,



is obtained.

*5-Nitro-6-methylamino-2-oxy-3-methylpyrimidine* forms a bulky mass of hair-like crystals, m. p. 203°, to a colourless oil.

The picrate of *5-amino-6-methylamino-2-oxy-3-methylpyrimidine* crystallises in long prisms, m. p. 200° (decomp.).

*2:8-Dioxy-1:9-dimethylpurine* crystallises in small, irregular plates, which do not melt or char at 320°.

*2-Oxy-6 : 8-dimethylpurine* separates in small prisms with square ends, which slowly turn brown at 315°; they give a murexide reaction.

E. F. A.

**Azomethines and Azo-dyes.** CAMILLE G. VERNET (*Arch. Sci. phys. nat.*, 1913, [iv], 35, 148—172).—The azomethines derived from a number of diamines and benzaldehyde or its derivatives are described. In general they are formed quantitatively, the amount isolated depending on the manner in which the condensation is effected and the dilution of the solvents employed.

2-Mononitrobenzidine forms with benzaldehyde a yellowish-brown compound, m. p. 157°; with one molecule of *p*-nitrobenzaldehyde the product is red, m. p. 200—201°, with two molecules it is yellow, m. p. 205—206°; with dimethyl-*p*-aminobenzaldehyde it is yellow with an ill-defined melting point; with *o*-vanillin it is red, m. p. 200°.

*m*-Dinitrobenzidine and *o*-vanillin yield a reddish-brown product.

Benzidinesulphone combines with one molecule of benzaldehyde to a yellow compound, m. p. 259—260°; with *p*-nitrobenzaldehyde to a brown compound, m. p. 302—304°; with dimethyl-*p*-aminobenzaldehyde the compound is yellow, m. p. 318°; with *o*-vanillin it is yellowish-red.

Diaminodiphenylamine and benzaldehyde form a yellow compound, m. p. 184—185°; with *p*-nitrobenzaldehyde the compound is black with a metallic lustre, m. p. 219°; with dimethyl-*p*-aminobenzaldehyde it is very similar, m. p. 222°; with *o*-vanillin it is brick-red, m. p. 207—208°.

3 : 3'-Diaminocarbazole and benzaldehyde yield a yellow substance, m. p. 186°; the product with *p*-nitrobenzaldehyde is red, m. p. 306—307°; with dimethyl-*p*-aminobenzaldehyde it is yellowish-brown, m. p. 266—268°; with *o*-vanillin it is brick-red, m. p. 254—255°.

*trans*-*o*-Diaminostilbene and benzaldehyde form a yellow product, m. p. 188°; with *p*-nitrobenzaldehyde it is orange-red, m. p. 228°; with

dimethyl-*p*-aminobenzaldehyde it is yellow, m. p. 227°, and with *o*-vanillin it is red, m. p. 228°.

*p*-Diaminostilbene yields a yellow compound with benzaldehyde, m. p. 254°; an orange-red compound with *p*-nitrobenzaldehyde, m. p. 242°; a reddish-yellow product with dimethyl-*p*-aminobenzaldehyde, m. p. 233°, and a red product with *o*-vanillin.

These azomethines are all very similar; the nitro-group has a greater effect in intensifying the colour than the substituted amino-group.

Most of the compounds have a normal composition with both amino-groups condensed, but traces of the condensation products with a single molecule of aldehyde are formed at the same time.

A comparison is made of the colours obtained by soaking the material impregnated with sodium-β-naphthoxide in the diazotised solutions of a number of diamines. Whereas benzidine gives a brown, thiobenzidine and benzidinesulphone give reddish-brown shades, mononitrobenzidine gives a red, *m*-dinitrobenzidine an orange, and the *o*-dinitro-derivative a garnet-red. With 2:2'- or 3:3'-diamino-carbazole the colour is almost black, and *p*-diaminostilbene gives a similar colour. The replacement of an atom of hydrogen by a univalent grouping has more influence on the colour than when two atoms of hydrogen are replaced by a bivalent substituent.

Each of the diamino-bases studied has been coupled with five acid compounds, namely, H-acid, chromotropic acid, Neville and Winther's acid, resorcinol, and naphthoic acid. The resulting compounds have not been analysed, but were directly utilised for dyeing tests. The colours obtained are detailed in tabular form; they act as substantive colours for cotton, and dye wool from acid solutions.

E. F. A.

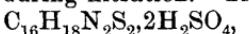
**Thiophenols. III. *pp'*-Azophenyl Methyl- and *pp'*-Azophenyl Ethyl-sulphide.** KURT BRAND and ADOLF WIRSING (*Ber.*, 1913, **46**, 820—829).—The authors have extended their previous work on *pp'*-azophenyl methyl sulphide (A., 1912, i, 666), and have investigated the corresponding ethyl derivative.

A concentrated aqueous solution of sodium hydroxide and sodium sulphide is gradually added to a boiling alcoholic solution of di-*p*-nitro-diphenyl disulphide. From the cooled reaction mixture, the sodium derivative of *p*-nitrophenyl mercaptan,  $C_6H_4O_2NSNa, 2H_2O$ , separates in golden leaflets, which decompose when heated slightly above 100°. The salt dissolves in water, forming a yellow solution, which, on addition of acid, becomes colourless and deposits *p*-nitrophenyl mercaptan. The solution absorbs oxygen with the formation of the disulphide. When warmed with an excess of ethyl bromide, the above sodium salt is transformed into *p*-nitrophenyl ethyl sulphide, m. p. 48° (Blanksma, A., 1902, i, 282, gives 40°; L. Gattermann, 44°). *pp'*-Azoxyphenyl ethyl sulphide,  $ON_2(C_6H_4'SEt)_2$ , is obtained when a methyl-alcoholic solution of *p*-nitrophenyl ethyl sulphide is added to a boiling solution of sodium methoxide in methyl alcohol. It forms pale yellow needles, m. p. 97—98°. A sulphinium compound could not be obtained from it by the action of methyl sulphate.

*pp'*-Hydrazophenyl ethyl sulphide, m. p. 76°, is obtained in the same manner as the corresponding methyl compound (*loc. cit.*). In alkaline alcoholic solution it is more readily oxidised by air than the

latter compound, and forms *pp'-azophenyl ethyl sulphide*, m. p. 132°. Treatment with concentrated hydrochloric acid transforms *pp'-hydrazophenyl ethyl sulphide* into *p-aminophenyl ethyl sulphide hydrochloride*, which readily gives up a portion of the hydrogen chloride. The free base, obtained from the hydrochloride by means of ammonia, has b. p. 165°/12 mm. (compare Auwers and Beger, A., 1894, i, 466; Monier-Williams, T., 1906, 89, 278; Gattermann, A., 1912, i, 986). *p-Acetylaminophenyl ethyl sulphide*, m. p. 116°, is obtained by shaking an aqueous solution of *p-aminophenyl ethyl sulphide hydrochloride* with sodium acetate and acetic anhydride, or by boiling the free base with the same reagents.

*pp'-Azophenyl ethyl sulphide*,  $N_2(C_6H_4 \cdot S\text{Et})_2$ , orange leaflets, m. p. 132°, is obtained by reduction of *p-nitrophenyl ethyl sulphide* by means of zinc and sodium hydroxide and oxidation of the hot, filtered solution by passing air through it. With mineral acids and strong organic acids it yields intensely blue solutions. The crystalline *hydrochloride* and *trichloroacetate* could not be obtained in the pure state, as they decompose during filtration. The *sulphate*,



green metallic needles, is obtained by the addition of sulphuric acid to a solution of *pp'-azophenyl ethyl sulphide* in glacial acetic acid. The following double salts have been obtained :  $C_{16}H_{18}N_2S_2 \cdot HCl \cdot HgCl_2$ , dark violet needles ;  $C_{16}H_{18}N_2S_2 \cdot HCl \cdot FeCl_3$ , green leaflets ;  $[C_{16}H_{18}N_2S_2 \cdot HCl]_2 \cdot FeCl_3$ , dark green needles ;  $C_{16}H_{18}N_2S_2 \cdot HCl \cdot SnCl_4$ , green leaflets ;  $[C_{16}H_{18}N_2S_2 \cdot HCl]_2 \cdot SnCl_4$ ,

dark green needles. They were prepared by mixing *pp'-azophenyl ethyl sulphide* with the metallic chloride in hot glacial acetic acid solution, addition of hydrochloric acid being necessary in the first, third, and fifth cases. They are immediately decomposed by water.

When *pp'-azophenyl ethyl sulphide* is heated with methyl sulphate and the reaction mixture treated with alcohol, light red crystals, m. p. 158°, are obtained. The aqueous solution yields, on addition of potassium iodide, a sulphinium iodide, m. p. 158—160°, analyses of which give results from which the authors conclude that the substance is *pp'-azophenyldimethylsulphinium iodide*. The discrepancy between the m. p. now found and that previously given (174—175°, *loc. cit.*) is attributed to impurity of the specimen.

In extension of their previous work, the authors have prepared the double salt,  $(C_{14}H_{14}N_2S_2 \cdot HCl)_2 \cdot SnCl_4$ , green needles by the action of stannic chloride and hydrochloric acid on a solution of *pp'-azophenyl methyl sulphide* in glacial acetic acid. They also find that *pp'-azophenyldimethylsulphinium methyl sulphate* is more conveniently prepared by heating *p'-azophenyl methyl sulphide* and methyl sulphate for an instant at the boiling point and treatment of the resulting product with alcohol. When this salt is treated with sodium hydroxide, it forms a new compound,  $C_{18}H_{26}O_8N_2S_4$ , investigation of which is not yet completed.

H. W.

**The Lakes of Hydroxylic Dyes.** RICHARD MÖHLAU (*Ber.*, 1913, 46, 443—456).—[With JOHANNES MAETZEL]—A brief account is first

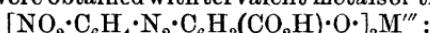
given of previous investigations of the compounds of dyes with mordants.

A number of compounds were prepared from various metallic mordants and hydroxylic dyes by precipitation. For the production of simple lakes derived from tervalent metals, solutions of a salt of the metal and of the potassium derivative of the dye were mixed. In order to obtain more complex lakes containing both tervalent and bivalent metals, the tervalent metal derivative was first prepared, and its solution in ammonium hydroxide was then treated with a solution of an equivalent amount of the salt of the bivalent metal (compare Liechti and Suida, A., 1884, 794; 1885, 315; Liebermann and Michaelis, A., 1895, i, 108, 671; Biltz, A., 1906, ii, 78).

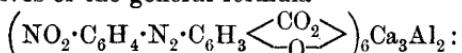
The fact that the lakes with the tervalent metals will dissolve readily in ammonium hydroxide indicates that the metallic atom is attached to hydroxylic oxygen, producing phenolic salts; the further introduction of the bivalent metallic atoms is then due to replacement of the hydrogen of the carboxyl or remaining hydroxyl group.

The following lakes of alizarin with tervalent metals were prepared, of the type  $\text{Me}''(\text{C}_{14}\text{H}_7\text{O}_4)_3$ : *aluminium*, dark brown powder; *chromium*, yellow powder; *iron*, bluish-black powder. These could give calcium derivatives of the general formula  $\text{Me}_2''\text{Ca}_3(\text{C}_{14}\text{H}_6\text{O}_4)_6$ ; *aluminium calcium*, violet-brown; *chromium calcium*, deep violet; *iron calcium*, bluish-violet.

Of *p*-nitrobenzeneazosalicylic acid (the acid of alizarin-yellow-R), the following lakes were obtained with tervalent metals of the general formula



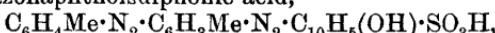
*aluminium*, red; *chromium*, brown; *iron*, chocolate. These gave calcium derivatives of the general formula



*aluminium calcium*, brownish-red; *chromium calcium*, brown; *iron calcium*, brownish-black.

The simple tervalent metallic lakes are more stable towards dilute acid and alkali than the more complex lakes containing two metals; of the latter, the aluminium calcium lakes are most stable and the iron calcium least, and those of alizarin are more stable than the corresponding derivatives of *p*-nitrobenzeneazosalicylic acid.

Benzeneazonaphtholsulphonic acid,  $\text{N}_2\text{Ph} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{SO}_3\text{H}$ , and azo-*o*-toluene-azonaphtholsulphonic acid,



give unstable *chromium* lakes, brownish-red and claret-red respectively, which are decomposed by dilute alkali or mineral acid; they are consequently regarded as being normal chromium salts and not phenolic derivatives. Complex lakes containing two metals could not be prepared from them.

D. F. T.

**Preparation of Acetyl Derivatives of Aminoazobenzene, its Homologues and Analogues. KALLE & Co. (D.R.-P. 253884).—** Acetyl derivatives of aminoazobenzene and of the aminoazo compound prepared from *o*-toluidine have been described previously; it is now

found that by prolonged heating with excess of the reagent, diacetyl derivatives are formed.

*Diacetylaminoazotoluene* exists in two modifications, long, reddish-yellow needles, m. p. 65°, and in crystals, resembling potassium dichromate with m. p. 75°; *diacetylaminoazobenzene* forms long, thin plates, m. p. 103—104°.

F. M. G. M.

**Density and Solution Volume of Certain Proteins.** (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 69—71).—From measurements of the density of casein, crystallised egg-albumin, crystallised serum-albumin and serum-globulin, and of the corresponding solution volumes in aqueous solution, it has been found that the density of the dissolved substance is in all cases greater than that of the free protein, the increase in density varying from 5 to 8%. In the case of serum-albumin and serum-globulin, the solution volume of the protein is independent of the concentration, whereas the contraction, which attends the dissolution of casein, diminishes as the concentration increases. H. M. D.

**The Amount of *l*-Tyrosine in Proteins and the Accuracy of its Estimation.** EMIL ABBERHALDEN and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, 83, 468—473).—The colorimetric method proposed for the estimation of *l*-tyrosine by Folin and Denis (A., 1912, ii, 1012) is shown to include other amino-acids, and to be untrustworthy. It is possible by crystallisation to separate completely the tyrosine from the products of protein hydrolysis, particularly when the necessary concentration of the liquids is effected under reduced pressure. Most of the published determinations of tyrosine in proteins have been made with insufficient care.

E. F. A.

**Colloidal Solutions. I. Certain Metallic Peptonates.** EMANUELE PATERNÒ and FLORENTIN MEDIGRECEANU (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 65—68).—Solutions of iron, copper, zinc, and barium peptonate were subjected to prolonged dialysis, and after making up the volumes of the dialysed and residual solutions to the volume of the original solutions, measurements were made of the freezing point, total solids, ash, total nitrogen, and metal for each portion, the data being compared with the corresponding numbers for the original solutions. The observations seem to show that the substances formed by combination of peptone with the metal are, at any rate in the case of iron and copper, of colloidal nature.

H. M. D.

**Porphyrinogen.** HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1913, 46, 511—514).—By the action of a mixture of glacial acetic acid and hydrogen iodide in presence of phosphonium iodide on haemin in the cold, a colourless, crystalline reduction product,  $C_{33}H_{42}O_4N_4$ , of high molecular weight is obtained. This is termed porphyrinogen in view of its ready conversion into a red product having the spectroscopic properties of porphyrin.

Sodium methoxide acts on porphyrinogen forming phyllopyrrole;

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also a porphyrin, of which the hydrochloride crystallises in centrically grouped needles—probably mesoporphyrin.

On oxidation, porphyrinogen yields methyl ethylmaleimide and haematinic acid.

The colourless porphyrinogen behaves as a sensitising agent when injected into mice exposed to light rays. E. F. A.

**Pepsin. II.** SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 194—200. Compare A., 1910, i, 449).—The pepsin prepared according to the method previously described contains very little chlorine, and the author now finds that by suitable purification this element can be removed almost completely without diminishing the activity of the product. It appears, therefore, that the statements of previous authors that chlorine is a constituent of the substance are incorrect. R. V. S.

**Some Properties of Koji-diastase.** G. KITA (*J. Ind. Eng. Chem.*, 1913, **5**, 220—222).—It has been generally assumed that koji (a culture of *Aspergillus oryzae* on steamed rice) contains two different saccharifying enzymes only, namely, amylase and glucase, and that the dextrose present in a liquid saccharified by means of koji is produced by these two enzymes. Comparative experiments on starch and maltose showed, however, that more dextrose was produced from the starch than from maltose, and the author concludes that koji contains a third enzyme which produces dextrose directly from starch without the aid of glucase.

Sodium chloride has a protecting action on koji-diastase when heated, but not on malt-diastase, whilst sodium phosphate, asparagine, and sulphuric acid impair its activity more quickly. The inhibitory action of the sodium chloride depends on the concentration of the diastase; in a dilute solution of the enzyme it is very marked, but not in a concentrated solution. The activity of koji-diastase may be conserved in brine solution for a long period. T. S. P.

**The Reversibility of the Ferment Action of Emulsin.** ÉMILE BOURQUELOT and J. COIRRE (*Compt. rend.*, 1913, **156**, 643—646; *J. Pharm. Chim.*, 1913, [vii], **7**, 236—240. Compare A., 1912, i, 928; this vol., i, 212).—The state of equilibrium attained during the synthesis or hydrolysis of a glucoside in alcoholic solution under the influence of emulsin is independent of the amount of emulsin used and depends solely on the proportions of the components of the glucoside in the solution. The action is thus a true reversible reaction, the only effect of varying the concentration of the emulsin being to vary the rate at which equilibrium is reached. W. G.

**Hydrolysis of Amygdalin Under the Influence of Emulsin.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, **251**, 85—89).—Krieble's observation (A., 1912, i, 482) that certain kinds of emulsin react with amygdalin to give *l*-benzaldehydecyanohydrin is confirmed, and a series of experiments has been made to determine the mode of formation of the latter. It is shown that a portion of the benzaldehyde and

hydrogen cyanide which result from the gradual breaking down of amygdalin through mandelonitrile-glucoside and *d*-benzaldehydecyanohydrin re-combine to form *i*-benzaldehydecyanohydrin, and if an emulsin such as that from cherry kernels, which is very rich in *d*-oxynitrilase, is used, hydrolysis of the *d*-component of the inactive cyanohydrin ensues, *l*-benzaldehydecyanohydrin being left unaltered.

T. A. H.

**Distribution of Emulsin-like Enzymes.** LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, 251, 56—84).—The work done in recent years on “emulsin” shows that the latter may include different enzymes depending on its origin (A., 1910, i, 800; Armstrong and others, A., 1912, i, 816). The author has, therefore, investigated a large number of plants, particularly those which are known to be cyano-genetic, with a view to ascertaining which of the ordinary components of “almond emulsin” they contain. For this purpose the mixture of enzymes prepared from the plant was mixed with (1) a solution of amygdalin, (2) a mixture of benzaldehyde and hydrocyanic acid (A., 1909, i, 74, 622), and (3) *dl*-benzaldehydecyanohydrin (Feist, A., 1909, i, 589), and the products of the reaction, if any, investigated. The results are described in detail in the original, and are also tabulated for convenience of reference. The following points of special interest are recorded. Enzymes capable of producing asymmetric synthesis or decomposition (reactions 2 and 3 above) are widespread in plants, although less so that those capable of decomposing amygdalin; this apparent difference may, however, be due to the fact that enzymes of the last-mentioned type are easier to detect by means of their product of reaction. Enzymes of these types may occur in plants which do not yield hydrogen cyanide, but in such cases they are not found in the leaves. These enzymes are not identical with those which decompose amygdalin, since in certain cases, such as *Hydnocarpus Wightiana* seeds, *Pangium edule* seeds, and *Prunus laurocerasus* leaves, negative results were obtained in reaction (1) and positive results with (2) and (3). Similarly, in other cases positive results were obtained for reaction (2) and negative results for reaction (3). An enzyme preparation from the seeds of *Taraktogenos Blumei* furnished in reaction (2) *l*-benzaldehydecyanohydrin instead of the *d*-isomeride furnished by enzymes derived from plants of the order Prunaceæ; these seeds therefore appear to contain a *l*-oxynitrilese, which may also be present in the flowers of *Achillea millefolium*. No enzyme capable of producing optically active nitriles from ketones and hydrocyanic acid was observed. The enzyme of *Taraktogenos Blumei* is soluble in brine, but not in water.

T. A. H.

**Oxydases. VI. Tyrosinase is also a Deamidising Enzyme.** ROBERT CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1913, 35, 140—147. Compare A., 1912, ii, 399, 611).—It has been shown previously that for the completion of the colour reaction between tyrosinase and *p*-cresol, the presence of an amino-acid is necessary. It is now proved that tyrosinase has a deamidising action on glycine, which it converts into carbon dioxide, ammonia, and formaldehyde.

The change is greatly facilitated by the addition of lime water. The formation of formaldehyde is identified by means of Rimini's reagent (phenylhydrazine hydrochloride and potassium ferrocyanide), that of ammonia by means of Nessler's and Trilliat's reagents. The interaction of *p*-cresol, glycine, and tyrosinase is prevented by the addition of calcium hydroxide; in its absence the blue coloration is obtained, and formaldehyde and ammonia are detected amongst the products of reaction.

With alanine and tyrosinase, acetaldehyde is formed in place of formaldehyde. Benzaldehyde is obtained from phenylglycine and tyrosinase.

The presence of formaldehyde in plant tissues does not necessarily indicate photo-synthesis. Attention is drawn to the parallelism between the action of tyrosinase and of hydrogen peroxide on glycine (compare Dakin, A., 1906-1911). E. F. A.

**Preparation of Derivatives of Nitrohydroxy- and Amino-hydroxy-arylarsinic Acids Containing Sulphur.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253757).—When an alkaline solution of 3-nitro-4-hydroxyphenylarsinic acid is saturated with hydrogen sulphide at the ordinary temperature, it gives rise to *nitrohydroxyphenylarsenosquisulphide*,  $[NO_2 \cdot C_6H_3(OH) \cdot As]_2S_3$ , which crystallises from xylene in hard, yellow, nodular crystals, m. p. 160° (about).

Compounds obtained by the action of sodium sulphide on 3-nitro-4-hydroxyphenylarsinic acid (a pale brown powder), of hydrogen sulphide on 3-amino-4-hydroxyphenylarsinic acid, and on its hydrochloride are also described. F. M. G. M.

**Aromatic Arsenic Compounds. IV. Preparation of 3-Nitro-4-dimethylaminophenylarsinic Acid and of 3-Nitro-4-hydroxyphenylarsinic Acid.** P. KARRER (*Ber.*, 1913, **46**, 515-517).—*p*-Dimethylaminophenylarsinic acid is readily nitrated on solution in a mixture of acetic and nitric acids. When the mono-nitrodimethylaminophenylarsinic acid,  $NO_2 \cdot C_6H_3(NMe_2) \cdot AsO_3H_2$ , is warmed with sodium hydroxide, it is converted into 3-nitro-4-hydroxyphenylarsinic acid (Benda and Bertheim, A., 1911, i, 63), which in turn, when reduced, gives rise to the base,

$NH_2 \cdot C_6H_3(OH) \cdot As \cdot As \cdot C_6H_3(OH) \cdot NH_2$ ,  
corresponding with salvarsan.

When 3-nitro-4-dimethylaminophenylarsinic acid is similarly reduced, tetramethyltetra-aminoarsenobenzene,  
 $NMe_2 \cdot C_6H_3(NH_2) \cdot As \cdot As \cdot C_6H_3(NH_2) \cdot NMe_2$ , is obtained. This compound has no curative action towards mice infected with trypanosomes.

*3-Nitro-4-dimethylaminophenylarsinic acid* crystallises in lustrous, yellow needles.

The hydrochloride of tetramethyltetra-aminoarsenobenzene is a yellowish-white powder. E. F. A.

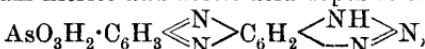
**Aromatic Arsenic Compounds. III. Triazoarylarsinic Acids and Some of their Derivatives.** P. KARRER (*Ber.*, 1913, **46**, 249-255).—Some triazophenylarsinic acids have been prepared

by the addition of sodium azoimide to the corresponding diazotised amines. They are very stable towards dilute sulphuric acid, and cannot be hydrolysed to aminophenols, but the *o*-nitrated azoimides give up nitrogen when heated and undergo rearrangement to *o*-dinitroso-compounds (compare Zincke and Schwarz, A., 1899, i, 751), which can be readily condensed with dimethylaniline to phenazine derivatives.

*p-Triazophenylarsinic acid*,  $N_3 \cdot C_6H_4 \cdot AsO_3H_2$ , from *p*-aminophenylarsinic acid, crystallises in stout, white crystals, and gives a mono-sodium salt. *3-Iodo-4-triazophenylarsinic acid* forms white crystals, and *3-nitro-4-triazophenylarsenic oxide*,  $N_3 \cdot C_6H_3(NO_2) \cdot AsO$ , prepared from *3-nitro-4-aminophenylarsenic dichloride*, which, in turn, is obtained from the arsanic acid, is a yellow, crystalline powder. *3-Nitro-4-triazophenylarsinic acid*, a yellow, crystalline powder, loses nitrogen at  $75^\circ$ , and changes into *3 : 4-dinitrosophenylarsinic acid*,  $C_6H_3(NO)_2 \cdot AsO_3H_2$ ; this condenses with dimethylaniline to form *2-(or 3)-dimethylaminophenazine-7-arsinic acid*,  $C_{14}H_{12}O_3N_3As$ , as a blue dye which is very soluble in acetic acid and in sodium hydroxide. *2-Nitro-3-triazophenylarsinic acid* also condenses with dimethylaniline, but *2-(or 3)-dimethylaminophenazine-8-arsinic acid* is insoluble in sodium hydroxide and has a reddish tinge.

*3-Nitro-4-triazophenylarsinic acid* can also be condensed with *o*-phenylenediamine in glacial acetic acid, when the *acetate* of *2 : 3-diaminophenazine-7-arsinic acid* separates as a brick-red powder. The free base (annexed formula) is yellow,

gives a *diacetyl* derivative as a yellowish-brown powder, and when treated with sodium nitrite and acetic acid deposits the compound,



in the form of a brown powder.

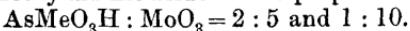
J. C. W.

### Iso- and Hetero-poly-salts. VIII. Alkylarsinomolybdates.

ARTHUR ROSENHEIM and ROBERT BILECKI (*Ber.*, 1913, **46**, 539—557. Compare A., 1911, i, 109, 265; ii, 116, 612; this vol., ii, 59).—In order to examine further the extension of Werner's co-ordination theory to poly-acids by Miolati and Pizzighelli (A., 1908, ii, 595), the authors have prepared a series of alkylarsinomolybdates. They find that the number of  $MoO_4$  or  $Mo_2O_7$  radicles which unite with the alkylarsenates to form complex compounds is intimately connected with the number of oxygen atoms in the arsenite anion, and diminishes as the number of alkyl radicles present increases. The basicity of the hetero-poly-acids so formed is either equal to, or, generally, higher than, that of the corresponding alkylarsenates. Normal hetero-poly-salts could not in all cases be obtained. This is attributed to the fact that the acids contain weakly electro-negative complex ions which are hydrolysed on neutralisation of the solutions. The composition of the hetero-poly-salts is found to depend on the electro-affinity of the central atom; more powerfully electronegative anions, such as the phenylarsinate- and *p*-hydroxyphenylarsinate-anions unite with  $MoO_4$

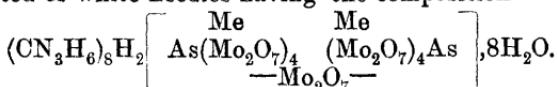
radicles, whilst the weaker electronegative anions, such as the dialkylarsinate-anion, unite with  $\text{Mo}_2\text{O}_7$  radicles.

The authors' experiments on solutions of cacodylic and molybdic acids agree with those of Miolati (*loc. cit.*). The latter, however, found breaks in the graph for the electrical conductivity of solutions of molybdic and methylarsinic acids at the proportions



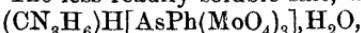
Since these figures did not agree with those obtained by the authors, the latter have plotted Miolati's graph on a larger scale, and find that it is not exact, somewhat weak breaks actually occurring at the proportions  $\text{AsMeO}_3\text{H} : \text{MoO}_3 = 1 : 6$  and  $1 : 9$ . The corrected result agrees with the authors' determinations.

A boiling aqueous solution of sodium methylarsinate was saturated with molybdic acid, and, after concentration, an excess of guanidinium chloride was added. Two *guanidinium* salts were thereby obtained, the less soluble of which was composed of rectangular plates having the formula  $(\text{CN}_3\text{H}_6)_2[\text{AsMe}(\text{Mo}_2\text{O}_7)_3], 11\text{H}_2\text{O}$ , whilst the more soluble salt consisted of white needles having the composition

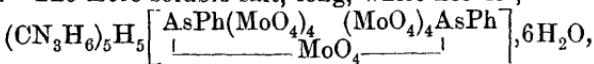


In alkaline solution only the latter salt was obtained.

Sodium phenylarsinate, when similarly treated, also yielded two *guanidinium* salts. The less readily soluble salt, white leaflets,



did not yield a neutral salt when boiled with excess of guanidinium carbonate. The more soluble salt, long, white needles,

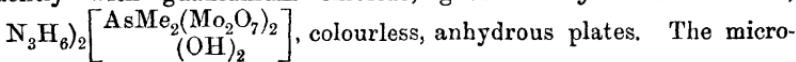


behaved according to conductivity measurements as the salt of a normal pentabasic substance. The hydrogen atoms could not be replaced by base in aqueous solution. In faintly alkaline solution, the more soluble salt was exclusively formed. When the latter salt was suspended in water and gently heated with guanidinium carbonate,

the salt,  $(\text{CN}_3\text{H}_6)_6\text{H}_2 \left[ \begin{array}{c} \text{AsPh}(\text{MoO}_4)_3 & (\text{MoO}_4)_3\text{AsPh} \\ | & | \\ \text{OH} & \text{MoO}_4 & \text{OH} \\ & | & \end{array} \right] , 4\text{H}_2\text{O}$ , was obtained.

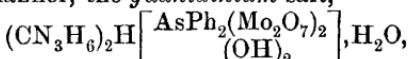
Precisely similar salts were obtained from those derivatives of phenylarsinic acid which did not form too powerfully electronegative anions; thus, from sodium *p*-aminophenylarsinate, the *guanidinium* salt,  $(\text{CN}_3\text{H}_6)_2 \left[ \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{NH}_2 \\ | \\ \text{As}(\text{MoO}_4)_3 \end{array} \right] , 5\text{H}_2\text{O}$ , pale yellow leaflets, was prepared, whilst sodium *p*-hydroxyphenylarsinate yielded a *guanidinium* salt,  $(\text{CN}_3\text{H}_6)_2 \left[ \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{OH} \\ | \\ \text{As}(\text{MoO}_4)_3 \end{array} \right] , 2\text{H}_2\text{O}$ , white needles, and also a more soluble salt, crystallising in small plates. A complex salt derived from *p*-carboxyphenylarsinic acid could not be isolated.

Sodium cacodylate, when treated with molybdic acid and subsequently with guanidinium chloride, gave the *guanidinium* salt,



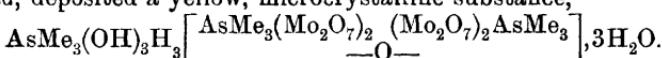
crystalline *lead*, *copper*, and *silver* salts were also prepared. The *potassium* salt, prepared from potassium cacodylate in the usual manner, formed microscopic needles of the formula  $K_2H\left[\frac{AsMe_2(Mo_2O_7)_2}{(OH)_2}\right]$ . The corresponding *barium* salt was obtained by the action of barium chloride on the sodium salt.

In a similar manner, the *guanidinium* salt,

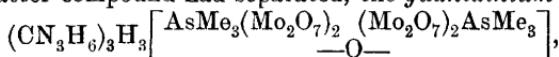


white, hexagonal plates, was obtained from sodium diphenylarsinate.

An aqueous solution of trimethylarsonium hydroxide was saturated with molybdic acid at its boiling point. The solution, when concentrated, deposited a yellow, microcrystalline substance,



When, however, guanidinium chloride was added to the above solution before the latter compound had separated, the *guanidinium* salt,

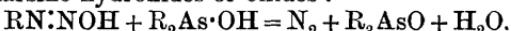


was obtained as microscopic, white plates.

When triphenylarsine oxide was dissolved in boiling aqueous sodium molybdate solution and the latter acidified by gradual addition of hydrochloric acid, a yellow, amorphous *substance*,  $\left[\frac{AsPh_3}{Mo_2O_7}\right]$ , was obtained.

H. W

**Preparation of Organic Arsenic Compounds.** HEINRICH BART (D.R.-P. 254345. Compare this vol., i, 115).—When solutions of *iso-diazo*-compounds react with diarylarsenious oxides (or acids) they give rise to triarylarsine hydroxides or oxides :



A 10% solution of sodium *p*-nitroisodiazobenzene is slowly treated with dinitrodiphenylarsenious acid and sodium hydroxide (1 mol.) ; on slowly heating to 75—80°, nitrogen is evolved, and on the addition of acid the trinitrotriphenylarsine oxide separates as a brown precipitate.

The required *dinitrodiphenylarsenious acid* is obtained by the careful reduction of dinitrodiphenylarsinic acid with hydrogen iodide in acetic acid solution ; when heated it decomposes energetically without fusion.

F. M. G. M.

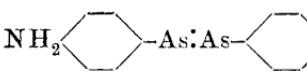
**Preparation of Unsymmetrical Arseno-compounds.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253226).—Unsymmetrical aromatic arseno-compounds have previously been prepared (this vol., i, 116), and this reaction has now been extended to the case of compounds containing both aliphatic and aromatic residues.

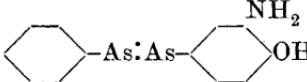
3-Amino-4-hydroxybenzenearsenomethane (annexed formula), a yellow powder soluble in dilute acids and alkaline hydroxides, is obtained when a methyl-alcoholic solution of 3-amino-4-hydroxyphenylarsenious oxide is treated with a similar solution of methyl arsenious oxide (A., 1906, i, 488), water added, and the mixture reduced with sodium hyposulphite.

One or both of the arsenious oxides in the foregoing reaction can be replaced by the corresponding acids, in which case the reduction is carried out with stannous chloride and hydrogen iodide at  $-10^{\circ}$  to  $-20^{\circ}$ .

F. M. G. M.

**Preparation of Aromatic Arseno-compounds.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254187). Compare A., 1909, i, 347; 1910, i, 148).—When aromatic arsinic acids are reduced in strongly acid solution they give rise to primary arsines of general formula  $R\cdot AsH_2$  ( $R$  = aryl), which can be condensed with aryl-arsenious oxides or haloids to yield aromatic arseno-derivatives (this vol., i, 117) :  $R\cdot AsH_2 + R\cdot AsO = R\cdot As\cdot As\cdot R + H_2O$ ;  $R\cdot AsH_2 + R\cdot AsCl_2 = R\cdot As\cdot As\cdot R + 2HCl$ .

 *4-Amino-4'-hydroxyarsenobenzene* (annexed formula), a yellow powder, decomposes at about  $200^{\circ}$ ; *3-amino-4-hydroxy-4'-glycylarsenobenzene* (this vol., i, 116) darkens at  $120^{\circ}$  and decomposes violently at  $150^{\circ}$ , and *3-amino-4-hydroxyarsenobenzene* (annexed formula) forms a yellow powder.

 Other compounds mentioned as being prepared by this method are *4:4'-diamino-arsenobenzene* and *3:3'-diamino-4:4'-dihydroxyarsenobenzene*.

F. M. G. M.

**Preparation of Aromatic Stibinic Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 254421). Compare Trans., 1911, 99, 2286).—Phenylstibinic acid has previously been prepared (Hasenbäumer and others) by a somewhat complicated series of reactions; the following simple method is now described.

Antimony trioxide (140 parts) is dissolved at the ordinary temperature in 764 parts of hydrochloric acid (D 1.123), treated with sodium hydroxide (600 parts) in water (3000 parts), and rapidly cooled to  $0^{\circ}$ , when part of the sodium antimonite separates. A solution of aniline-diazonium sulphate (prepared from 93 parts of aniline and 147 parts of sulphuric acid) is then rapidly stirred in, either with or without the addition of copper paste; after some hours the mixture is carefully neutralised with sulphuric acid, filtered, and the phenylstibinic acid precipitated by the addition of hydrochloric acid. To purify the product from antimony trioxide it is dissolved in hot hydrochloric acid (D 1.123), and the solution saturated with solid ammonium chloride, when on cooling *phenylstibinic oxychloride* separates in glistening leaflets; this is isolated, decomposed with sodium carbonate, and the pure phenylstibinic acid precipitated with hydrochloric acid. As thus prepared, phenylstibinic acid is stable at  $250^{\circ}$  (Hasenbäumer gives decomp. point  $200^{\circ}$ ).

*p-Hydroxyphenylstibinic acid* and *p-acetylaminophenylstibinic acid* are similarly prepared from *p*-aminophenol and monoacetyl-*p*-phenylene diamine respectively; the sodium salt of the latter dissolves in water with a neutral reaction. *p-Aminophenylstibinic acid*, obtained by the hydrolysis of the foregoing acid, combines readily with aldehydes

(salicylaldehyde) to furnish hydroxybenzylidene derivatives or on diazotisation gives rise to a red azo-derivative with alkaline  $\beta$ -naphthol.

F. M. G. M.

**Preparation of Nuclear Substituted Mercury Derivatives of Aromatic Hydroxy-acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 255030).—The following therapeutically active organic derivatives of mercury have now been prepared.

*Mercurydisalicylic acid*,  $Hg[C_6H_3(OH)\cdot CO_2H]_2$ , a colourless powder, insoluble in water, is obtained by the reduction of *o*-hydroxymercurisalicylic anhydride with sodium formaldehydesulphenate, and is employed in the form of its neutral alkali salts.

*Mercury-bis-sulphosalicylic acid*, also employed in the form of its sodium salt, is similarly prepared from sodium mercurisulphosalicylate.

*Mercury-bis-arsenosalicylic acid*, a colourless powder, is obtained from mercury arsenosalicylic acid.

*Sodium mercuri-bis-2-naphthol-3 : 6-disulphonic acid* and *mercury-bis-4-hydroxy-m-tolyl-1-arsinic acid* are also employed in the form of their crystalline sodium salts.

F. M. G. M.