Organic Chemistry.

Dibromoacetylene; Purification, Cryoscopy, Analysis. PAUL LEMOULT (*Compt. rend.*, 1903, **137**, 55—56. Compare this vol., i, 595).—Pure dibromoacetylene is prepared by distilling a mixture of tribromoethylene and alcoholic potassium hydroxide in a current of nitrogen, and collecting the heavy drops which distil at 76—77° under boiled-out water.

The molecular weight found by depression of the freezing point of acetic acid was 183·3, whilst CBr⋮CBr requires 184. A Carius estimation of the bromine gave 87·57 per cent. of Br, whilst C_2Br_2 requires 86·95. It is therefore proved that dibromoacetylene can be obtained pure when fractionated as soon as it is formed. J. McC.

Preparation of Primary Alcohols by means of the Corresponding Acids. LOUIS BOUVEAULT and GUSTAVE BLANC (*Compt. rend.*, 1903, **137**, 60—62. Compare this vol., i, 597).—The reduction previously described (*loc. cit.*) can also be applied to the lower acids. With these, however, the experimental difficulties are greater. Amyl acetate, when reduced in amyl alcohol solution with sodium, gives ethyl alcohol.

Methyl butyrate in ethyl alcoholic solution with sodium gives *n*-butyl alcohol, which is separated with difficulty from the ethyl alcohol. Its presence is identified by the formation of its phenylurethane.

Methyl decoate is easily reduced by this method, and gives a good yield of *n*-decyl alcohol, which boils at 120° under 12 mm. pressure.

Methyl myristate is also easily reduced, but the separation of the reduction product from the sodium myristate, which is simultaneously formed, is difficult. The alcohol formed is *n*-tetradecyl alcohol; it melts at 38° and boils at 160° under 10 mm. pressure.

Ethyl benzoate, or other aromatic ester with the carboxyl group directly linked to the benzene nucleus, is not reduced. On the other hand, ethyl phenylacetate gives a good yield of phenylethyl alcohol, the phenylurethane of which melts at 80°.

Ethyl hexahydrobenzoate, on reduction with sodium, gives *hexahydrobenzyl alcohol* as a viscid oil with characteristic odour which boils at 82° under 11 mm. pressure. Its *phenylurethane* forms acicular crystals, melts at 82°, is soluble in the common organic solvents, but is insoluble in light petroleum. J. McC.

Removal of Water from Secondary Alcohols of High Molecular Weight. HERMANN THOMS and C. MANNICH (*Ber.*, 1903, **36**, 2544—2550).—Methyl nonyl ketone condenses with aminoguanidine to form a *compound* which separates in minute, fatty scales, and melts at 79°; its *picrate* melts at 148—149°. The *aminoguanidine*-derivative of methyl heptyl ketone melts at 66—67° and its picrate at 154°.

Good yields of methylnonylcarbinol and methylheptylcarbinol can be obtained by reducing the ketones with sodium and alcohol. Methylnonylcarbinol is a viscous liquid, boils at 120° under 14 mm. pressure, has sp. gr. 0·8263 at 18°, and when boiled with 60 per cent. sulphuric acid yields the ether, $O(CHMe\cdot C_9H_{19})_2$, and Δ^β-undecylene, $CH_3\cdot CH{:}CH\cdot C_8H_{17}$, which is oxidised by potassium permanganate to pelargonic acid; about 4 per cent. of Δ^α-undecylene, $CH_2{:}CH\cdot C_9H_{19}$, is also produced; the hydrocarbons could not be separated directly, but were converted into dibromides, and these by alcoholic potash into hydrocarbons of the acetylene series; the undecinene (nonylacetylene), $CH{:}C\cdot C_9H_{19}$, was separated with alcoholic silver nitrate (compare this vol., i, 678).

Methylheptylcarbinol, $C_7H_{15}\cdot CHMe\cdot OH$, boils at 193—194° under atmospheric pressure, and at 87·5° under 10 mm. pressure; it gives a nonylene boiling at 147—148°, which is oxidised to heptoic acid.

T. M. L.

Chlorohydrin and Oxide of αδ-Dihydroxypentane. BRUNO POSSANNER VON EHRENTHAL (*Monatsh.*, 1903, **24**, 351—356).—Acetylpropyl alcohol, prepared by the interaction of sodium ethoxide, ethyl acetoacetate, and ethylene dibromide under conditions unsuitable for the formation of ethyl diacetyladipate (compare Lipp, Abstr., 1889, 843), was reduced by sodium amalgam to αδ-dihydroxypentane (compare Perkin and Freer, Trans., 1887, **51**, 836). *αδ-Dihydroxypentanechlorohydrin*, formed by heating αδ-dihydroxypentane at 100° with excess of hydrochloric acid, is a clear liquid, which boils at 70—80° under 12 mm. pressure. The oxide, prepared by heating it with powdered potassium hydroxide, boils at 77—79°, and is not reconverted into the glycol when heated with water for 6 hours at 120—130°. The oxide, when prepared in this manner, is identical with that obtained by heating the glycol either with water or with 60 per cent. sulphuric acid (compare Froebe and Hochstetter, this vol., i, 320). A. McK.

Esterification of the Hydracids. ANTOINE VILLIERS (*Compt. rend.*, 1903, **137**, 53—55. Compare this vol., i, 598, 599).—The velocity of esterification of hydrochloric acid is so slow at the ordinary temperature that solutions prepared 25 years ago seem not yet to have attained the limit; furthermore the results obtained by direct esterification are very different from those obtained by decomposition of the hydrochloric ester. Ordinary ether is produced with hydrochloric acid only at high temperatures.

For the monatomic alcohols the velocity of esterification with hydrochloric acid decreases as the molecular weight of the alcohol rises: it is noticeable, however, that the velocity for amyl alcohol is greater than for *iso*propyl alcohol. Butyl alcohol is esterified exceptionally slowly, and the limit is probably less at the ordinary temperature than at 100°.

The esterification of glycol and glycerol with hydrochloric acid is much more rapid than that of ethyl alcohol. The limit attained is probably less than that reached at 100°, but is the same as that at 44°, and this suggests a difference in the mode of action of the hydrochloric acid hydrates on glycol and glycerol from that on ethyl alcohol. J. McC.

Fatty Acids of Egg-lecithin. H. Cousin (*Compt. rend.*, 1903, **137**, 68—70).—The acids were obtained from lecithin by saponifying with alcoholic potassium hydroxide and then acidifying with hydrochloric acid. They were formerly supposed to be oleic, stearic, and palmitic, but the iodine value of the unsaturated acid was found to be higher than that corresponding with oleic acid. The mixture, therefore, contains an acid which is less saturated than oleic acid.

A quantity of the mixed acids was transformed into the barium salts, and the mixed salts were treated with a mixture of benzene and alcohol; the acid regenerated from the dissolved part was proved to be linoleic acid, because when oxidised in alkaline solution with permanganate it gave tetrahydroxystearic acid, melting at 171—172°.

The undissolved residue was converted into lead salt, and this was treated with ether. From the ethereal solution oleic acid was obtained. From the lead salt insoluble in ether a mixture of stearic and palmitic acids was obtained. The quantity of stearic acid varied from 30 to 40 per cent., and that of palmitic acid from 60 to 70 per cent., in different specimens.

No other acids than these mentioned could be found in the egg-lecithin. J. McC.

A Possible Method of preparing Organic Sulphur Compounds. Alwin Mittasch (*J. pr. Chem.*, 1903, [ii], **68**, 103—104).—When a current of hydrogen or coal gas is passed through carbon disulphide and then through a moderately heated combustion tube filled with nickel powder, an organic sulphur compound, which is either a mercaptan or a thio-ether, is formed. It forms a derivative with mercuric oxide, which melts at 65—70°. G. Y.

Organo-mineral Anhydrides. Amé Pictet (*Arch. Sci. phys. nat.*, 1903, [iv], **15**, 589—611).—By the direct union of nitric, phosphoric, pyrophosphoric, arsenious, sulphuric, chromic, or boric acid with various organic acids, mixed anhydrides are formed. Of these, the anhydride of nitric and acetic acids is described.

[With Paul Genequand.]—A cryoscopic determination of the molecular weight of *diacetylorthonitric acid* (Abstr., 1902, i, 584) in ethylene dibromide and in bromoform shows that it has the formula $C_4H_9O_7N$. A vapour density determination by Meyer's method, using xylene (138°) in the outer bath, shows that the compound is completely dissociated about 10° above its boiling point. By the action of varying quantities of acetic acid on nitric acid, it was proved that the greatest development of heat takes place when molecular quantities are mixed, and no compound other than $N(OAc)_2(OH)_3$ is produced.

With E. I. Klein.]—Attempts have been made to prepare salts of acetonitric acid by acting on nitrates with acetic acid, and on acetates with nitric acid. In the cases of potassium, sodium, ammonium, calcium, strontium, barium, magnesium, copper, and lead, no derivatives were obtained in this way. Silver nitrate is soluble in glacial acetic acid, and from the solution long, colourless, homogeneous crystals separate. This *diargentic acetonitrate*, $N(OAc)_2(OAg)_2{\cdot}OH$, exhibits no definite melting point, but explodes when heated slowly to 172°.

When mercurous nitrate is boiled with acetic acid, solution takes place, and, on cooling, colourless, transparent crystals of *mercuric acetonitrate*, $N(OAc)_2(O_2Hg)\cdot OH$, separate. This salt melts at 205°, and undergoes no change when heated at 110°. The silver salt decomposes easily in the air, but the mercuric salt is much more stable. The mercuric salt is insoluble in alcohol and ether, but is soluble in acids.

No esters of acetonitric acid are formed by the interaction of esters of nitric acid and acetic acid, or by the action of acetic acid on nitric esters, or of nitric acid on acetic esters. J. McC.

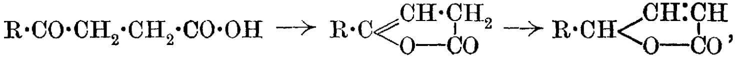
A New Fatty Acid. γγγ-Trimethylbutyric Acid [γγ-Dimethylvaleric Acid]. Charles Moureu and Raymond Delange (*Bull. Soc. chim.*, 1903, [iii], **29**, 664—666).—γγ-Dimethylvaleric acid, prepared as already described (this vol., i, 314), has sp. gr. 0·9129 at 20° and 0·9238 at 0°; the amide (*loc. cit.*) crystallises in rectangular lamellæ. T. A. H.

Amylchloroacrylic Esters [β-Chloro-Δ^α-octenoic Esters]. Charles Moureu and Raymond Delange (*Bull. Soc. chim.*, 1903, [iii], **29**, 677—678. Compare Abstr., 1901, i, 360).—When a solution of amylpropiolic acid in ethyl alcohol is saturated with hydrogen chloride, there is formed *ethyl β-chloro-*Δ^α*-octenoate*, $C_5H_{11}\cdot CCl{:}CH\cdot CO_2Et$, a colourless oil which boils at 123—128° under 18 mm. pressure. The chlorine atom is assumed to be in the β-position in this substance, since, on treatment with potassium hydroxide in alcohol, methyl amyl ketone is formed, whereas the α-substituted acid would, with this reagent, give rise to normal heptaldehyde. T. A. H.

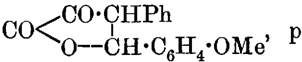
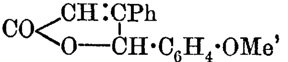
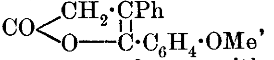
Nitrates of Hydroxy-acids. H. Duval (*Bull. Soc. chim.*, 1903, [iii], **29**, 678—680. Compare this vol., i, 603).—From the crude product obtained by the action of nitric acid on glycollic acid there has been isolated, in addition to the nitrate of glycollic acid (*loc. cit.*), *acetoxyacetic acid nitrate*, $NO_2\cdot O\cdot CH_2\cdot CO\cdot O\cdot CH_2\cdot CO_2H$, a yellow oil soluble in water and alcohol, but insoluble in benzene. A similar condensation appears to be produced by the action of nitric acid on lactic and α-hydroxybutyric acids.

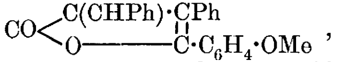
Malic acid nitrate, similarly prepared, crystallises in colourless needles, melts and decomposes at 115°, is soluble in water and alcohol, but insoluble in benzene and light petroleum. T. A. H.

Labile and Stable Crotonolactones. Emil Erlenmeyer, jun. (*Ber.*, 1903, **36**, 2523—2525).—Thiele has shown (Abstr., 1899, i, 611) that γ-ketonic acids yield first labile βγ- and then stable αβ-unsaturated crotonolactones,



$$R\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot OH \longrightarrow R\cdot C{<}\begin{matrix}CH\cdot CH_2\\ |\qquad |\\ O{-}CO\end{matrix} \longrightarrow R\cdot CH{<}\begin{matrix}CH{:}CH\\ |\qquad |\\ O{-}CO\end{matrix},$$

whilst in the α-oxylactones the isomeric change, if it takes place, is from the αβ- to the βγ-unsaturated lactone (compare this vol., i, 419). Proof of this has been obtained (jointly with Lattermann) in the case of the *α-oxylactone*,  $\mathrm{CO}<\begin{matrix}\mathrm{CO\cdot CHPh}\\ \mathrm{O{-}{-}CH\cdot C_6H_4\cdot OMe}\end{matrix}$, prepared from anisaldehyde and phenylpyruvic acid, which is reduced by zinc dust and acetic acid to two isomeric unsaturated lactones. The *labile* lactone  $\mathrm{CO}<\begin{matrix}\mathrm{CH{:}CPh}\\ \mathrm{O{-}{-}CH\cdot C_6H_4\cdot OMe}\end{matrix}$, melts at 105°, is unsaturated in the $\alpha\beta$-position, and is converted by heating with benzaldehyde and aniline only into the stable isomeride. The *stable* lactone,  $\mathrm{CO}<\begin{matrix}\mathrm{CH_2\cdot CPh}\\ \mathrm{O{-}{-}C\cdot C_6H_4\cdot OMe}\end{matrix}$, melts at 122°, is unsaturated in the $\beta\gamma$-position, and condenses with benzaldehyde to yield the *benzylidene*-derivative,



$$\mathrm{CO}<\begin{matrix}\mathrm{C(CHPh)\cdot CPh}\\ \mathrm{O{-}{-}{-}{-}C\cdot C_6H_4\cdot OMe}\end{matrix},$$

which forms orange-yellow needles and melts at 195°. T. M. L.

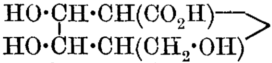
Action of Ammonia on a Mixture of Two α-Oxyacids. Emil Erlenmeyer, jun. (*Ber.*, 1903, **36**, 2525—2526).—By the action of ammonia on a mixture of glyoxylic and pyruvic acids, aceturic acid, $\mathrm{CH_3\cdot CO\cdot NH\cdot CHMe\cdot CO_2H}$, was obtained as a condensation product from the pyruvic acid only. [A syrupy acid was obtained which might contain also the mixed condensation product.] Similarly, a mixture of pyruvic and phenylpyruvic acids gave only phenylacetylphenylalanine, $\mathrm{CH_2Ph\cdot CO\cdot NH\cdot CHPh\cdot CO_2H}$. T. M. L.

***iso*Nitrosomalonic Esters and their Transformation into Mesoxalic Esters.** Louis Bouveault and André Wahl (*Compt. rend.*, 1903, **137**, 196—198).—*Ethyl* iso*nitrosomalonate* is obtained by passing a current of methyl nitrite into a mixture of ethyl malonate and sodium ethoxide at 20—25°, distilling off the alcohol, and treating the residue first with water, then with hydrochloric acid; the ester is extracted with ether and purified by distillation under diminished pressure. It is a colourless, viscid liquid which boils at 172° under 12 mm. pressure, has a sp. gr. 1·206 at 4°/0°; it is insoluble in water, but soluble in the ordinary organic solvents. If in the preparation the residue, after the alcohol has been evaporated, is left to itself, white needles of the *hydrogen* salt, $\mathrm{NOH{:}C(CO_2Et)_2 + NONa{:}C(CO_2Et)_2}$, separate; this salt is easily dissociated by water. If a current of nitrogen peroxide be passed through the ester at 0°, vigorous action takes place. When the product is distilled under diminished pressure (12 to 15 mm.), ethyl mesoxalate and ethyl nitromalonate are obtained. The nitrogen peroxide therefore exerts two actions: (1) transformation of the oxime group into a ketonic group, and (2) direct oxidation.

Methyl iso*nitrosomalonate*, prepared in the same way, is a liquid which boils at 168° under 16 mm. pressure and crystallises when cooled. After recrystallisation from a mixture of ether and light petroleum it forms slender, white needles which melt at 67°. If water is added to the alkaline alcoholic solution in this preparation, crystals of the salt $\mathrm{NONa{:}C(CO_2Me)_2,2H_2O}$ are deposited. The principal product of the action of nitrogen peroxide on methyl *iso*nitrosomalonate is methyl mesoxalate and its hydrate, which crystallises from a mixture of ether and light petroleum in tabular crystals melting at 81°. At the same time a small quantity of methyl nitromalonate is formed.

J. McC.

Chitonic and Chitaric Acids. EMIL FISCHER and EDWARD ANDREAE (*Ber.*, 1903, **36**, 2587—2592. Compare Fischer and Tiemann, Abstr., 1894, i, 167).—When dried at 140° the calcium salt of chitonic acid has the formula $(C_6H_{11}O_7)_2Ca$. At this temperature in an exhausted receiver over phosphoric oxide it loses 2 molecules of water; thus the salt has the formula, $(C_6H_9O_6)_2Ca,2H_2O$, and chitonic acid, $C_6H_{10}O_6$, that is, it is the anhydride of a hexonic acid. When heated with acetic anhydride and sodium acetate, it forms an acid compound, $C_8H_8O_5$, *acetoxymethylpyromucic acid*, which melts at 115—117° (corr.), has a bitter taste and crystallises from chloroform in needles or prisms. When hydrolysed with barium hydroxide, it is converted into the hydroxymethylpyromucic acid, melting at 165—167°, described by Hill and Jennings (*Amer. Chem. J.*, 1893, **15**, 181). Similarly, chitaric acid is converted into acetoxymethylpyromucic acid, and thus both it and chitonic acid are represented by the structural formula,



$$\left.\begin{array}{l} HO\cdot CH\cdot CH(CO_2H)— \\ \quad\;| \\ HO\cdot CH\cdot CH(CH_2\cdot OH) \end{array}\right>O,$$

and differ from one another with respect to the spatial arrangement of the hydroxyl groups. This makes it probable that *iso*saccharic acid and chitose are also both hydrofurfuran derivatives. E. F. A.

Action of Hypophosphorous Acid on Diethyl Ketone and on Acetophenone. CHARLES MARIE (*Compt. rend.*, 1903, **137**, 124—125. Compare this vol., i, 328, 379).—Diethyl ketone (3 to 4 mols.) is boiled with hypophosphorous acid (1 mol.) in a reflux apparatus, the excess of ketone is distilled off, and the residue is converted into the *lead salt*, $Pb[COEt_2,H_2PO_2]_2$. The lead salt is decomposed in aqueous suspension with hydrogen sulphide, when the *acid* is obtained as a colourless syrup which does not solidify at $-20°$. On oxidation with bromine or mercuric chloride, it gives the oxyphosphinic acid, Et_2CO,H_3PO_3; this is soluble in water, alcohol, acetone, and ethyl acetate, but insoluble in benzene or chloroform. Its silver salt is insoluble in water.

If acetophenone (3 mols.) is heated on the water-bath with hypophosphorous acid, and the mixture treated with lead carbonate, the insoluble *lead salt*, $Pb[COMePh,H_2PO_2]_2$, is formed. When decomposed with hydrogen sulphide, it gives the *acid*, $COMePh,H_3PO_2$, as a syrup which slowly solidifies, and melts at 70°. When oxidised with mercuric chloride, it gives the oxyphosphinic acid, $COMePh,H_3PO_3$ (m. p. 170°), but when oxidised with bromine, the product isolated is $COMePh,H_3PO_3,HBr$, which melts at 190°. J. McC.

Conversion of Methyl Nonyl Ketone into the Isomeric Ethyl Octyl Ketone. C. MANNICH (*Ber.*, 1903, **36**, 2551—2553).—The hydrocarbon $C_{11}H_{20}$ (this vol., i, 674), which does not react with ammoniacal silver nitrate is Δ^{β}-*undecinene*, $CMe{:}C\cdot C_8H_{17}$, as, on oxidation with cold 4 per cent. permanganate solution, it yields acetic and pelargonic acids. It is a colourless oil with a disagreeable odour, distils at 199—201° under atmospheric, or at 81·5° under 10·5 mm. pressure, and is fairly readily volatile even at the ordinary temperature. In chloroform solution it combines with two atoms of bromine yielding an oily *dibromide*, $CMeBr\colon CBr\cdot C_8H_{17}$, distilling at 137—139° under 11 mm. pressure. When Δ^{β}-undecinene is poured into ice-cold 94 per cent. sulphuric acid, it absorbs the elements of water, and yields a mixture of two ketones, namely, methyl nonyl ketone (18 per cent.) and ethyl octyl ketone (82 per cent.). The two ketones can be separated by the aid of sodium hydrogen sulphite, as the methyl nonyl ketone forms an additive compound and the ethyl octyl ketone does not.

Ethyl octyl ketone is a colourless liquid with a pleasant odour, it distils at 104—106° under 11 mm. pressure, solidifies at 4·5°, and reacts with hydroxylamine and semicarbazide hydrochloride. The *oxime* is oily, and the *semicarbazone* has no sharp melting point. When oxidised with chromic mixture, it yields *n*-octoic acid.

As Δ^{β}-undecinene is obtained from methyl nonyl ketone (*loc. cit.*), it affords a simple method of transforming the ketone into the isomeric ethyl octyl ketone. J. J. S.

Condensation of Higher Aliphatic Ketones to Compounds of the Type of Mesityl Oxide. HERMANN THOMS and C. MANNICH (*Ber.*, 1903, **36**, 2555—2558).—When methyl nonyl ketone is saturated with hydrogen chloride and kept for some 6 weeks, condensation occurs. The mass is washed with water and potassium carbonate solution, dried and fractionated under reduced pressure. A considerable amount of hydrogen chloride is evolved during the distillation, and an *unsaturated ketone*, $C_9H_{19}\cdot CMe\colon CH\cdot CO\cdot C_9H_{19}$, passes over at 214—216° under 10 mm. pressure. It is a colourless, oily liquid with a faint odour, and has sp. gr. 0·8514 at 15°. It readily combines with hydrogen chloride to form an oily compound, which decomposes into its components on distillation even under reduced pressure.

The *oxime*, *phenylhydrazone*, and *semicarbazone* have only been obtained in the form of oils. The *picrate* of its *aminoguanidine derivative*, $C_{29}H_{49}O_7N_7$, melts at 125—126°.

When boiled with 60 per cent. sulphuric acid, the ketone is hydrolysed to methyl nonyl ketone. On oxidation with permanganate it yields decoic and carbonic acids with a small amount of acetic acid.

Methyl heptyl ketone condenses under the influence of hydrogen chloride to an *unsaturated ketone*, $C_7H_{15}\cdot CMe\colon CH\cdot CO\cdot C_7H_{15}$; it is difficult to obtain this free from chlorine, as it readily combines with hydrogen chloride, and the whole of this is not removed on distillation. The *picrate* of its *aminoguanidine derivative* melts at 130—131°.

J. J. S.

Transformation of Starch Paste. LÉON MAQUENNE (*Compt. rend.*, 1903, **137**, 88—90).—When a homogeneous starch jelly in an aseptic medium is kept for some days, the translucent mass becomes opaque, and finally deposits segregated nuclei. This change is due to a transformation of the starch, which passes into the form of amylocellulose described by Brown and Heron. The transformed substance is not coloured by iodine, is not attacked by malt, and is only very slowly hydrolysed by boiling dilute solutions of mineral acids. On the other hand, it is easily soluble in solutions of potassium hydroxide, and the neutralised solution gives a blue coloration with iodine. This behaviour seems to indicate that the amylocellulose has a lactonic character, which is probably due to a partial dehydration of the original starch molecule.

The transformation is progressive; its velocity slowly diminishes, and even after 20 days is not complete. The transformation is purely chemical, and entirely independent of enzymes or micro-organisms.

The velocity of the change appears to be greater if the starch jelly has not been heated. J. McC.

β-Aminoundecane and β-Aminononane. Hermann Thoms and C. Mannich (*Ber.*, 1903, **36**, 2554—2555).—These two compounds are obtained by the reduction of the oximes of methyl nonyl ketone and methyl heptyl ketone with sodium in a mixture of alcohol and acetic acid.

β-Aminoundecane is a light, colourless liquid distilling at 113—114° under 26 mm. pressure. It has strongly alkaline properties, and readily absorbs carbon dioxide. The *platinichloride*, $C_{22}H_{50}N_2,H_2PtCl_6$, crystallises in plates or needles, turns black at 240°, and is only very sparingly soluble in cold water. The *picrate* melts at 111°.

β-Aminononane distils at 69—69·5° under 11 mm. pressure. Its *hydrochloride* is extremely hygroscopic and is soluble in alcohol, ether, or acetone. The *platinichloride*, $C_{18}H_{42}N_2,H_2PtCl_6$, turns black at 210—220° when quickly heated, and the *picrate* melts at 108·5—109·5°. J. J. S.

Action of Ammonia on the Ethylene Oxide of β-*o*-*cyclo*-Hexanediol [*eso*Anhydride]. Léon Brunel (*Compt. rend.*, 1903, **137**, 198—199. Compare this vol., i, 338, and preceding abstract).—When the *eso*anhydride, $C_6H_{10}\!:\!O$, is heated in a sealed tube with a large excess of ammonia, *orthoaminocyclohexanol*, $OH\cdot C_6H_{10}\cdot NH_2$, is obtained as a colourless, crystalline mass with an odour of piperidine, which is not affected by light and is soluble in water and the ordinary solvents. It melts at 66° and boils at 219°; it is extremely hygroscopic and readily absorbs carbon dioxide. Its *hydrochloride* forms white needles which melt at 175°, and its *nitrate* melts at 144°.

If less ammonia is used, *dihydroxycyclohexylamine*, $NH(C_6H_{10}\cdot OH)_2$, is formed as well. This is obtained in two forms when the *eso*anhydride is heated in a sealed tube with twice its volume of an alcoholic solution of ammonia. On cooling, *β_1-dihydroxycyclohexylamine* crystallises out in colourless leaflets, which melt at 153°, and are sparingly soluble in water or alcohol. Its *hydrochloride* melts at 266°. It forms a *nitrosamine*, $NO\cdot N(C_6H_{10}\cdot OH)_2$, which crystallises in yellow prisms and melts at 148°. The alcoholic solution contains *β_2-dihydroxycyclohexylamine*, which on evaporating the alcohol, warming the residue with benzene, and cooling, separates in slender, colourless needles which melt at 114°. The *hydrochloride* melts at 192°, and the *nitrosamine* at 171°. J. McC.

Preparation of Secondary Amides. J. Tarbouriech (*Compt. rend.*, 1903, **137**, 128—130).—The author has prepared some secondary amides (1) by the action of acids on nitriles, and (2) by the action of acid chlorides on primary amides in sealed tubes.

n-*Dibutyramide* is obtained by heating together in a sealed tube *n*-butyrylnitrile and *n*-butyric acid at 205°; the product is subjected to distillation, and when the thermometer reaches 200° the heating is stopped; the residue solidifies on cooling and the dibutyramide is recrystallised from alcohol. The same compound is formed when molecular quantities of *n*-butyramide and *n*-butyryl chloride are heated in a sealed tube at 120—130° for 6 hours. It can be distilled under diminished pressure and melts at 107°.

*Di*iso*butyramide*, prepared in the same ways, forms large, colourless crystals, melts at 173—174°, and is almost insoluble in cold water or alcohol, but easily soluble in ether.

*Di*iso*valeramide* forms slender, white needles, and melts at 94°. *Di*-n-*valeramide* is a white, crystalline substance melting at 100°, sparingly soluble in cold alcohol, but easily in ether.

In the preparation of these amides, ammonium chloride is frequently formed in small quantity at the same time as a very small amount of a tertiary amide. J. McC.

[Physico-chemical Constants of] Organic Amides. (Constitution of Nitrosoalkylurethanes, Acid Amides, Anthranil, Regularities in the Boiling Points of Acid Amides, Analogy between Formylamines and Nitrosoamines.) Otto Schmidt (*Ber.*, 1903, **36**, 2459—2482).—The following compounds were examined:

I. Monoacylamines. (*a*) *Primary.*

	M. p.	t.	$d^{t/4}$.	n^{t}_{D}.	$\mathfrak{M}_{\mathrm{D}}$.
Methyl carbamate	57—58°	55·6°	1·1361	1·41253	16·448
Ethyl ,,	49	52·0	1·0560	1·41439	21·078
iso*Butyl* ,,	64—65	76·2	0·9556	1·40978	30·320
iso*Amyl* ,,	64	70·6	0·9438	1·41754	34·945

(*b*) *Secondary.*

	B. p.	p.	t.	$d^{t/4}$.	n^{t}_{D}.	$\mathfrak{M}_{\mathrm{D}}$.
*Formyl*iso*butylamine*	111°	12 mm.	17°	0·9092	1·43957	29·262
*Formyl*iso*amylamine*	123·5—124	10	13·2	0·9049	1·44513	33·833
Formanilide (m. p. 47°)	166	14	24	1·13958	1·58786	35·728
			25·6	1·13811	1·58763	35·775
			17·3	1·14366	1·59012	35·711
Methyl anthranilate	126·2—126·8	12	18·6	1·16822	1·58435	43·280
Ethyl anthranilate	137·5—138	14	20·7	1·11792	1·56487	47·647
Methyl formylanthranilate (m. p. 42—43°)	169·8—170	13	37·6	1·23336	1·57776	48·146
Methyl methylcarbamate	64 — 65	14	20·6	1·06405	1·41584	20·982
Ethyl methylcarbamate	79·8— 80·6	14·5	18·9	1·00874	1·42004	25·842
Ethyl ethylcarbamate	74 — 75	14	19·6	0·97645	1·42254	30·484

(*b*) *Secondary*—continued.

	B. p.	*p*.	*t*.	$d^{t/4}$.	*n*.	$\mathfrak{M}_D$.
Ethyl iso*butylcarbamate*	95 — 96°	15 mm.	16·8	0·94452	1·43008	39·665
Ethyl iso*amylcarbamate*	122 —123	22	20·9	0·93258	1·43267	44·282
Ethyl phenylcarbamate (m. p. 53°)	152	14	30·4	1·10639	1·53764	46·626
iso*Formylanilinomethyl ether*	83 — 84	15	23·5	1·03474	1·53821	40·823
iso*Formanilinoethyl ether.*	107 —108	23	17·4	1·0090	1·52978	45·600

(*c*) *Tertiary.*

	B. p.	*p*.	*t*.	$d^{t/4}$.	*n*.	$\mathfrak{M}_D$.
Dipropylformylamine	96 — 97	14	19·8	0·8892	1·44094	38·305
*Dï*iso*butylformylamine*	109 —110	15	16·6	0·87472	1·44295	47·583
*Dï*iso*amylformylamine*	132 —132·6	13	20·4	0·86688	1·44556	56·863
			17·5	0·86876	1·44617	56·805
Formylmethylaniline	124·9—125·2	13	27·4	1·08930	1·55902	40·017
			23·0	1·09280	1·55780	39·815
Formylethylaniline	89·5— 91	14	22	1·05422	1·54313	44·561
Formyldiphenylamine (m. p. 72·2—72·6°)	189·5—190·5	13 ; was examined in toluene solution.				
Toluene	—	—	15·2	0·8702	1·49894	—
Solution (25·685 per cent.)			15·3	0·9315	1·52533	60·24
Ethyl diethylcarbamate	62 — 63	14	20·9	0·92824	1·42017	39·545
*Ethyl dï*iso*amylcarbamate*	129 —130	14	22·8	0·88038	1·43292	67·597
Ethyl phenylmethylcarbamate	127 —128	13	17·8	1·07585	1·51734	50·365
Ethyl phenylethylcarbamate	130 —130·5	14	18·4	1·04529	1·50765	55·005
Nitrosodipropylamine	95 — 95·6	18	16·8	0·9182	1·44535	37·708
*Nitrosodï*iso*amylamine*	132·4—132·8	14·5	15·6	0·88668	1·45029	56·406
			16·0	0·88720	1·45013	56·356
			15·6	0·88720	1·45036	56·380
Nitrosomethylaniline	120·9—121·5	13	25·5	1·1253	1·57567	39·976
Nitrosoethylaniline	119·5—120	15	22·0	1·0858	1·55947	44·636
Nitrosodiphenylamine (m. p. 67·2—67·6°) was examined in toluene solution.						
Solution (25·493 per cent.)			14·4	0·93449	1·52570	59·75

(*d*) *Other Compounds.*

	B. p.	*p*.	*t*.	$d^{t/4}$.	*n*.	$\mathfrak{M}_D$.
Anthranil	90·2	14·5	13·2	1·18810	1·58723	—
Phenylcarbimide	—	—	25·9	1·08870	1·53412	33·990

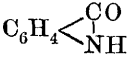
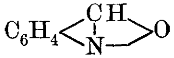
II. Diacylamines.

	B. p.	*p*.	*t*.	$d^{t/4}$.	*n*.	$\mathfrak{M}_D$.
Methyl nitrosomethylcarbamate	59·3—60	14	24·6	1·20419	1·44048	25·848
Nitrosomethylurethane	65 —65·5	13	18·8	1·13144	1·43852	30·659
Nitrosoethylurethane	69 —70	15	19·3	1·0854	1·43533	35·123

The constitution of acid amides has been studied by Auwers, Brühl, Claisen, and by Hantzsch and Dollfus (Abstr., 1902, i, 223). The latter maintain the correctness of the normal formulation, a result with which the author is also in agreement. The reactivity of the acyl grouping in the acylamines was also studied. Although amidine formation occurs with great ease in the case of acylanthranils, it was not found possible to obtain other acylamines with an equal reactivity. Ordinary monoacylamines are inert in this respect; thus, phenylhydrazine does not condense with acetanilide, whilst formanilide, when condensed with β-naphthol, yields only small quantities of a substance melting above 200°. Accordingly, arylalkylcarbamic chlorides are stable; by the action of phosphorus oxychloride, for instance, on phenylmethylurethane, the stable phenylmethylcarbamic chloride (m. p. 88—89°) was prepared.

With regard to the constitution of nitrosoalkylurethanes, the author's refractometric results lead him to the conclusion that nitrosoalkylurethanes are true nitrosoamines; this agrees with Hantzsch's conception (Abstr., 1900, i, 86), and is opposed to Brühl's (Abstr., 1900, i, 210).

From the values of the molecular refraction of the various acylamines examined, the refractometric constant of the acyl grouping can be calculated. Since the values in primary, secondary, and tertiary aliphatic formylamines and urethanes are practically the same, and since the tertiary compounds can possess the normal structure only, the normal structure may also be assigned to the primary and secondary compounds. With secondary, aromatic acylamines, the refractometric value of the acyl group is higher than with the tertiary compounds. From the values obtained with formanilide, on the one hand, and the iminoethers, *iso*formanilino-methyl and -ethyl ethers on the other, it is concluded that formanilide has the normal structure. In agreement with this, formanilide, when heated in a sealed tube for 4 hours at 100° with phenyl*iso*cyanate, gives an almost quantitative yield of *formyldiphenylcarbamide*, melting and decomposing at 103—104°, and giving diphenylcarbamide by the action of boiling hydrochloric acid. When hydrogen chloride is led into a solution of formanilide in dry xylene, the hydrochloride, NHPh·CHO,HCl, is formed; it is unstable and parts readily with hydrogen chloride.

According to Anschütz and Schmidt, anthranil has the constitution  $C_6H_4<\begin{array}{l}CO\\ \vert\\ NH\end{array}$ (this vol., i, 56), whilst Bamberger prefers  $C_6H_4<\begin{array}{l}CH\\ \vert\\ N\end{array}>O$ (this vol., i, 432). From the comparison of the refractometric values of anthranil, formanilide, and phenylcarbimide, the former constitution is justified.

Various regularities in the boiling points of amides are indicated. The hydrogen atom attached to nitrogen in a secondary or primary acylamine has the same character as the hydrogen of a hydroxyl group.

In physical properties, tertiary formylamines are very closely allied to their corresponding nitrosoamines, the boiling points, refractometric constants, and molecular volumes of various compounds are quoted. In some cases, as, for instance, with formyldiphenylamine and nitrosodiphenylamine, the crystallographic structure is nearly identical.

The molecular refraction of nitrosoaniline is calculated, and found to agree with that of formanilide. Like true nitrosoamines, formanilide is comparatively inert, whilst the ethers derived from the *iso*-form are much more chemically active. Phenylhydrazine was found by the author to condense with *iso*formanilinomethyl ether to form the corresponding diazohydrazide. A. McK.

Constitution of Allyl Cyanide. Robert Lespieau (*Compt. rend.*, 1903, **137**, 262—263).—By the action of a chloroform solution of bromine on a chloroform solution of dried allyl cyanide at -14° to -10° for 9 hours, hydrogen bromide is evolved and the residue can be separated into a fraction boiling at 60—100° and one boiling at 125—135° under 13 mm. pressure. The latter consists essentially of $\beta\gamma$-dibromobutyronitrile, $CH_2Br\cdot CHBr\cdot CH_2\cdot CN$ (compare this vol., i, 547). The fraction of lower boiling point was refractionated and the molecular weight of the various fractions determined; it apparently consists of a monobromo-substitution product of allyl cyanide ($C_4H_5BrO_2$). The author concludes that the constitution of allyl cyanide is best represented by the formula $CH_2{:}CH\cdot CH_2\cdot CN$.

J. McC.

Double Cyanides of Zinc with Potassium and with Sodium. William J. Sharwood (*J. Amer. Chem. Soc.*, 1903, **25**, 570—596).—In the precipitation of gold and silver by the addition of zinc to the solutions obtained in the cyanide process of extraction, a certain amount of zinc is dissolved. The present investigation was undertaken in order to ascertain the nature of the zinc compound thus produced.

When an alkaline solution containing the cyanides of zinc and potassium is concentrated, potassium zinc cyanide, $K_2Zn(CN)_4$, is obtained, which crystallises in regular octahedra, and is soluble to the extent of 11 grams in 100 c.c. of water at 20°, and is nearly insoluble in alcohol. The same salt is formed by the action of potassium cyanide on zinc oxide or of potassium hydroxide on excess of zinc cyanide.

If a solution of sodium and zinc cyanides is concentrated, a hydrated form of sodium zinc cyanide, $NaZn(CN)_3$, is produced, which crystallises with difficulty, and is partially decomposed by the addition of water with precipitation of a basic zinc cyanide. This salt does not seem to exist in the solution, for the mother liquor contains Zn : CN approximately in the ratio 1 : 4. When dilute solutions of sodium cyanide react with zinc cyanide or zinc oxide, or when sodium hydroxide reacts with an excess of zinc cyanide, the ratio of zinc to cyanogen in the resulting solution is approximately that required by the compound $Na_2Zn(CN)_4$.

When $N/10$ solutions of the hydroxides of sodium or potassium are shaken with zinc oxide, very little of the latter is dissolved, and the zinc oxide formed is largely decomposed on boiling.

Zinc cyanide is dissolved by dilute solution of potassium cyanide with the formation of a solution of double cyanide, $K_2Zn(CN)_4$, which is little affected by boiling or by the presence of carbonic acid. A similar solution is obtained by the action of sodium cyanide on zinc cyanide.

Zinc oxide is dissolved by $N/10$ potassium cyanide solution in the proportion of 3 mols. of the former to 10 mols. of the latter; on boiling the solution thus formed, decomposition occurs with precipitation of zinc oxide. Dilute solutions of sodium cyanide behave in a similar manner.

Zinc cyanide (1 mol.) is dissolved by a dilute solution of potassium hydroxide (2 mols.) with formation of a solution which is decomposed on heating, zinc oxide being precipitated and potassium hydroxide remaining in the solution. A solution can be also prepared containing zinc cyanide and potassium hydroxide in molecular proportion, but zinc oxide soon begins to separate. Sodium hydroxide reacts in similar manner with zinc cyanide.

The solvent action of a solution of potassium zinc cyanide on gold is less than that of a simple solution of potassium cyanide containing half the amount of cyanogen per unit volume. If potassium hydroxide is added to such a solution, the solvent power is greatly increased. It is evident, therefore, that potassium zinc cyanide in dilute solutions is partially decomposed by potassium hydroxide with formation of potassium cyanide. E. G.

Prussian and Turnbull's Blues. A New Class of Complex Cyanides. PAUL CHRÉTIEN (*Compt. rend.*, 1903, **137**, 191—194).—When hydroferricyanic acid spontaneously decomposes at about 20°, *hydrodiferrocyanic acid*, $HFe_2(CN)_6,3H_2O$, is formed. The decomposition is greatly assisted by the presence of bromine. The liquid soon gelatinises, but the acid can be again obtained in a soluble form by dialysis. When treated with alkaline salts hydrogen salts of the type $RH[Fe_2(CN)_6]_2,6H_2O$ are formed; the silver salt has $7H_2O$. With salts of barium, manganese, cobalt, or iron, coagulation of the acid takes place and no salt is produced.

The following thermochemical values have been determined: $HFe_2(CN)_6,3H_2O$ (solid) + 4KOH (dissolved) = $K_4Fe(CN)_6$ (dissolved) + $Fe(OH)_3$ (solid) + 25·4 Cal.; from this it is deduced that the heat of formation of the solid acid is 122·15 Cal. This value is in good agreement with that obtained from the heat changes involved in the decomposition of the soluble Prussian blues. J. McC.

Diazomethane. RUDOLF WEGSCHEIDER and HEINRICH GEHRINGER (*Monatsh.*, 1903, **24**, 364—366).—In the preparation of various acid esters by the aid of diazomethane, it was observed that the yield of ester formed was greater than that calculated from the amount of diazomethane used. The diazomethane was employed in ethereal solution, the strength of which was estimated by titration with standard iodine solution according to von Pechmann (Abstr., 1894, i, 438), who supposed that the action took place according to the equation $CH_2N_2 + I_2 = CH_2I_2 + N_2$. The authors have studied the esterification of benzoic acid by diazomethane. Accepting von Pechmann's view, and taking a quantity of benzoic acid corresponding with $C_7H_6O_2 + CH_2N_2 = C_8H_8O_2 + N_2$, they find that the benzoic acid is completely esterified, but that some diazomethane remains unattacked. In the one experiment quoted, the diazomethane used esterified twice as much benzoic acid as it should do according to the above equations. A. McK.

Action of Nitrogen Peroxide on Organo-Magnesium Compounds. HEINRICH WIELAND (*Ber.*, 1903, **36**, 2315—2319).—Grignard has shown (Abstr., 1902, i, 142) that, by the action of magnesium-alkyl iodides, carbon dioxide may be converted into carboxylic acids and sulphur dioxide into sulphinic acids. With the object of preparing the corresponding nitrogen acids, the author has studied the action of magnesium-alkyl iodides on nitrogen peroxide. Instead, however, of obtaining acids of the type R·N:O·OH, he obtained ββ-dialkylated hydroxylamines of the type NRR·OH, the same products which result from nitroparaffins and organic zinc or magnesium compounds.

A violent action ensues when nitrogen peroxide is passed into an ethereal solution of the magnesium compound at the ordinary temperature. A strongly cooled solution of magnesium in ethyl iodide was added very gradually to an ethereal solution containing 5 per cent. of nitrogen peroxide, the latter solution being immersed in a freezing mixture. After careful decomposition of the resulting double compound with water and subsequent extraction with ether, the base *diethylhydroxylamine* was obtained, which was converted into its *oxalate*: this crystallises from methyl alcohol in needles melting at 138° (compare Dunstan and Goulding, Trans., 1899, **75**, 800). The *hydrochloride* is deliquescent and melts at 63°. The free base, obtained from the oxalate or the hydrochloride, boils at 76° under 86 mm. pressure, and has the properties assigned to it by Dunstan and others. Further, it readily reduces alkaline copper and silver solutions as well as gold and platinic chlorides.

The action of nitrogen peroxide on magnesium phenyl bromide is also violent, and is being further studied by the author in the hope of isolating diphenylhydroxylamine. A. McK.

Action of Sulphur on Organo-Magnesium Compounds.

HENRI WUYTS and G. COSYNS (*Bull. Soc. chim.*, 1903, [iii], **29**, 689—693. Compare Bodroux, this vol., i, 121, 249, 521).—When magnesium ethyl iodide in ethereal solution is treated with sulphur and the resulting product decomposed with water, hydrogen sulphide is evolved, and there is formed ethyl mercaptan and small quantities of ethyl disulphide and of an unidentified oily sulphur compound. Magnesium phenyl bromide reacts with sulphur under these conditions to form thiophenol, diphenyl sulphide, and diphenyl disulphide. By reducing the crude product with powdered zinc and dilute hydrochloric acid, a yield of 66 per cent. of thiophenol can be obtained, and the reaction is recommended as a method of preparing this substance.

It is suggested that the first products of reaction in these cases are compounds of the type RSMgX and RS_2MgX, which are decomposed by water, giving rise to substances of the type RSH and RS_2H respectively, which interact with each other to form the sulphides RS_2R and RS_3R.

Selenium and tellurium react similarly with organo-magnesium compounds. T. A. H.

*cyclo*Hexane and its Chloro-derivatives.

PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1903, **137**, 240—242).—When benzene is hydrogenated by the catalytic process, cyclo*hexane*, C_6H_{12}, is produced identical with that which occurs in Caucasian petroleum. It melts at 6·5°, boils at 81° under 755 mm. pressure, has a sp. gr. 0·7843 at 13·5° and 0·7551 at 44·6°, and n_α 1·42777, n_β 1·43531, n_γ 1·43972. The existence of the benzene nucleus in it has been established by the fact that with bromine it gives tetrabromobenzene. When passed over reduced nickel at 270—280°, it gives benzene and methane ($3C_6H_{12} = 2C_6H_6 + 6CH_4$).

When chlorine is passed through it at 0° substitution takes place, and the action is energetic. The presence of iodine chloride or antimony chloride has no effect on the action, but if aluminium chloride be present condensed products are obtained. After chlorination, the product was washed with dilute potassium hydroxide solution, then dried and fractionated under 50 mm. pressure, when di-, tri-, and tetrachloro-derivatives were separated.

*Chloro*cyclo*hexane* is a colourless liquid with a pleasant odour, which boils at 141·6—142·6° under 749 mm. pressure, and has a sp. gr. 1·0161 at 0°/0°, and 0·9976 at 22°/0°. When boiled with alcoholic potassium hydroxide it gives *cyclo*hexene.

*Dichloro*cyclo*hexanes* were obtained in two fractions under 50 mm. pressure. Of the first, the one boiling at 105·4—106·4° has a sp. gr. 1·2056 at 0°/0°, and at 106·4—107·4° has a sp. gr. 1·2060 at 0°/0°. Under 761 mm. pressure, it boils at 189° with decomposition and evolution of hydrogen chloride. When cooled in solid carbon dioxide it solidifies, and melts at 93°. When heated for a long time with alcoholic potassium hydroxide it gives naphthylene chloride, C_6H_9Cl, which gives a red coloration with sulphuric acid. At the same time a small quantity of a hexaterpene, C_6H_8, is formed.

The second liquid boils at 112·4—113·4° under 50 mm. pressure, and at 196° under 760 mm. pressure, and has a sp. gr. 1·2222 at 0°/0°; this is probably the 1 : 2 derivative.

Two liquid *trichloro*cyclo*hexanes* have been isolated. They possess a disagreeable odour. The first boils at 139·5—141·5° under 50 mm. and at 221° with much decomposition at 745 mm. pressure, and has a sp. gr. 1·3535 at 0°/0°. The second boils at 143·5—145·5° under 50 mm. and at 226° with decomposition under 745 mm. pressure, and has a sp. gr. 1·3611 at 0°/0°. A solid *trichloro*cyclo*hexane*, which was also obtained, forms colourless crystals which are very soluble in chloroform, melts at 66°, boils at 150·4—151·4° under 50 mm. pressure, and has a sp. gr. 1·5103 at 0°/0°. When heated at 100° in a sealed tube with alcoholic potassium hydroxide, it loses 3 mols. of hydrogen chloride and gives benzene; it is probably the 1 : 3 : 5-derivative.

The continued action of chlorine in the sunlight on *cyclo*hexane leads to *tetrachloro*cyclo*hexane*. This crystallises from chloroform in long prisms, melts at 173°, and can be volatilised, has a sp. gr. 1·6404 at 0°/0°, and when heated with alcoholic potassium hydroxide loses 3 mols. of hydrogen chloride and gives chlorobenzene. The liquid from which this compound is deposited gives a residue, and by fractionally distilling this under 50 mm. pressure a liquid *tetrachloro*cyclo*hexane* is obtained boiling at 170·5—172·5°. J. McC.

Action of Sodium on Carbon Tetrachloride and Chlorobenzene; Formation of Triphenylmethane and Hexaphenylethane. JULES SCHMIDLIN (*Compt. rend.*, 1903, **137**, 59—60).—The action of sodium on a mixture of carbon tetrachloride and chlorobenzene in benzene solution is slow at the ordinary temperature, but after about a day the reaction becomes violent. Triphenylmethane and hexaphenylethane were identified in the product, and were separated by acetic acid, in which the latter is insoluble. Hydrogen chloride is evolved during the reaction. In the first place triphenylchloromethane is formed: $3PhCl + CCl_4 + 6Na = Ph_3{:}C{\cdot}Cl + 6NaCl$, and then undergoes the actions: $Ph_3{:}C{\cdot}Cl + H_2 = Ph_3{\cdot}CH + HCl$ and $2Ph_3{:}C{\cdot}Cl + 2Na = 2NaCl + Ph_3{:}C{\cdot}C{:}Ph_3$. Diphenyl was isolated from the more volatile portions.

Tetraphenylmethane was not formed. J. McC.

Allylbenzene. AUGUST KLAGES (*Ber.*, 1903, **36**, 2572—2574).—A reply to Kunckell (this vol., i, 331). Allylbenzene has been prepared by the two methods previously described (this vol., i, 329, and Abstr., 1902, i, 666), and has been proved to possess the physical data previously given, namely, sp. gr. 0·9141 at 20°/4°, n_D 1·5497 at 12°, and boiling point 176—178° at 754 mm. These data agree with those given by Perkin (Trans., 1891, **59**, 1010), but not with Kunckell's numbers. This is due either to the presence of small amounts of *n*-propyl benzene in Kunckell's preparation or to the presence of an isomeric hydrocarbon, such as phenyltrimethylene, in the author's samples. J. J. S.

Phenylpropargylidene Chloride, $CPh{:}C{\cdot}CHCl_2$. ERNEST CHARON and EDGAR DUGOUJON (*Compt. rend.*, 1903, **137**, 125—128. Compare this vol., i, 472) —Phenylpropargylaldehyde was prepared by a modified form of Moureu and Delange's method (Abstr., 1901, i, 581). Ethyl formate dissolved in anhydrous ether was cooled to 0°, and the sodium derivative of phenylacetylene was added to it; acetic acid was then added in slight excess, then, after diluting with water, the aldehyde was extracted with ether. The chloro-derivative was obtained from the aldehyde by the action of phosphorus pentachloride. *Phenylpropargylidene chloride* is a colourless liquid which boils at 131—132° under 22 mm. pressure, does not solidify at $-14°$, and has a sp. gr. 1·2435 at 0°. In the air it slowly becomes yellow, but is much more stable than cinnamylidene chloride; it is only slowly decomposed by water. With chlorine, it gives a solid having the formula,

$$CHPhCl{\cdot}CHCl{\cdot}CHCl_2,$$

which boils at 165—167° under 28 mm. pressure, and is very stable in the air and under water. By the action of bromine in acetic acid or chloroform, the propargylidene compound gives slender needles of the bromide, $CHPhBr{\cdot}CHBr{\cdot}CHCl_2$, which are extremely stable.

The authors discuss the stability relationships of these compounds containing double and treble linkings. J. McC.

Certain Nitro-derivatives of Vicinal Tribromobenzene. C. LORING JACKSON and AUGUSTUS H. FISKE (*Amer. Chem. J.*, 1903, **30**, 53—80).—3 : 4 : 5-Tribromo-1-nitrobenzene melts at 112°. When treated with dilute sodium methoxide, it is converted into 2 : 6-dibromo-4-nitroanisole, melting at 122°, which was first prepared by Körner (Abstr., 1876, i, 228) by the action of methyl iodide on the silver derivative of 2 : 6-dibromo-4-nitrophenol.

3 : 5-*Dibromo*-4-*methoxyazoxybenzene*, $ON_2(C_6H_2Br_2\cdot OMe)_2$, obtained by the action of a strong solution of sodium methoxide on 3 : 4 : 5-tribromonitrobenzene, crystallises from benzene in groups of yellowish-white needles, melts at 214°, and is soluble in chloroform or benzene; this compound may also be prepared by the action of sodium methoxide on 2 : 6-dibromo-4-nitroanisole. When 2 : 6-dibromo-4-nitroanisole is reduced with tin and hydrochloric acid, it is converted into 2 : 6-dibromo-4-anisidine, which melts at 64—65°.

By the action of a dilute solution of sodium ethoxide on 3 : 4 : 5-tribromonitrobenzene, 2 : 6-dibromo-4-nitrophenetole is obtained, which crystallises in white, slender needles, melts at 58—59°, and not at 108° as stated by Staedel (Abstr., 1883, 663), and is very soluble in ether, benzene, chloroform, or acetone. When 3 : 4 : 5-tribromonitrobenzene is treated with a strong solution of sodium ethoxide, 3 : 5-*dibromo*-4-*ethoxyazoxybenzene*, $ON_2(C_6H_2Br_2\cdot OEt)_2$, is produced, which crystallises from benzene in long, slender, yellowish-white needles, melts at 163°, and is soluble in chloroform; this substance may also be prepared by the action of sodium ethoxide on 2 : 6-dibromo-4-nitrophenetole. By the reduction of 2 : 6-dibromo-4-nitrophenetole with tin and hydrochloric acid, 2 : 6-dibromo-4-phenetidine is formed, which crystallises in white plates and melts at 107° instead of 67° as given by Staedel (*loc. cit.*); its *hydrochloride* was prepared and analysed.

When 3 : 4 : 5-tribromonitrobenzene is boiled with a dilute solution of potassium carbonate, very little action takes place, but by the action of sodium hydroxide, 2 : 6-dibromo-4-nitrophenol is produced.

3 : 4 : 5-*Tribromo*-1 : 2-*dinitrobenzene*, obtained by nitration of 3 : 4 : 5-tribromo-1-nitrobenzene, forms large, yellowish-white prisms, melts at 160°, and is readily soluble in benzene, chloroform, acetone, or glacial acetic acid. 2 : 3 : 4-*Tribromo*-6-*nitroanisole*, prepared by the action of dilute sodium methoxide on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene, crystallises from alcohol in white, slender needles, melts at 109—110°, and is freely soluble in ether, benzene, chloroform, or acetone. *Dibromonitrodimethoxybenzene*, $NO_2\cdot C_6HBr_2(OMe)_2$, formed by the action of boiling sodium methoxide solution on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene or on 2 : 3 : 4-tribromo-6-nitroanisole, crystallises in white, slender needles, melts at 81°, and is readily soluble in alcohol, ether, benzene, chloroform, or acetone.

2 : 3 : 4-*Tribromo*-6-*nitrophenetole*, $NO_2\cdot C_6HBr_3\cdot OEt$, obtained by the action of cold sodium ethoxide on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene, crystallises in small, white rosettes, melts at 74°, is freely soluble in ether, benzene, chloroform, or acetone, and on exposure to the air gradually becomes yellow and afterwards brown.

When 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene is boiled with aqueous sodium hydroxide, 2 : 3 : 4-*tribromo*-6-*nitrophenol* is produced, which crystallises in thick, yellow prisms, melts at 120—121°, and is readily soluble in chloroform, acetone, or hot benzene; the *sodium* and *silver* derivatives were prepared and analysed. By the action of methyl iodide on the silver salt, the corresponding anisole melting at 109° is produced.

Ethyl sodiomalonate reacts with 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with formation of a red salt which is converted by acids into a *substance*, probably $C_6HBr_2(NO_2)_2{\cdot}CH(CO_2Et)_2$, which melts at 103—104°. A similar red salt is produced by the action of ethyl sodioacetoacetate.

2 : 3 : 4-*Tribromo*-6-*nitroaniline*, $NO_2{\cdot}C_6HBr_3{\cdot}NH_2$, obtained by the action of alcoholic ammonia on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene at the ordinary temperature, crystallises from benzene in bright yellow, radiating needles, melts at 161°, and dissolves readily in benzene, chloroform, or acetone. 2 : 4-*Dibromo*-6-*nitro*-m-*phenylenediamine*, $NO_2{\cdot}C_6HBr_2(NH_2)_2$, formed by heating 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with alcoholic ammonia in a sealed tube for 3 days at 100°, crystallises in bright yellow needles, melts at 189—190°, and is soluble in acetone, alcohol, ether, chloroform, or glacial acetic acid.

2 : 3 : 4-*Tribromo*-6-*nitrodiphenylamine*, $NO_2{\cdot}C_6HBr_3{\cdot}NHPh$, obtained by the action of aniline on 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene, crystallises from alcohol in red prisms, melts at 138—139°, and is soluble in ether, benzene, chloroform, or acetone.

3 : 4 : 5-*Tribromo*-o-*phenylenediamine*, $C_6HBr_3(NH_2)_2$, formed by the reduction of 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with tin and hydrochloric acid, melts at about 91°, becomes brown on exposure to the air, and is freely soluble in ether or acetone ; its *hydrochloride* was prepared and analysed. By the condensation of this diamine with phenanthraquinone, *diphenylene*-3 : 4 : 5-*tribromoquinoxaline* is produced as a yellow solid which does not melt below 250°. By condensation of the diamine with benzil, *diphenyl*-3 : 4 : 5-*tribromoquinoxaline* is obtained, which forms a light, brick-red powder and dissolves readily in benzene or chloroform. E. G.

m-Nitronitrosobenzene. FREDERICK J. ALWAY (*Ber.*, 1903, **36**, 2530—2531).—m-*Nitronitrosobenzene*, $NO{\cdot}C_6H_4{\cdot}NO_2$, prepared by reducing *m*-dinitrobenzene to the hydroxylamino-compound and oxidising, crystallises from alcohol in a white or bluish-green powder and melts at 85° (corr.) ; it condenses with aniline to *m*-nitroazobenzene.

T. M. L.

So-called Styrene Nitrosites. Preparation of Hyponitrous Acid. HEINRICH WIELAND (*Ber.*, 1903, **36**, 2558—2567).—Styrene pseudonitrosite, Sommer's α-styrene nitrosite (Abstr., 1895, i, 456 ; 1896, i, 294) is best obtained by passing nitrous gases from white arsenic and nitric acid of sp. gr. 1·38 into a well-cooled ethereal solution of styrene until the solution has a light green colour. The mixture is kept for two hours and the crystals then removed. It melts and decomposes at 129° and not at 158°, and is decomposed when boiled with any of the ordinary solvents. Boiling with water or alcohol largely transforms it into Sommer's β-styrene nitrosite, which is now shown to be α-nitroacetophenone oxime, $OH{\cdot}N{:}CPh{\cdot}CH_2{\cdot}NO_2$. When boiled with concentrated hydrochloric acid, the oxime yields a considerable amount of benzonitrile and benzoic acid. Styrene pseudonitrosite has the double molecular formula, and is undoubtedly a nitrobisnitroso-compound, $N_2O_2{\cdot}(CHPh{\cdot}CH_2{\cdot}NO_2)_2$, and its conversion into α-nitroacetophenone oxime is exactly analogous to the conversion of bisnitrosylbenzyl into benzaldoxime (Behrend and König, Abstr., 1890, 1132).

Aniline converts the pseudonitrosite into a base,

$NO_2 \cdot CH_2 \cdot CHPh \cdot NHPh$,

and nitrous oxide. Piperidine and phenylhydrazine behave in a similar manner.

Sodium hydroxide reacts with the pseudonitrosite yielding benzaldehyde, nitromethane, hyponitrous acid, and a small amount of nitrous oxide. Sodium ethoxide reacts in a similar manner; the hyponitrous acid has been obtained in the form of its silver salt, which is not explosive (compare Divers, Proc., 1899, **14**, 223). The formation of the hyponitrous acid is due to the elimination of the bisnitroso-group by the metal and the production of the sodium salt of phenylnitroethanol ether, $OEt \cdot CHPh \cdot CH{:}NO_2Na$, which further decomposes into benzaldehyde and sodionitromethane. J. J. S.

9-Nitrophenanthrene and its Reduction Products (Studies in the Phenanthrene Series. VI). JULIUS SCHMIDT and MAX STROBEL (*Ber.*, 1903, **36**, 2508—2518).—9-*Nitrophenanthrene* has already been prepared by Schmidt (Abstr., 1901, i, 76) from sodium methoxide and nitrobisdihydrophenanthrene oxide. A more convenient method is to nitrate phenanthrene dissolved in glacial acetic acid in presence of acetic anhydride (compare Pictet and Genequand, Abstr., 1902, i, 584). The product, when crystallised from alcohol, melted at 116—117°, and was further identified by its conversion into 9-amino- and 9-hydroxy-phenanthrenes and by its oxidation with chromic acid. The *picrate* softens at 96° and melts at 98—99°.

9-*Azoxyphenanthrene*, $ON_2(C_{14}H_9)_2$, crystallising with $1C_2H_6O$, is prepared by the electrolytic reduction of 9-nitrophenanthrene in hot alcoholic alkaline solution. It forms minute, bordeaux-red needles which melt and decompose at 254—255°; when dissolved in cold concentrated sulphuric acid, it exhibits an intensely blue colour. When 9-nitrophenanthrene is reduced by zinc dust and potassium hydroxide solution in presence of alcohol, 9-*azophenanthrene* is produced in small quantity. It crystallises in coloured needles, begins to decompose at 270°, and does not completely melt at 320°. It also gives, with concentrated sulphuric acid, a blue coloration with a tinge of red.

9-Azoxyphenanthrene and 9-azophenanthrene are the first representatives of their kind in the phenanthrene series.

When 9-nitrophenanthrene is reduced with zinc dust and alcoholic ammonia, 9-aminophenanthrene is generally formed. In some experiments, however, a product melting and decomposing at 220—221° was isolated, and was probably 9-hydrazophenanthrene.

9-*Aminophenanthrene* has been previously described (Schmidt and Strobel, Abstr., 1901, i, 464. Compare Japp and Findlay, Trans., 1897, **71**, 1123). Its *sulphate* crystallises in needles of a silvery lustre and melts at about 230°; the *nitrate* forms white needles melting and decomposing at 163°; the *oxalate* forms yellowish-white needles melting and decomposing at 215°. Its *monobenzenesulphonyl* derivative, $C_{14}H_9NH \cdot SO_2Ph$, crystallises from alcohol in glistening, white needles which melt at 194—195°. The *dibenzenesulphonyl* derivative, formed as a bye-product from the preceding preparation, crystallises from alcohol in white needles which melt at 263—264°.

s-*Di-9-phenanthrylthiocarbamide*, $S:C:(NHC_{14}H_9)_2$, prepared from 9-aminophenanthrene, alcohol, and carbon disulphide, separates in quadratic prisms and pyramids melting at 229°.

9-*Dimethylaminophenanthrene methiodide*, prepared from a methyl alcoholic solution of 9-aminophenanthrene and methyl iodide in presence of sodium methoxide, forms transparent, brown prisms which melt and decompose at 217°.

When 9-aminophenanthrene is diazotised, bye-products, consisting mainly of 9-azoxy- and 9-azo-phenanthrenes, are formed. The diazonium compound yields the known 9-hydroxyphenanthrene melting at 149°, which was further identified by conversion into its acetyl derivative melting at 77°. By the action of diazophenanthrene sulphate on an alkaline solution of β-naphthol, 9-*phenanthreneazo-β-naphthol* is produced; it forms dark reddish-brown crystals which soften at 200° and melt completely at about 240°. A. McK.

New Formation of Diphenylamine Derivatives. FRITZ ULLMANN (*Ber.*, 1903, **36**, 2382—2384).—When *o*-chlorobenzoic acid is heated with aniline and copper powder, condensation takes place, and phenylanthranilic acid, $NHPh\cdot C_6H_4\cdot CO_2H$, is formed. The presence of copper is necessary to the reaction, which may also be extended to other aromatic amines.

m-Nitrophenylanthranilic acid, $NO_2\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot CO_2H$, from *m*-nitroaniline and *o*-chlorobenzoic acid, forms yellow needles melting at 215°, insoluble in water, but dissolving readily in alcohol.

C. H. D.

Diphenyldimethylammonium Salts. S. GADOMSKA and HERMAN DECKER (*Ber.*, 1903, **36**, 2487—2489).—It was formerly generally supposed that the existence of quaternary diphenylammonium salts was improbable, since no additive product could be prepared from alkyl haloids and methyldiphenylamine. When, however, molecular quantities of methyl sulphate and methyldiphenylamine are heated for two hours at 140—150°, the main product is *diphenyldimethylammonium methyl sulphate*, which forms deliquescent, colourless crystals with all the characteristics of true quaternary salts. On treatment first with water and then with a saturated aqueous solution of potassium iodide it is converted into *diphenyldimethylammonium iodide*, colourless needles which melt at 163° and, at a higher temperature, decompose to form methyl iodide and methyldiphenylamine. A. McK.

Molecular Rearrangement of Iminoacid Anhydrides. HENRY L. WHEELER and TREAT B. JOHNSON (*Amer. Chem. J.*, 1903, **30**, 24—39).—The experiments described in this paper were undertaken with the object of investigating the formation and properties of some iminoacid anhydrides of the type of the hypothetical iminoformic anhydride, $NH:CH\cdot O\cdot CH:O$. It was expected that such compounds would undergo a molecular rearrangement into diacylamides of the type CHO·NH·CHO, and similarly that derivatives of di-iminoformic anhydride would be transformed into acylamidines,

$$NH{:}CH{\cdot}O{\cdot}CH{:}NH \rightarrow CHO{\cdot}NH{\cdot}CH{:}NH.$$

By the interaction of phenyl-α-chlorobenzylideneamine with silver *p*-bromobenzoate, p-*bromobenzoylbenzanilide*, $NPhBz{\cdot}CO{\cdot}C_6H_4Br$, is produced, which crystallises in colourless prisms, melts at 150°, and is readily soluble in hot alcohol or benzene. The same compound is obtained when α-chloro-*p*-bromobenzylideneaniline is treated with silver benzoate. It follows, therefore, that the iminoacid anhydrides first formed in these reactions undergo a molecular rearrangement in the cold.

p-*Bromobenzanilidimide chloride* [*α-chloro-*p*-bromobenzylideneaniline*], $C_6H_4Br{\cdot}CCl{:}NPh$, prepared by the action of phosphorus pentachloride on *p*-bromobenzanilide, crystallises in needles, melts at about 78°, boils at 205—207° under 12 mm. pressure, and is readily soluble in benzene or light petroleum.

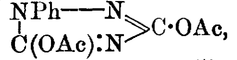
When α-chlorobenzylideneaniline is treated with silver acetate, acetylbenzanilide is produced. By the action of silver benzoate on ethyl phenyliminochloroformate or of ethyl chlorocarbonate on phenyliminoethyl benzoate, *benzoylphenylurethane*, $NPhBz{\cdot}CO_2Et$, is formed, which crystallises in prisms and melts at 67°.

When a mixture of α-chlorobenzylideneaniline and silver anisate is suspended in dry ether and left for 16 hours, anisic anhydride is produced, together with *benzoylanisanilide*, which crystallises in six-sided tablets, melts at 162—163°, and is very soluble in alcohol or benzene; the latter substance can also be prepared by the action of anisyl chloride on phenyliminoethyl benzoate. If a mixture of α-chlorobenzylideneaniline and silver anisate is boiled with ether for 2½ hours, benzoyldiphenylbenzenylamidine (Lander, Trans., 1902, **81**, 594) is produced.

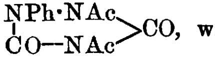
α-Chloroanisylideneaniline, $MeO{\cdot}C_6H_4{\cdot}CCl{:}NPh$, distils and decomposes at 220—230° under 17 mm. pressure, crystallises from petroleum in colourless prisms, melts at 70°, and by the action of water is converted into anisanilide

By the action of silver *m*-nitrobenzoate on α-chlorobenzylideneaniline, m-*nitrobenzoylbenzanilide*, $PhBzN{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2$, is obtained, which crystallises in colourless prisms and melts at 139°.

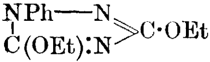
By the action of acetyl chloride on the silver salt of phenylurazole, Acree (Abstr., 1902, i, 242) obtained 3-acetyl-1-phenylurazole. On repeating this experiment, it was found that a labile *diacetylphenylurazole*,



$\begin{array}{l}NPh{-}{-}N\\ \;|\\ C(OAc){:}N\end{array}\!>\!C{\cdot}OAc$, is produced, which is very soluble in benzene; it melts at 115° and is thereby converted into the stable form,



$\begin{array}{l}NPh{\cdot}NAc\\ \;|\\ CO{-}NAc\end{array}\!>\!CO$, which melts at 162°, and is identical with the diacetyl derivative obtained by Thiele and Schleussner (Abstr., 1897, i, 380). When silver phenylurazole is treated with ethyl iodide, ethoxyphenylurazole (Acree, *loc. cit.*) is not produced, but phenylurazole is obtained together with 1-*phenyl*-3 : 5-*diethylurazole*,



$$\begin{matrix}NPh—N\\ \vert \qquad\quad \\ C(OEt){:}N\end{matrix}\!\!>\!C\cdot OEt$$, which crystallises in colourless needles and melts at 46—47°. E. G.

Derivatives of Dipeptides and their Behaviour towards Pancreas Ferments. EMIL FISCHER and PETER BERGELL (*Ber.*, 1903, **36**, 2592—2608).—*β-Naphthalenesulphoglycyl*-d-*alanine*,

$C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$,

prepared in the manner already described (this vol., i, 467) from naphthalenesulphoglycine, thionyl chloride and *d*-alanine ethyl ester, crystallises from water in tiny needles or glistening plates, melts at 154—155° (corr.) and in alkaline solution has $[\alpha]_D + 7\cdot11°$. It is soluble in 50 parts of boiling water and in about 2012 parts at 20°; it forms easily soluble calcium and barium salts and amorphous, sparingly soluble silver and lead compounds.

β-Naphthalenesulpho-d-*alanylglycine*,

$C_{10}H_7\cdot SO_2\cdot NH\cdot CHMe\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$,

crystallises in glistening plates, melts at 180·5—181·5° (corr.) and in alkaline solution has $[\alpha]_D - 63\cdot71°$; it is soluble in 50 parts of boiling or about 711 parts of water at 20°. The silver and lead salts are sparingly soluble, as also are the calcium and barium compounds, which crystallise in needles grouped in stellate aggregates. The *ethyl* ester crystallises in long needles from dilute alcohol and melts at 103°. The difference in solubility of the calcium and barium salts of these two acids facilitates their separation. They are of interest, as by the successive hydrolysis of silk-fibroin with hydrochloric acid, trypsin, and barium hydroxide, a product is formed, which appears to be a compound of glycine and alanine. It is, however, not identical with either of the acids described above, although possibly a mixture of the two.

β-Naphthalenesulphoglycyltyrosine,

$C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4\cdot OH$,

crystallises from dilute alcohol in needles, sinters at 157—158°, melts at 163—163·5°, has $[\alpha]_D + 17\cdot9°$ at 20° in alkaline solution and is very sparingly soluble in water. With Millon's reagent it gives a faintly red precipitate, the solution itself remaining colourless.

β-Naphthalenesulphoglycyl-dl-*leucine*,

$C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CHMe_2$,

crystallises from 20 per cent. alcohol in long needles, melts sharply at 123—123·7° and is very sparingly soluble in water.

The analogous *l*-leucine compound was not obtained quite pure. It melts at 144—145° and has $[\alpha]_D$ about + 13°.

Carbethoxyglycyl-dl-*leucine*,

$CO_2Et\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH(CO_2H)\cdot CH_2\cdot CHMe_2$,

crystallises in plates from acetone or in needles from alcohol and water, melts at 134—135° and is soluble in 9 parts of boiling and about 100 parts of cold water.

Carbethoxyglycyltyrosine was only obtained as a syrup.

The *sodium* salt of *di-β-naphthalenesulphotyrosine*,

$C_{10}H_7\cdot SO_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot SO_2\cdot C_{10}H_7$, obtained on shaking an alkaline solution of tyrosine with β-naphthalenesulphonic chloride, crystallises in long needles from methyl alcohol, sinters at 250°, and melts at 252—254°. The acid crystallises from alcohol in rosettes of fine needles and on heating forms an oil at 100°, which becomes liquid at 120° and froths at 145—150° without decomcomposing. The ammonium and barium salts are sparingly soluble and crystallise in needles.

*Di-β-naphthalenesulphotyrosyl-*dl*-leucine*, formed by the interaction of the sodium salt just described with thionyl chloride and leucine ethyl ester, forms stellate aggregates of small needles, sinters at 90° and melts at 100—105°.

In the tryptic digestion of albumins, tyrosine and leucine are always the first products formed, in fact, in the case of the digestion of the peptone from silk-fibroin, their presence can be detected in 15 minutes. Similar observations have been made with the synthetic derivatives of dipeptides. These were brought into solution with a little ammonia if necessary, and digested at 37° with pancreatin in presence of toluene. Under these conditions, the glycine derivatives, namely, glycylglycine, naphthalenesulpho-*d*-alanylglycine, and naphthalenesulphoglycyl-*d*-alanine, as also hippuric acid, were not affected, whereas naphthalenesulphoglycyl-*l*-tyrosine was hydrolysed to naphthalenesulphoglycine and *l*-tyrosine almost completely in the space of 13 hours. Especially interesting results were obtained with carbethoxyglycyl-*dl*-leucine, which was hydrolysed into *l*-leucine and carbethoxyglycine, the carbethoxyglycyl-*d*-leucine remaining unattacked. E. F. A.

Oxide from β-*cyclo*Hexane-1 : 2-diol and its Derivatives. LÉON BRUNEL (*Compt. rend.*, 1903, **137**, 62—64. Compare this vol., i, 338). —An oxide is formed under various circumstances from hexahydrobenzene monoiodohydrin, $C_6H_{10}I\cdot OH$. For its preparation, the hydrin is dissolved in dry ether and the solution is shaken with powdered potassium hydroxide. On fractionation of the product, a small quantity of *cyclo*hexane is obtained at 83—85°, and the portion boiling at 131—132° is the pure *oxide*, $C_6H_{10}{:}O$. This internal oxide of β-*cyclo*hexane-1 : 2-diol is a colourless, mobile liquid with a strong odour and a burning taste ; it has a sp. gr. 0·975 at 15°, does not solidify at – 10°, and is insoluble in water, but readily soluble in alcohol, ether, acetone, or acetic acid. The vapour density corresponds with the simple formula $C_6H_{10}{:}O$.

Reduction of the oxide with sodium amalgam gave no satisfactory result, but when hydrogen charged with its vapour was conducted over reduced nickel at 170—180°, reduction to *cyclo*hexanol, $C_6H_{11}\cdot OH$, takes place almost quantitatively.

The oxide can be easily hydrated ; the action commences at 80° and is rapid at 110—115°, β-*cyclo*hexane-1 : 2-diol being formed.

When the oxide is agitated with a solution of sodium hydrogen sulphite, *sodium β-*cyclo*hexan-1-ol-2-sulphonate*, $OH\cdot C_6H_{10}\cdot SO_3Na$, is formed. The action takes place more readily at a higher temperature, and the salt is best prepared in a sealed tube at 110—115°. When crystallised from water it separates with H_2O, which it loses at 100°; it is sparingly soluble in water and almost insoluble in alcohol. J. McC.

Attempts at an Asymmetric Synthesis. Emil Fischer and Max Slimmer (*Ber.*, 1903, 36, 2575—2587).—Most of the results described have been published previously (compare Abstr., 1902, i, 621). Gluco-*o*-hydroxyphenylethylcarbinol (*loc. cit.*), when hydrolysed with 1—3 per cent. sulphuric acid and extracted with ether, yields a syrup having $[\alpha]_D$ $-10°$ to $-15°$ at 20°, from which, on distillation under 0·3 mm. pressure, a colourless oil having $[\alpha]_D$ $-9·83°$ at 20° was obtained. This was at first believed to be active o-*hydroxyphenylethylcarbinol.* However, hydrolysis of the glucoside with emulsin yielded an inactive carbinol, and on careful fractionation of the active carbinol under 0·3 mm. pressure an optically active, less volatile fraction was obtained, together with the inactive carbinol. Apparently a condensation product, soluble in ether, is formed even by the dilute acid acting on the glucoside, which distils along with the carbinol and thus imparts to it the apparent optical activity. E. F. A.

Nitrosobenzoates. Frederick J. Alway and Arthur B. Walker (*Ber.*, 1903, 36, 2312—2314).—By the action of light on *o*-nitrosobenzaldehyde, Ciamician and Silber (Abstr., 1901, i, 547; 1902, i, 378, 433; this vol., i, 39) have obtained *o*-nitrosobenzoic acid, and from solutions of this aldehyde in methyl and ethyl alcohols respectively they have obtained the corresponding benzoates. The authors have prepared the latter esters and others by the action of zinc dust and acetic acid on nitrobenzoates. The hydroxyamino-compounds initially formed were directly oxidised to the mixture of azoxybenzoates and nitrosobenzoates, which are readily separable by steam distillation. *Methyl* o-*nitrosobenzoate* crystallises from glacial acetic acid in colourless needles and melts at 153°. *Ethyl* o-*nitrosobenzoate* melts at 120—121°. *Methyl* m-*nitrosobenzoate* forms white crystals and melts at 93° (corr.). *Methyl* m-*azoxybenzoate* crystallises from glacial acetic acid in orange-coloured needles and melts at 136—136·5° (corr.).

Methyl p-*nitrosobenzoate* crystallises from alcohol in yellow needles and melts at 128—129·5° (corr.). *Methyl* p-*azoxybenzoate* crystallises from alcohol in flesh-coloured needles melting at 206·5—207·5° (corr.) (compare Meyer and Dahlem, this vol., i, 448). A. McK.

Formation of Ester-acids. Robert Kahn (*Ber.*, 1903, 36, 2531—2534).—Controversial, in reply to Wegscheider (this vol., i, 559. Compare the following abstract). T. M. L.

Action of Alcohols on Mixed Anhydrides. Robert Kahn (*Ber.*, 1903, 36, 2535—2538).—3-*Acetylaminophthalic anhydride*, $C_{10}H_7O_4N$, separates from benzene in yellow crystals and melts at 181°.

Benzoic p-*nitrobenzoic anhydride*, $C_6H_5·CO·O·CO·C_6H_4·NO_2$, separates from carbon disulphide in white crystals, melts at 130°, and is hydrolysed by ethyl alcohol to benzoic acid and ethyl *p*-nitrobenzoate, the ester being derived from the stronger acid, which is also the acid in which substitution has taken place. Benzoic *iso*cuminic anhydride, $C_6H_5\cdot CO\cdot O\cdot CO\cdot C_6H_4\cdot CHMe_2$, in which the acids are of almost equal strength, gives a mixed product when acted on by alcohol. The isomeric *benzoic mesitylcarboxylic anhydride*, $C_6H_5\cdot CO\cdot O\cdot CO\cdot C_6H_2Me_3$, separates from carbon disulphide in white crystals, melts at 105°, and gives benzoic acid and ethyl mesitylcarboxylate; in this case, the substituted acid is esterified, although it is probably the weaker acid.

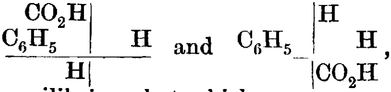
T. M. L.

Action of Cyanogen Bromide on Benzyl Cyanide. Julius von Braun (*Ber.*, 1903, **36**, 2651—2653).—Cyanogen bromide reacts with an alcoholic solution of benzyl cyanide in presence of sodium ethoxide forming a faintly red precipitate almost entirely soluble in water. The insoluble portion is diphenylmaleonitrile; on hydrolysis, it forms diphenylmaleic anhydride melting at 156°. The portion soluble in water is chiefly sodium cyanide. The original alcoholic solution yields, on evaporation, the brominated benzyl cyanide, $C_6H_5\cdot CHBr\cdot CN$, described by Reimer (Abstr., 1881, 47).

Thus cyanogen bromide here acts as a brominating agent.

E. F. A.

A New Isomerism of Ethylene Derivatives. Emil Erlenmeyer, jun. (*Ber.*, 1903, **36**, 2340—2344).—If cinnamic acid be written $\frac{C_6H_5 \quad H}{H \quad CO_2H}$, and one of the three isomeric cinnamic acids $\frac{C_6H_5 \quad H}{CO_2H \quad H}$, then in passing from the latter form into the former (stable) form, rotation of one half of the molecule must take place, and according to the direction of rotation, two intermediate configurations are possible,



$$\begin{array}{c|c} CO_2H & \\ \underline{C_6H_5} & \underline{\ H\ } \\ & H \end{array} \quad \text{and} \quad \begin{array}{c|c} & H \\ \underline{C_6H_5} & \ H \\ & CO_2H \end{array}$$

, in which the molecule will be in equilibrium, but which can pass readily into the more stable configurations. These two forms may also combine to a single molecule in the same way as two oppositely active isomerides. This hypothesis suggests the existence of a larger number of isomeric ethylene derivatives than is accounted for by van't Hoff's theory.

When cinnamaldehyde is condensed with racemic *iso*-α-hydroxy-αβ-diphenylethylamine (this vol., i, 412), a single product,

$$\begin{array}{l} Ph\cdot CH\cdot OH \\ Ph\cdot \overset{|}{C}H\cdot N\!:\!CH\cdot CH\!:\!CHPh \end{array}$$

melting at 186°, is obtained. If, on the other hand, the *l*-base be employed, the product may be separated by successive crystallisation from benzene and light petroleum into two dextrorotatory compounds giving the same figures on analysis, and melting at 189—190° and 131° respectively. The *d*-base similarly yields two lævorotatory condensation products melting at 189—190° and 131° respectively. The condensation products of the active bases with benzaldehyde, on the other hand, both melt at 137° and rotate the plane of polarisation in the same direction as the corresponding base.

C. H. D.

isoCinnamic Acid. Arthur Michael (*Ber.*, 1903, **36**, 2497—2498. Compare this vol., i, 418).—A reply to Liebermann (this vol., i, 485).

A. McK.

Some Derivatives of p-Sulphocinnamic Acid. F. J. Moore (*J. Amer. Chem. Soc.*, 1903, **25**, 622—629).—The *aniline* salt of *p*-sulphocinnamic acid melts at 246°; the *acid sodium* salt crystallises with $2H_2O$.

By the action of bromine on *p*-sulphocinnamic acid, p-*sulphodibromodihydrocinnamic acid* is produced, which crystallises with $2H_2O$ and is soluble in water at 20° to the extent of 53—57 per cent.; its *barium, copper, sodium,* and *ammonium* salts were prepared. The *aniline, diethylaniline,* and *dimethylaniline* salts melt at 192°, 160°, and 150° respectively. The *amide* crystallises from hot water in scales and melts at 208° (uncorr.). When silver nitrate is added to an aqueous solution of the acid sodium salt of *p*-sulphodibromodihydrocinnamic acid, a white precipitate is produced which rapidly changes into silver bromide; if the filtrate is evaporated in a vacuum, a crystalline *substance* is obtained, which is probably the acid sodium salt of *p*-sulphobromocinnamic acid.

p-Sulphocinnamic acid dissolves in warm concentrated hydrobromic acid, and, on cooling, separates in thin needles containing $3H_2O$; the ordinary form of the acid, described by Rudnew (Abstr., 1875, 76), crystallises with $5H_2O$.

E. G.

Formation and Transformation of Cinnamylformic Acid [Styrylglyoxylic Acid]. Emil Erlenmeyer, jun. (*Ber.*, 1903, **36**, 2527—2530. Compare Claisen, Abstr., 1881, 169; 1882, 520).—Styrylglyoxylic acid, $CHPh{:}CH\cdot CO\cdot CO_2H$, can be prepared in a crystalline form by condensing pyruvic acid and benzaldehyde with sodium hydroxide, thoroughly draining the sodium salt formed, dissolving, and acidifying; the acid crystallises with $1H_2O$ and melts at 54°, or, when anhydrous, at 57°; the dibromide decomposes at 138°, and the phenylhydrazone at 158°. On reduction, it gives Fittig's α-hydroxyphenyl*iso*crotonic acid, and not benzylpyruvic acid; the reduced acid, when boiled with dilute hydrochloric acid, gives benzoylpropionic acid.

T. M. L.

Condensation of Acetylenic Esters with Alcohols. Charles Moureu (*Compt. rend.*, 1903, **137**, 259—261. Compare this vol., i, 399).—When methyl phenylpropiolate is treated with sodium methoxide in methyl alcohol solution, reaction takes place, and, according to the conditions, either 1 or 2 mols. of methyl alcohol condense with the acetylenic ester. When methyl phenylpropiolate is carefully added to a solution of sodium methoxide in methyl alcohol and the mixture heated for 15 hours in a reflux apparatus, then introduced into a sealed tube and heated at 125° for 4 hours, a colourless, limpid liquid is obtained. This was poured into an excess of ice-water and at once extracted with ether and rectified under diminished pressure. In this way, *methyl αα-dimethoxydihydrocinnamate*, $CPh(OMe)_2\cdot CH_2\cdot CO_2Me$, was obtained. It is a highly refractive oil with an agreeable odour, boils at 146—147° under 16 mm. pressure, has a sp. gr. 1·112 at 21°/0° and n_D 1·5004 at 21°. A cryoscopic determination showed that it has the simple formula $C_{12}H_{16}O_4$. The molecular refraction is in agreement with the constitution given. Ferric chloride tinges an alcoholic solution of it yellow, which slowly passes into red; this change can be attributed to the hydrolysis of the acetal function. When saponified in the cold with sodium hydroxide, it gives crystals of *sodium αα-dimethoxydihydrocinnamate* with $5H_2O$, from which the free acid is obtained in prismatic crystals by treatment with the requisite quantity of dilute sulphuric acid at 0°. At the ordinary temperature, the acid loses carbon dioxide, and at the same time an oil having an aromatic odour is formed. The latter distils at about 94° under 23 mm. pressure, and was found to be a mixture of the *dimethylacetal* of *acetophenone*, $CMePh(OMe)_2$, and *α-methoxystyrene*, $OMe\cdot CPh\colon CH_2$. When the oil is treated with acetyl chloride in presence of pyridine, methoxystyrene is obtained as an aromatic liquid, which boils at 197° (corr.), has a sp. gr. 1·0158 at 0°, n_D 1·3958 at 21°, and on hydrolysis gives acetophenone.

If methyl phenylpropiolate acts on sodium methoxide at a high temperature, there is always formed a monomethoxy-derivative, $OMe\cdot CPh\colon CH\cdot CO_2Me$, which, on saponification, gives *α-methoxycinnamic acid*, $OMe\cdot CPh\colon CH\cdot CO_2H$, which can be separated from the dimethoxy-acid by aid of its sparing solubility in ether and alcohol. The acid is obtained in microscopic crystals which decompose at 160°. J. McC.

3-Nitrophthalyl Chloride and its Action with Ammonia and with Aromatic Amines. VICTOR JOHN CHAMBERS (*J. Amer. Chem. Soc.*, 1903, **25**, 601—612. Compare Bogert and Boroschek, Abstr., 1902, i, 98).—*3-Nitrophthalyl chloride*, $NO_2\cdot C_6H_3(COCl)_2$, obtained by the action of phosphorus pentachloride on 3-nitrophthalic acid, crystallises in colourless, transparent prisms, melts at 76—77°, and is readily soluble in ether or chloroform. When a stream of dry ammonia is passed over it, 3-nitrophthalimide is produced. By the action of dilute aqueous ammonia on a solution of the chloride in chloroform, 3-nitrophthalamic acid is formed. If dry ammonia gas is led into a dry ethereal solution of the chloride, 2 : 6-*nitrocyanobenzoic acid*, $NO_2\cdot C_6H_3(CN)\cdot CO_2H$, is obtained, which crystallises in clusters of white, slender needles, melts at 99—100°, and is converted by the action of heat into 3-nitrophthalimide. 3-*Nitrophthalanilide* melts at 211—212°, the corresponding p-*toluidide* melts at 223—225°, and the m- and p-*nitroanilides* melt and decompose at 225—230° and at 197—200° respectively. E. G.

Action of the Sodium Salts of Dibasic Acids on Aniline Hydrochloride, and of Aniline on Phthalyl Chloride and Succinyl Chloride. FREDERICK L. DUNLAP and FREDERICK W. CUMMER (*J. Amer. Chem. Soc.*, 1903, **25**, 612—621).—When dry sodium phthalate is heated with aniline hydrochloride for 6 hours in a sealed tube at 200°, phthalanil is produced, but no phthalanilide can be isolated. If a mixture of sodium succinate and aniline hydrochloride is treated in the same way, succinanilide and succinanil are formed; the higher the temperature at which the reaction takes place, the larger is the proportion of succinanil obtained.

By the action of phthalyl chloride on an ethereal solution of aniline at the ordinary temperature, aniline hydrochloride, phthalanilide, and phthalanil are produced (compare Rogoff, Abstr., 1897, i, 470, and Kuhara and Fukui, Abstr., 1902, i, 34). When succinyl chloride reacts with an ethereal solution of aniline at the ordinary temperature, succinanilide and aniline hydrochloride are produced, but no succinanil can be isolated. E. G.

3-Aminophthalimide. HUGO KAUFFMANN and ALFRED BEISSWENGER (*Ber.*, 1903, 36, 2494—2497).—When 3-nitrophthalic acid is reduced by ferrous hydrate, the amino-acid is formed (Onnertz, Abstr., 1902, i, 99). When, however, the ammonium salt, obtained in the course of the preparation, is decomposed by a slight excess of glacial acetic acid, white crystals of *ammonium hydrogen 3-aminophthalate* separate which melt and decompose at 117—118°. On exposure for several hours, the mother liquor begins to darken and to fluoresce, and a yellow product (possibly 3-aminophthalic anhydride), which does not melt at 280°, is obtained. When this substance, which may also be prepared by heating ammonium hydrogen 3-aminophthalate with glacial acetic acid, is boiled with ammonia, it forms *3-aminophthalimide*, which crystallises from water in minute, yellow needles, melting at 256—257°, and forms strongly fluorescent solutions. It may also be prepared by the reduction of 3-nitrophthalimide with tin and hydrochloric acid, by treatment of 3-nitrophthalic acid with ammonium sulphide, by passing ammonia over fused 3-nitrophthalic acid, or by heating 3-nitrophthalic acid with ammonium thiocyanate at 170—180°.

3-Aminophthalimide probably exists in two tautomeric forms, the one yellow and exhibiting green fluorescence, the other colourless and exhibiting violent fluorescence. A. McK.

Phenylitaconic Acid. JOSEF HECHT (*Monatsh.*, 1903, 24, 367—374).—Stobbe and Klöppel (Abstr., 1894, i, 594) obtained a small yield of phenylitaconic acid by condensing ethyl succinate with benzaldehyde in the presence of sodium ethoxide. A convenient modification of the method is described by the author. The preparation is conducted in alcoholic solution, and by using molecular proportions of ethyl succinate and benzaldehyde it is found that the formation of an acid, melting at 203°, which was observed by Stobbe and Klöppel, is to a large degree prevented.

The *dimethyl ester*, prepared by the hydrogen chloride method, is a viscid oil which boils at 186° under 19 mm. pressure. It unites with hydrogen cyanide, and, on hydrolysis of the product, *a-phenyltricarballylic acid* is obtained; this crystallises from water in short, transparent prisms melting at 110°. A. McK.

[Formation of Carbon Rings.] ARTHUR KÖTZ (*J. pr. Chem.*, 1903, [ii], 68, 148—152. Compare Kötz and Speiss, Abstr., 1902, i, 12).—A *résumé* of the work of various authors on the formation of carbon rings by the action of halogens and dihaloids on disodium derivatives of the esters of ethane and other tetracarboxylic acids.

The action of methylene di-iodide on ethyl disodioethanetetracarboxylate leads to the formation of ethyl *cyclo*trimethylenetetracarboxylate. The action of *meta-* and *para*-xylyldibromides does not lead to the formation of ring compounds.

A 6 : 7 double-ring *compound*, $C_6H_4{<}\begin{matrix}CH_2\cdot C(CO_2Et)_2\\ CH_2\cdot C(CO_2Et)_2\end{matrix}{>}CH_2$, is formed by the action of *o*-xylyl dibromide on ethyl disodiopropanetetracarboxylate. G. Y.

Action of Hydrated Bismuth Oxide on Isomerides of Gallic Acid. Bismutho-pyrogallolcarboxylic Acid. PAUL THIBAULT (*Bull. Soc. chim.*, 1903, [ii], 29, 680—682. Compare Abstr., 1902, i, 101, 240, and this vol., i, 633).

—*Bismutho-pyrogallolcarboxylic acid*, prepared by the long-continued action of gelatinous bismuth oxide on pyrogallolcarboxylic acid in closed vessels at the ordinary temperature, crystallises in golden-yellow, prismatic needles, decomposes at 195—200°, and has sp. gr. 3·51 at 18°. An aqueous solution of ferric chloride at first colours the acid blue, and finally dissolves it, forming a colourless liquid. The *ammonium* and *sodium* salts are crystalline; the anilide could not be prepared. When pyrogallolcarboxylic acid is digested with hydrated bismuth oxide at 100°, there is formed a brown powder of the composition $C_6H_3O_6Bi_3,2H_2O$, which is partially soluble in sodium hydroxide solution. Phloroglucinolcarboxylic acid does not react at the ordinary temperature with hydrated bismuth oxide, but at 100° a brick-red powder of the composition $C_6H_3O_6Bi_3$ is produced. T. A. H.

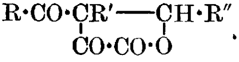
Constitution of α-Oxylactones. EMIL ERLENMEYER, jun. (*Ber.*, 1903, 36, 2344—2348).

—The α-oxylactones may be formulated either as ketonic or enolic compounds:

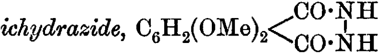

I. II.

The first formula contains two asymmetric carbon atoms, and two racemic modifications are therefore possible. The second contains only one asymmetric carbon atom and a double linking, and, a closed ring being present, only one pair of optically active modifications is possible. The discovery of geometrical isomerides of α-oxylactones would therefore be evidence for the keto-formula (compare Abstr., 1902, i, 543).

The condensation of piperonal with phenylpyruvic acid yields two *α-oxylactones* of the formula $CO{<}\begin{matrix}CHPh\\ CO-O\end{matrix}{>}CH\cdot C_6H_3{:}O_2{:}CH_2$, which may be separated by their different solubility in alcohol. The more soluble lactone melts at 208°, its *acetyl* derivative at 135°, and its *benzoyl* derivative at 177°, the less soluble form melts at 205°, and its *acetyl* and *benzoyl* derivatives at 130° and 172° respectively. The acetyl and benzoyl derivatives of the two lactones are thus not identical, and must therefore also be derived from the ketonic form,

 $\begin{array}{l}R\cdot CO\cdot CR'\text{——}CH\cdot R'' \\ \qquad\;\; CO\cdot CO\cdot O\end{array}$. Reduction of the *a*-oxylactones, melting at 208° and 205°, yields *a-hydroxylactones* melting at 155° and 153° respectively.

The *a*-oxylactones obtained from cuminaldehyde and phenylpyruvic acid (this vol., i, 419) behave similarly. The *acetyl* and *benzoyl* derivatives of the lactone melting at 186° melt at 120° and 140° respectively, while the lactone melting at 198° forms an *acetyl* derivative melting at 156° and a *benzoyl* derivative melting at 126°. C. H. D.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XI. Behaviour of Acid-esters of Hemipinic Acid towards Hydrazine Hydrate and Thionylchloride. Rudolf Wegscheider and Peter von Rušnov (*Monatsh.*, 1903, **24**, 375—390).—*Hemipinicdihydrazide*, $C_6H_2(OMe)_2\cdot(CO\cdot NH\cdot NH_2)_2$, formed by boiling *a*-methyl hydrogen hemipinate with hydrazine hydrate, melts in a closed capillary tube at 215°, and is partially decomposed by heating with water or with ether. When repeatedly crystallised from alcohol, it forms *hemipinichydrazide*,  $C_6H_2(OMe)_2<\begin{array}{l}CO\cdot NH\\ CO\cdot NH\end{array}$, which melts at 218—221° on being slowly heated in a closed capillary tube. When strongly heated, methylamine is evolved, the dihydrazide behaving similarly. At the laboratory temperature, *a*-methyl hydrogen hemipinate interacts with hydrazine hydrate to form the hydrazine salt, a trace of dihydrazide being also produced.

The behaviour of *b*-methyl hydrogen hemipinate towards hydrazine hydrate is similar. In both cases, therefore, hydrazine hydrate interacts not only with the CO_2Me group but also with the carboxyl group. Hemipinic anhydride is formed by the action of thionyl chloride on *b*-methyl hydrogen hemipinate. The ester chloride, owing to its instability, could not be isolated; it undergoes considerable transformation into the isomeric *a*-chloride. By the action of ammonia on a mixture of thionyl chloride and *b*-methyl hydrogen hemipinate, no amide formation was observed, but *a*- and *b*-methyl hydrogen hemipinates were respectively isolated and were identified by their melting points and by determinations of their electrical conductivities. A similar transformation of *b*-acid-ester into the *a*-isomeride by means of a solution of hydrogen chloride in methyl alcohol has been previously noted by Wegscheider (Abstr., 1895, i, 420), the reaction proceeding slowly with the intermediate formation of normal ester. In the case now studied, the change was rapid and no appreciable amount of normal ester was formed. In addition to the acid-esters formed from ammonia, thionyl chloride, and *b*-methyl hydrogen hemipinate, a substance of the constitution $C_{10}H_{14}O_5N_2$ was isolated. A. McK.

Lichens and their Characteristic Constituents. VIII. Oswald Hesse (*J. pr. Chem.*, 1903, [ii], **68**, 1—71. Compare Abstr., 1902, i, 680).—The author claims to have been the first to obtain barbatic acid from *Usnea longissima* (Abstr., 1897, i, 255. Compare Zopf, Abstr., 1898, i, 89; 1902, i, 788). Barbatic acid is best characterised by its potassium salt.

Usnea ceratina, from the Black Forest, contains *d*-usnic acid, barbatic acid, and barbatin; that from Java cinchona bark contains *d*-usnic acid, usnaric acid, parellic acid, and ceratin (compare Zopf, Abstr., 1902, i, 789).

Usnea barbata (α) *florida*, from Bolivian cinchona bark, contains *d*-usnic acid, usnaric acid, plicatic acid, usnetic acid, and an *acid* which resembles usnaric acid, but is tasteless.

The author replies to Widman (Abstr., 1903, i, 96).

Usnea barbata (β) *hirta*, from Bolivian cinchona bark, contains *d*-usnic acid and barbatic acid, the latter in larger proportion.

Stenhouse and Groves's formula, $C_{19}H_{20}O_7$, for barbatic acid is confirmed. The sodium salt, $C_{19}H_{19}O_7Na,2H_2O$, crystallises when pure in glistening, straight-sided leaflets (Zopf, Abstr., 1902, i, 789). The action of acetic anhydride on barbatic acid leads to the formation of a *substance*, probably the lactone of acetylbarbatic acid, which melts at 250°, and, on recrystallisation from glacial acetic acid, yields *acetylbarbatic acid*. This crystallises in small, white needles, melts at 172°, is soluble in ether, alcohol, acetone, or aqueous alkalis or alkaline carbonates, gives a brownish-yellow coloration with ferric chloride in alcoholic solution, and forms an amorphous potassium salt. Hydrolysis of acetylbarbatic acid or of barbatic acid with aqueous alkalis leads to the formation of betorcinol and rhizoninic acid. Rhizonic acid is identical with barbatic acid (Abstr., 1899, i, 385).

Usnea barbata (γ) *dasypoga* contains alectoric acid, contrary to Zopf's statement (Abstr., 1902, i, 789). Alectoric acid is distinguished from barbatic acid by its smaller solubility in ether and by its conversion into alectorinic acid on treatment with aqueous barium hydroxide (Abstr., 1901, i, 149). Alectorinic acid, $C_{27}H_{24}O_{13},2H_2O$, has a neutral reaction, neutralises aqueous potassium hydroxide in boiling alcoholic solution, the acid crystallising out unchanged on cooling, and gives a brownish-red coloration with ferric chloride in alcoholic solution.

Evernia furfuracea (Zopf, Abstr., 1901, i, 88) contains atranorin, evernuric acid, and traces of furevernic acid. The formula of evernuric acid is now given as $C_{24}H_{26}O_9$; the *potassium* salt,

$$C_{24}H_{25}O_9K,2H_2O,$$

crystallises in short, colourless prisms. The action of barium hydroxide on the acid leads to the formation of *evernurol*, $C_{23}H_{26}O_7$, which crystallises in short, white prisms, melts at 196°, and is soluble in ether, alcohol, or hot chloroform, but less so in benzene. The alcoholic solution is neutral, and gives a greenish-brown coloration with ferric chloride and a blood-red coloration with bleaching powder. *Furevernic acid* crystallises in small, white prisms, melts and decomposes at 197°, is easily soluble in ether, alcohol, or aqueous alkalis, and dissolves in concentrated sulphuric acid to a colourless solution which gradually becomes brown.

Ramalina farinacea contains *d*-usnic acid and *ramalic acid*, $C_{30}H_{26}O_{15}$. The new acid forms small, white needles, melts and decomposes at 240—245°, has a bitter taste, and is moderately soluble in hot glacial acetic acid or alcohol. The alcoholic solution has an acid reaction and gives a purple-red coloration with ferric chloride. It dissolves in concentrated sulphuric acid to a yellow solution which becomes blood-red, and, on addition of water, yields an orange-coloured, flocculent decomposition *product.*

Cetraria islandica, from the Gerlinger Höhe, contains protocetraric acid and proto-α-lichesteric acid. The moss previously obtained from Stuttgart and Frankfurt (Abstr., 1898, i, 534) contained protocetraric acid and protolichesteric acid. Protolichesteric acid melts at 108—109° and is converted by acetic anhydride into lichesteric acid (m. p. 124°) (Sinnhold, Abstr., 1899, i, 13). Proto-α-lichesteric acid, $C_{18}H_{30}O_5$, melts at 106—107°, is converted by acetic anhydride into α-lichesteric acid, which melts at 122°, and is identical with Zopf's protolichesteric acid (Abstr., 1902, i, 788). The protolichesteric acids form very soluble ammonium salts, and their potassium salts are easily oxidised by potassium permanganate; the lichesteric acids form crystalline ammonium salts and are not easily oxidised by potassium permanganate. *Methyl proto-α-lichesterate* crystallises in glistening leaflets and melts at 33°. The action of aqueous barium hydroxide solution on the acid leads to the formation of lichestronic acid, which melts at 80° (Abstr., 1901, i, 87). β-Lichesteric acid is identical with α-lichesteric acid, as is also probably γ-lichesteric acid. Böhme's results (Abstr., 1903, i, 316) are due to his method of extraction, which ensures changes taking place in the product. From Böhme's Iceland moss, the author obtains proto-α-lichesteric acid.

Parmelia conspersa, from Wildbad, contains *d*-usnic acid and conspersaic acid, but no usnetic acid (Abstr., 1898, i, 90, 680). *Conspersaic acid* forms granular aggregates of microscopic needles, melts and decomposes at 252°, has a bitter taste, is slightly soluble in hot alcohol or acetone, and gives a purple coloration with ferric chloride in alcoholic solution. The ammoniacal solution gives a white, flocculent precipitate with barium chloride; the solution in warm aqueous potassium hydrogen carbonate, on cooling, deposits small, white needles which assume an orange-colour; on addition of water, the solution in concentrated sulphuric acid yields a red, flocculent precipitate mixed with colourless needles.

Parmelia saxatilis retiruga, from Reunbachtale (Wildbad), contains atranorin, protocetraric acid, and *saxatic acid,* $C_{25}H_{40}O_8$, which crystallises in colourless leaflets, melts at 115°, is soluble in alcohol, acetone, or ether, and dissolves in aqueous alkali carbonates to colourless solutions which become yellow on warming; the solution in concentrated sulphuric acid becomes brown on warming; the ammoniacal solution gives an amorphous precipitate with barium chloride.

Parmelia saxatilis omphalodes contains atranorin, saxatic acid, and an acid resembling protocetraric acid.

Parmelia cetrata, from Java cinchona bark, contains *cetrataic acid,* $C_{29}H_{24}O_{14}$, which crystallises in small, white, six-sided needles, melts and decomposes at 178—180°, is soluble in alcohol, less so in ether, has a bitter taste, and gives a purple coloration with ferric chloride in alcoholic solution. The solution in concentrated sulphuric acid is yellow, slowly darkening, and becoming blood-red and brown on warming.

Lecanoric acid is not contained in *Parmelia perlata,* its presence in a previous specimen (Abstr., 1901, i, 151) being due to admixture of small amounts of *P. tinctorum,* which contains lecanoric acid and atranorin. The moss previously supposed to be *P. olivetorum* is found to be *P. tinctorum.*

Parmelia olivetorum contains atranorin, olivetorin, and olivetoric acid (Zopf, Abstr., 1901, i, 88). Olivetoric acid is considered to have the formula $C_{21}H_{26}O_7$ (Zopf, $C_{27}H_{34}O_8$). *Olivetorin* crystallises in delicate, white needles, melts at 143°, and is soluble in alcohol or warm benzene; the alcoholic solution gives, with ferric chloride, a purple-violet, with bleaching-powder a blood-red coloration.

Parmelia olivacea is now found to contain olivacein and olivaceic acid. *Olivacein,* $C_{17}H_{22}O_6,H_2O$, crystallises in red needles, melts at 156°, and is easily soluble in alcohol, acetone, ether, benzene, or glacial acetic acid, moderately so in boiling water; the alcoholic solution gives with ferric chloride a purple-violet, with bleaching-powder a blood-red coloration. *Olivaceic acid,* $C_{16}H_{19}O_5{\cdot}OMe$, crystallises in small leaflets, melts at 138°, and is easily soluble in ether, acetone, or alcohol; the alcoholic solution gives purple-violet and blood-red colorations with ferric chloride and bleaching powder respectively. The *potassium* salt crystallises in small, white nodules; the *barium* salt is easily soluble in water.

Gasparrinia medians is now found to contain calycin and pulvic lactone (Abstr., 1898, i, 681).

The orange-red needles, obtained by extracting *Gyalolechia epixantha* (Ach), contain calycin and pulvic lactone and melt at 228°. The following compounds of calycin and pulvic lactone have been prepared synthetically: $C_{18}H_{10}O_4,C_{18}H_{12}O_5$, melting at 216—217°; $2C_{18}H_{10}O_4,C_{18}H_{12}O_5$, melting at 211—213°; $C_{18}H_{10}O_4,2C_{18}H_{12}O_5$, melting at 226—228°.

Contrary to Zopf's statement (Abstr., 1902, i, 790), *Urceolaria scruposa* contains lecanoric acid. The distillation in steam of pannaric acid (Abstr., 1901, i, 596) leads to the formation of *pannarol,* $C_8H_8O_2$, which crystallises in small, white needles, melts at 176°, is volatile without decomposition, is easily soluble in ether, alcohol, or acetone, gives a blue coloration with ferric chloride in alcoholic solution, and, when heated with concentrated sulphuric acid, yields the steel-blue *substance,* $C_8H_6O_3,3H_2O$, which is also obtained from pannaric acid.

Pertusaria rupestris = P. communis (β) *areolata* contains areolatin, areolin, and gyrophoric acid, $C_{16}H_{14}O_7$. *Areolatin,* $C_{11}H_7O_6{\cdot}OMe$, crystallises in green masses of needles, melts at 270°, and is only slightly soluble in boiling alcohol, more so in hot glacial acetic acid; the alcoholic solution, on addition of ferric chloride, is dark green by transmitted, reddish-violet by reflected light. When heated with concentrated hydriodic acid, areolatin yields *areolatol,* $C_9H_8O_4,H_2O$, which crystallises in delicate, white needles, sublimes without melting at 220°, and is easily soluble in alcohol; the alcoholic solution gives a brownish-purple coloration with ferric chloride; the solution in aqueous sodium hydroxide gives a flocculent precipitate on the addition of hydrochloric acid.

Areolin crystallises in white, globular aggregates, melts at 243°, and gives a purple-red coloration with ferric chloride in alcoholic solution.

Petrusaria glomerata, from Wildbad, contains porin and porinic acid.

Porin, $C_{42}H_{67}O_9\cdot OMe$, crystallises in small, yellow leaflets, melts at 166°, is easily soluble in hot alcohol, insoluble in aqueous alkalis, and gives no coloration with ferric chloride or bleaching-powder. The mother liquor from the methoxyl determination with porin contains *porinin*, $(C_3H_6O)_n$, which crystallises in colourless needles and melts at 70—71°. *Porinic acid*, $2C_{11}H_{12}O_4,H_2O$, crystallises in microscopic needles, loses H_2O at 100°, and melts and decomposes at 218°; the alcoholic solution gives with ferric chloride a brownish-violet, with bleaching-powder a blood-red coloration. When boiled with aqueous barium hydroxide, the acid yields a *substance*, $C_{10}H_{12}O_2$, which crystallises in flat, colourless needles, melts at 58°, after drying in a desiccator at 92°, and gives a blood-red coloration with bleaching-powder, but no colour with ferric chloride.

Calycium chlorinum, from Bastei, contains vulpic acid and calycin, but no leprarin (Abstr., 1901, i, 86).

Lepraria latebrarum contains *d*-usnic acid, atranorin, hydroxyroccellic acid, lepraric acid, and talebraric acid (compare Zopf, Abstr., 1901, i, 87).

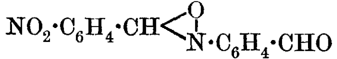
Talebraric acid crystallises in light yellow, four-sided prisms, melts and decomposes at 208°, is slightly soluble in alcohol, ether, or glacial acetic acid, and easily so in aqueous alkalis or alkaline carbonates or ammonia; the alcoholic solution gives a dark brownish-red coloration with ferric chloride. The action of concentrated sulphuric acid and water leads to the formation of *talebrarinic acid*, which forms a yellow powder or glistening needles, melts at 182°, and gives a dark green coloration with ferric chloride.

Zopf's lepraridin, leprarinin, and lepralid are the ethyl, methyl, and *n*-propyl esters of lepraric acid. The action of hydriodic acid on lepraric acid leads to the formation of *norlepraric acid*, which crystallises in small, white needles, melts at 215°, and gives a purple-red coloration with ferric chloride. G. Y.

Nitrosobenzaldehyde. FREDERICK J. ALWAY (*Ber.*, 1903, **36**, 2303—2311. Compare this vol., i, 425).—p-*Hydroxylaminobenzaldehyde*, $OH\cdot NH\cdot C_6H_4\cdot CHO$, has been prepared in small yield by Kalle and Co. (D.R.-P. 89978) by the action of zinc dust and an aqueous solution of an ammonium salt on *p*-nitrobenzaldehyde. A better method is now described, in which zinc dust is added to *p*-nitrobenzaldehyde dissolved in alcohol and glacial acetic acid.

When *p*-hydroxylaminobenzaldehyde is oxidised by sulphuric acid and potassium dichromate, a mixture of *p*-nitrosobenzaldehyde and *p*-azoxybenzaldehyde is produced.

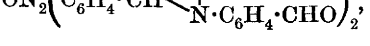
p-*Nitrobenzaldoxime*-N-p-*formylphenyl ether*,



$$NO_2\cdot C_6H_4\cdot CH\Big<\begin{array}{l}O\\ \mid\\ N\cdot C_6H_4\cdot CHO\end{array},$$

is prepared by adding zinc dust to a solution of *p*-nitrobenzaldehyde in glacial acetic acid or by adding a solution of *p*-nitrobenzaldehyde in sulphuric acid to an alcoholic solution of *p*-hydroxylaminobenzaldehyde.

p-*Azoxybenzaldoxime*-N-p-*formylphenyl ether*,



$$ON_2\left(C_6H_4\cdot CH\Big<\begin{array}{l}O\\ \mid\\ N\cdot C_6H_4\cdot CHO\end{array}\right)_2,$$

has been prepared by the electrolytic reduction of *p*-nitrobenzaldoxime-N-*p*-formylphenyl ether in sulphuric acid solution, by the action of air on *p*-hydroxylaminobenzaldehyde, by the action of zinc dust on a solution of *p*-nitrobenzaldehyde in glacial acetic acid, and by condensation of *p*-hydroxylaminobenzaldehyde (2 mols.) with *p*-azoxybenzaldehyde (1 mol.) by means of sulphuric acid. On oxidation, it yields *p*-nitrosobenzaldehyde and *p*-azoxybenzaldehyde, whilst on being boiled with dilute acids it forms *p*-azoxybenzaldehyde only.

p-Nitrosobenzaldehyde was prepared from *p*-nitrobenzaldehyde in a manner analogous to the preparation of *p*-hydroxylaminobenzaldehyde. It may also be prepared by adding zinc dust to *p*-nitrobenzyl chloride, dissolved in alcohol and glacial acetic acid.

m-*Nitrobenzaldoxime*-N-m-*formylphenyl ether* was prepared by the reduction of *m*-nitrobenzaldehyde. It melts at 189—190° and is identical with the product obtained by the electrolytic reduction of *m*-nitrobenzaldehyde. The crude reduction product, obtained from *m*-nitrobenzaldehyde and zinc dust, gave, on oxidation, *m*-nitrosobenzaldehyde.

p-*Tolueneazo*-p-*benzylidene*-p-*toluidine*,

$$\mathrm{C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}C_6H_4Me},$$

prepared from *p*-nitrosobenzaldehyde, *p*-toluidine, and acetic acid, forms orange-red leaflets melting at 170—171° (corr.). By the action of nitric acid, it yields p-*tolueneazo*-p-*benzaldehyde*, $\mathrm{C_6H_4Me{\cdot}N_2{\cdot}C_6H_4{\cdot}CHO}$, which crystallises from glacial acetic acid in red needles melting at 177·5° (corr.). A. McK.

The Addition of Hydrogen Chloride to Dibenzylideneacetone. Johannes Thiele and Fritz Straus (*Ber.*, 1903, **36**, 2375—2378. Compare Vorländer and Mumme, this vol., i, 495).—The compound of dibenzylideneacetone with hydrogen chloride, $\mathrm{C_{17}H_{15}OCl}$, crystallises from ether or carbon disulphide in colourless leaflets which decompose on heating. It combines with bromine in chloroform solution to form a *dibromide*, $\mathrm{C_{17}H_{15}OClBr_2}$, crystallising from a mixture of chloroform and light petroleum in groups of colourless needles which melt at 128°. Vorländer's red dihydrochloride forms the known colourless tetrabromide when treated with excess of bromine in carbon tetrachloride solution, the hydrogen chloride being eliminated.

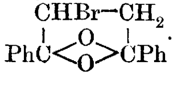
The constitution of the colourless hydrochloride must be

$$\mathrm{CHPhCl{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CHPh},$$

the hydrogen chloride in the dihydrochloride, on the other hand, must be differently combined, since both molecules are eliminated in contact with air or water, without intermediate formation of the monohydrochloride. C. H. D.

Chloro- and Bromo-diphenacyls. Carl Paal and Heinrich Schulze (*Ber.*, 1903, **36**, 2386—2404. Compare Abstr., 1902, i, 228).—The formulæ I—V are possible for the bromodiphenacyls:

I. $\mathrm{COPh{\cdot}CHBr{\cdot}CH_2{\cdot}COPh}$; II. $\mathrm{OH{\cdot}CPh{:}CBr{\cdot}CH_2{\cdot}COPh}$;
III. $\mathrm{COPh{\cdot}CHBr{\cdot}CH{:}CPh{\cdot}OH}$; IV. $\mathrm{OH{\cdot}CPh{:}CBr{\cdot}CH{:}CPh{\cdot}OH}$;

V. 

$$\begin{array}{c}\mathrm{CHBr{-}CH_2}\\ \mathrm{|\quad O\quad |}\\ \mathrm{PhC{<}_{O}^{\,}{>}CPh}\end{array}.$$

Of these, I is assigned to γ-bromodiphenacyl, leaving II—V for the α- and β-derivatives. α- and β-Chloro- and bromo-diphenacyls, unlike the γ-compounds, combine with acetyl chloride and bromide to form stable compounds (compare Paal and Stern, Abstr., 1902, i, 476). The compound from β-chlorodiphenacyl and acetyl bromide is identical with that from β-bromodiphenacyl and acetyl chloride, and the two halogen atoms must be attached to the same carbon atom. This excludes formulæ III and V. Assuming formula II for the β-derivatives, the enolic hydroxyl is first acetylated, and the hydrogen haloid formed is then taken up at the double linking. The formula II must be rejected for the α-derivatives, since the products from α- and β-chlorodiphenacyls and acetyl chloride are not identical. The properties of α- and β-halogendiphenacyls are best represented by the formula IV, of which four configurations are possible. This explains the existence of four iododiphenacyls (compare following abstract).

α-Chloro- and α-bromo-diphenacyls are isomorphous, and crystallise from ethyl acetate in large, rhombic tablets. β-Chloro- and β-bromodiphenacyls are also isomorphous, and form large, probably monoclinic, tablets. The following additive products are described:

	α-Chlorodiphenacyl.	β-Chlorodiphenacyl.
Acetyl chloride	Needles, m. p. 106°	Tablets, m. p. 98°
Acetyl bromide	Tablets, m. p. 104° Needles, m. p. 114° (dimorphous)	Identical with the product from β-bromodiphenacyl and acetyl chloride (*loc. cit.*), m. p. 90°.
Hydrogen chloride...	—	Needles, m. p. 164°
Hydrogen bromide...	—	Needles, m. p. 155°

	α-Bromodiphenacyl.	β-Bromodiphenacyl.
Acetyl bromide	Needles, m. p. 124°	Prisms, m. p. 103°
Hydrogen chloride...	—	Needles, m. p. 160°
Hydrogen bromide...	—	Needles, m. p. 145°

Ethyl chlorocarbonate reacts in boiling glacial acetic acid solution, forming the hydrogen chloride addition compounds.

The mother liquor from the crystallisation of α- and β-chlorodiphenacyls contains a small quantity of a *compound*, $C_{16}H_{13}O_2Cl$, crystallising from alcohol in white needles melting at 189°, isomeric with the chlorodiphenacyls, but yielding no diphenacyl on reduction. C. H. D.

Iododiphenacyls. Carl Paal and Heinrich Schulze (*Ber.*, 1903, 36, 2405—2415).—The iododiphenacyls are prepared by the action of potassium iodide on the corresponding chloro- or bromo-diphenacyls. *α-Iododiphenacyl*, OH·CPh⁚CI·CH⁚CPh·OH, crystallises from chloroform in rosettes of tablets and from ethyl acetate in rhombic tablets, isomorphous with the α-chloro- and α-bromo-compounds, and melts at 70—90° according to the rate of heating. No additive product could be obtained with acetyl chloride, as decomposition occurred. *β-Iododiphenacyl*, prepared from β-bromodiphenacyl and potassium iodide, or mixed with tribenzoyltrimethylene, from ω-iodoacetophenone and sodium ethoxide (compare Paal and Stern, Abstr., 1899, i, 367), crystallises from alcohol in long needles, from methyl alcohol in short prisms, and from chloroform or ethyl acetate in large crystals, isomorphous with the β-chloro- and β-bromo-compounds, and decomposes at 104—116°. *γ-Iododiphenacyl* is formed, together with some *trans*-dibenzoylethylene, by the action of potassium iodide on γ-chlorodiphenacyl, and crystallises from alcohol in white needles melting at 121°. Its solution in warm concentrated sulphuric acid, unlike that of the other isomerides, is not fluorescent. *δ-Iododiphenacyl*, prepared by the action of alcoholic ammonia or organic bases on the β-compound, crystallises from ethyl acetate in large, colourless, triclinic prisms, melting at 150—153° and decomposing shortly after.

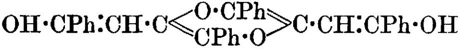
An acetic acid solution of hydrogen chloride converts α-iododiphenacyl into an oily product. β- and δ-Iododiphenacyls, on the other hand, yield identical *additive* products, $OH\cdot CHPh\cdot CCl\cdot CH{:}CPh\cdot OH$, crystallising from anhydrous solvents in white, glistening needles, which melt and decompose at about 133—134°. C. H. D.

Cyanodiphenacyl. Carl Paal and Heinrich Schulze (*Ber.*, 1903, **36**, 2415—2416).—*β-Cyanodiphenacyl*,

$$OH\cdot CPh{:}C(CN)\cdot CH{:}CPh\cdot OH,$$

prepared by heating either α- or β-bromodiphenacyl with potassium cyanide in alcoholic solution, crystallises from dilute alcohol in long, colourless needles and melts at 118°, and from ethyl acetate in large tables resembling those of β chloro- and β-bromo-diphenacyls.

C. H. D.

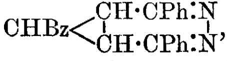
Action of Silver Acetate on Halogen-diphenacyls. Carl Paal and Heinrich Schulze (*Ber.*, 1903, **36**, 2416—2424).—When β-iodo- or β-bromo-diphenacyl is heated with silver acetate in glacial acetic acid, *acetoxydiphenacyl*, $COPh\cdot CH(OAc)\cdot CH{:}CPh\cdot OH$, is formed, crystallising from alcohol in white needles which melt at 98° and dissolve in concentrated sulphuric acid to a yellow solution with a brilliant green fluorescence. The same product is obtained from δ-iododiphenacyl. α-Bromodiphenacyl, on the other hand, loses water to form a *compound* with the molecular formula $C_{32}H_{24}O_4$, probably  $OH\cdot CPh{:}CH\cdot C{<}\genfrac{}{}{0pt}{}{O\cdot CPh}{CPh\cdot O}{>}C\cdot CH{:}CPh\cdot OH$ crystallising from dilute acetone in small, concentrically grouped needles, which melt when rapidly heated, undergoing isomeric change, and then again solidify, finally melting at 279°. A small quantity of this isomeride is also produced in the preparation of the compound from α-bromodiphenacyl, and crystallises from nitrobenzene or chloroform in small, white prisms melting at 279°.

Acetoxydiphenacyl is hydrolysed by heating with alcoholic potassium hydroxide, forming the *ketodiol*, $COPh\cdot CH(OH)\cdot CH{:}CPh\cdot OH$, a yellow oil, exhibiting the same green fluorescence in sulphuric acid as the acetyl compound. Heating with acetic anhydride and sodium acetate converts it again into acetoxydiphenacyl. C. H. D.

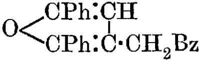
Quinonoid Diketones. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1903, **137**, 263—264).—The action of concentrated sulphuric acid on several diketo-compounds has been studied. Anthraquinone is fairly stable, but carbon dioxide and sulphur dioxide are evolved; alizarin is somewhat less resistant than anthraquinone; purpurin is less resistant than alizarin. Phenanthraquinone and *α*-naphthaquinone are both very resistant, but evolve carbon dioxide and sulphur dioxide. It is concluded that, at a definite temperature under the action of sulphuric acid, quinonoid diketones and quinone-phenols suffer fission between the carbonyl and phenyl groups; then the phenyl groups act by their CH constituents on the acid and reduce it.

From the relative powers of resistance, it is concluded that all substitution in an aromatic molecule decreases the stability. J. McC.

Synthesis of *s*-Tribenzoyl*cyclo*trimethylenes. CARL PAAL and HEINRICH SCHULZE (*Ber.*, 1903, **36**, 2425—2436).—When sodium acts on an ethereal solution of *ω*-iodoacetophenone, a mixture of *cis*- and *trans*-tribenzoyl*cyclo*trimethylenes is formed, the former preponderating. cis-1 : 2 : 3-*Tribenzoyl*cyclo*trimethylene* crystallises from alcohol, chloroform, or ethyl acetate in silky needles melting at 215°, sparingly soluble in ether. trans-1 : 2 : 3-*Tribenzoyl*cyclo*trimethylene* is more readily soluble in ether, insoluble in chloroform, and crystallises from ethyl acetate in small, white needles melting at 292°. Both forms are unattacked by bromine or potassium permanganate. A conversion of the *cis*- into the *trans*-form by boiling with quinoline could not be effected. Boiling with hydrazine hydrate converts both forms into 4 : 5-*benzoylmethylene*-4 : 5-*dihydro*-3 : 6-*diphenylpyridazine*,



$$\mathrm{CHBz}\Big<\begin{array}{l}\mathrm{CH\cdot CPh{:}N}\\ \mathrm{CH\cdot CPh{:}N}\end{array},$$

crystallising from alcohol or ethyl acetate in golden-yellow needles which melt at 235° and are not attacked by oxidising agents. Hydriodic acid converts *cis*- and *trans*-tribenzoyl*cyclo*trimethylenes into 2 : 5-*diphenyl*-3-*phenacylfurfuran*,  $\mathrm{O}\Big<\begin{array}{l}\mathrm{CPh{:}CH}\\ \mathrm{CPh{:}C\cdot CH_2Bz}\end{array}$, which crystallises from alcohol in long, white, glistening needles melting at 118°, and reacting with hydrazine hydrate to form a *ketazine*,

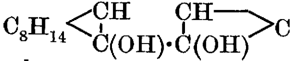
$$\mathrm{C_4OHPh_2\cdot CH_2\cdot CPh{:}N\cdot N{:}CPh\cdot CH_2\cdot C_4OHPh_2},$$

which crystallises from glacial acetic acid in small, yellow needles melting at 219—220°. When diphenylphenacylfurfuran is more strongly heated with hydriodic acid or warmed with phosphorus oxychloride, it loses water to form 2 : 5-*diphenyl-α-naphthafurfuran*, $(C_6H_5)_2C_{12}H_6O$, which crystallises from alcohol in slender, white needles melting at 120—121°, and dissolving in glacial acetic acid, ethyl acetate, chloroform or benzene to solutions having an intensely blue fluorescence. C. H. D.

Syntheses in the Camphor Group with Magnesium Powder. SIGNE M. MALMGREN (*Ber.*, 1903, **36**, 2608—2642. Compare this vol., i, 103).—When *α*-monobromocamphor dissolved in xylene is heated with magnesium powder, it yields camphor and a compound, $C_{20}H_{28}O_2$, melting at 192—193°, identical with Oddo's dicamphendione. In toluene solution, small quantities of dicamphor melting at 163—164° are also obtained. In ethereal solution, two reactions take place, the one giving rise to the formation of *magnesium bromocamphor*, which remains in solution, whilst the other forms *magnesium camphor* and magnesium bromide, which separate from the ether.

The solution and precipitate obtained in this manner are exceedingly reactive. Thus, if carbon dioxide is passed into the solution, it forms camphocarboxylic acid from the magnesium bromocamphor along with dicamphor and camphor from the magnesium camphor.

Alkyl haloids all bring about the formation of *dicamphor pinacone*,



$C_8H_{14}<\begin{matrix}CH & CH— \\ | & | \\ C(OH)\cdot & C(OH)\end{matrix}>C_8H_{14}$, which is easily soluble in most organic solvents and crystallises in flat, prismatic needles melting at 151°.

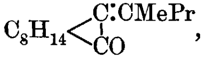
With acetaldehyde, the magnesium camphor reacts very violently, a *secondary alcohol*,

$C_8H_{14}<\begin{matrix}CH\cdot CHMe\cdot OH \\ | \\ CO\end{matrix}$, boiling at 223—226°, being formed in small quantities together with *acetylcamphor* boiling at 127° under 11 mm. pressure.

With benzaldehyde, a nearly theoretical yield of benzoylcamphor is formed.

Camphorylmethylpropylcarbinol,

$C_8H_{14}<\begin{matrix}CH\cdot CMePr\cdot OH \\ | \\ CO\end{matrix}$, prepared by condensation with methyl propyl ketone, loses water very easily, forming an unsaturated compound,



$C_8H_{14}<\begin{matrix}C{:}CMePr \\ | \\ CO\end{matrix}$, boiling at 253—260° under 756 mm. or at 158—163° under 10 mm. pressure.

With ethyl acetate, *dicamphorylmethylcarbinol*, $CMe(C_{10}H_{15}O)_2\cdot OH$, melting at 148—149° is formed along with acetylcamphor; this is a fairly strong acid, it develops a very marked coloration with iron chloride, and gives crystalline barium and copper salts. The *monoxime* crystallises in long, thin, colourless needles melting at 164°.

Dicamphorylethylcarbinol melts at 158—160°.

Propionylcamphor boils at 138·5° under 11 mm. pressure and develops an intense red coloration with iron chloride.

Butyrylcamphor boils at 146° under 12 mm. pressure.

Phenyldicamphorylcarbinol, obtained by condensation with benzoylchloride, crystallises from alcohol in plates or from light petroleum in tetrahedra and melts at 155—156°. E. F. A.

Action of Bromine on Pinene in Presence of Water. Paul Genvresse and P. Faivre (*Compt. rend.*, 1903, **137**, 130—131).—The products of the action of bromine on pinene in presence of water were distilled in a current of steam. At first, some unchanged pinene passes over, then a heavy oil, from which cymene was isolated and a white, crystalline solid. The solid was proved to be pinene dibromide, $C_{10}H_{16}Br_2$, which melts at 167—168°. J. McC.

Fenchyl Derivatives. Iwan L. Kondakoff and Julius Schindelmeiser (*J. pr. Chem.*, 1903, [ii], **68**, 105—119. Compare Abstr., 1900, i, 604; 1902, i, 478).—Secondary fenchyl chloride is now found to melt at 75°; it boils at 81—82° under 11 mm. and at 83—84° under 16 mm. pressure, has $[\alpha]_D$ +17°88′ and +15°39′ for *p* 11·79 and *p* 25·91 per cent. respectively, and, when acted on by concentrated alcoholic potassium hydroxide at 180°, yields fenchene, fenchyl alcohol, and traces of fenchyl ethyl ether (?); the fenchene boils at 159—161° and has $[\alpha]_D$ −9°65′; the fenchyl alcohol boils at 197—201° and has $[\alpha]_D$ −10°15′. The dichloride, obtained by the action of concentrated hydrochloric acid on fenchyl chloride, when free from the monochloride, crystallises in needles and leaflets, melts at 49—51°, and is optically inactive. The dibromide crystallises in two forms which melt at 49° and 52·5° respectively.

When acted on by alcoholic potassium hydroxide at 125°, the dichloride yields a hydrocarbon which boils at 181—184°, is optically inactive, has a sp. gr. 0·8524 at 21°/4°, and n_D 1·47713, has an odour resembling sylvestrene, gives the carvestrene reaction with acetic anhydride and sulphuric acid (Baeyer, Abstr., 1895, i, 153), and is not stable when exposed to air. With concentrated hydrobromic acid, it yields a *dibromide*, $C_{10}H_{18}Br_2$, which melts at 61—64°, at 59—60° after recrystallisation from light petroleum, is decomposed by alcohol, reacts with bromine, and is optically inactive in chloroform solution.

An attempt to prepare carvestrene by Baeyer's method from carone resulted in the formation of a mixture of hydrocarbons, which, with hydrobromic acid, yielded a mixture of bromides boiling at 85—138° under 11 mm. pressure. The action of alcoholic potassium hydroxide at 150° on the bromides led to the formation of a hydrocarbon which boils at 169—176°, is optically inactive, and yields a bromide boiling at 90—101° under 12 mm. pressure. The hydrocarbon corresponding with the less volatile part of the bromide mixture is decomposed by the alcoholic potassium hydroxide. Carvestrene, which has been considered stable, is decomposed by alkalis or acids, and has not yet been obtained in a state of purity.

Borneol and *iso*borneol yield a crystalline dibromide which boils at 139—142° under 12 mm. pressure and is optically inactive. The action of alcoholic potassium hydroxide on this dibromide leads to the formation of a hydrocarbon which boils at 173—175°, has a sp. gr. 0·843 at 20° and n_D 1·47586; the hydrocarbon obtained from another specimen boils at 174—179°, has a sp. gr. 0·844 at 20° and n_D 1·47588; both hydrocarbons are optically inactive. G. Y.

Resin from a Passion Flower. Henri Jumelle (*Compt. rend.*, 1903, **137**, 206—208).—The bark of *Ophiocaulon Firingalavense* is covered with a green, wax-like substance, which proves, however, to be really a resin and not a wax. In chloroform, it dissolves to the extent of 92 per cent., in carbon disulphide, ether, and benzene, 83 per cent., in cold alcohol and toluene, 81 per cent., and in acetone 78 per cent. In all cases, the solution leaves on evaporation an amorphous deposit resembling that obtained from the resin of *Gardenia* by the same treatment. In hot water, it begins to soften at 65°, and between 85° and 90° it is quite pasty. The fresh resin has a sp. gr. 0·980, but after fusion it has sp. gr. 1·014 to 1·020. The portion soluble in chloroform absorbs 34·7 per cent. of iodine. J. McC.

Glucoside Formation from Bioses. RICHARD FOERG (*Monatsh.*, 1903, **24**, 357—363).—By the action of alcoholic hydrogen chloride on bioses, hydrolysis occurred and glucosides of the monoses were formed, whilst no acetals could be detected. By interaction of maltose, methyl alcohol, and dry hydrogen chloride under varying conditions, α-methylglucoside was produced. The same glucoside was also isolated from lactose and from sucrose respectively. A. McK.

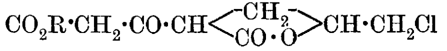
A New Colouring Matter from Ox-bile. WILHELM FRANZ LOEBISCH and MAX FISCHLER (*Monatsh.*, 1903, **24**, 335—350).—The product, obtained from ox-bile by extraction with alcohol, was dissolved in water, acidified with sulphuric acid, and extracted with ether. The ethereal solution was dried with calcium chloride and the ether expelled. The residue was then extracted, first with light petroleum and then with alcohol; the colouring matter, *bilipurpurin*, remained undissolved and formed dark violet, metallic scales on being crystallised from chloroform. Its solutions exhibit dichroism. The colouring matter does not melt or decompose at 330°; it is stable in air, and, when heated, decomposes, evolving an odour like that of pyridine. Its analysis accorded with the composition, $C_{32}H_{34}O_5N_4$, and the substance is considered to be the anhydride of bilirubin, $C_{32}H_{36}O_6N_4$. Crystallographic and spectroscopic determinations are quoted. Bilipurpurin dissolves in concentrated sulphuric acid to form a brilliant green solution, which gradually changes to bluish-green. Other colour reactions with acids and with alkalis are described. It was not found possible to convert bilirubin into bilipurpurin. Bilipurpurin is formed in the alcoholic extract from ox-bile even without addition of acid; its formation in the alcoholic extract requires, at the ordinary temperature, from 4 to 8 days, in the course of which, spectroscopic examination shows certain absorption bands, which indicate the formation of intermediate colouring matters. A. McK.

Brazilin and Hæmatoxylin. JOSEF HERZIG and JACQUES POLLAK (*Ber.*, 1903, **36**, 2319—2322. Compare this vol., i, 270).—By the action of potassium hydroxide on dinitrotetramethylhæmatoxylone, 6-nitrohomoveratrole and 4 : 5 : 4′ : 5-tetramethoxyl-2 : 2′-dinitrodibenzyl were isolated. From that portion of the product which was soluble in alkali, the authors have isolated Perkin and Yates' 2-carboxy-5 : 6-dimethoxyphenoxyacetic acid, $C_{11}H_{12}O_7$ (Trans., 1902, **81**, 235). The dinitro- and mononitro-compounds studied are soluble in dilute alkalis, the colour of the solutions being a reddish-violet, which disappears on dilution.

From hydroxylamine hydrochloride and β-trimethylbrazilone, a substance having the composition of an oxime has already been described (*loc. cit.*). Similarly, when hydroxylamine hydrochloride acts on nitrotrimethylbrazilone, an oxime is obtained which crystallises from alcohol in yellow needles melting at 159—162°. On treatment with alcoholic hydrogen chloride, it yields the original nitro-compound, which crystallises from glacial acetic acid in yellow needles and melts at 222—225°. A. McK.

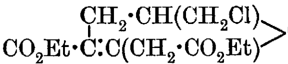
New Syntheses effected by means of Molecules containing a Methylene Group Associated with One or Two Negative Radicles. Action of Epichlorohydrin on the Sodium Derivatives of Acetonedicarboxylic Esters. III.

Albin Haller and F. March (*Compt. rend.*, 1903, **137**, 11—15. Compare this vol., i, 318).—By the action of epichlorohydrin on the methyl or ethyl ester of acetonedicarboxylic acid, a chloroketolactonic ester of the formula



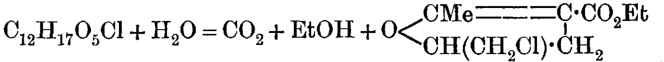
$CO_2R\cdot CH_2\cdot CO\cdot CH{<}\begin{matrix}CH_2\\ CO\cdot O\end{matrix}{>}CH\cdot CH_2Cl$

is formed. An alcoholic solution of the ethyl compound is saturated with hydrogen chloride, and after keeping for 48 hours the hydrogen chloride is removed under reduced pressure and the residue treated with water and extracted with ether. The ethereal solution yields an oil which has the formula $C_{12}H_{17}O_5Cl$, and boils at 198—199° under 17 mm. pressure. It gives no precipitate with cupric acetate, and does not form a semicarbazide: the ketonic function has, therefore, disappeared, and the complex $\cdot CO\cdot CH_2\cdot CO_2R$ has been changed. When boiled with an aqueous solution of potassium carbonate, it gives crystals the composition of which is represented by the formula $C_9H_{13}O_3Cl$. This melts at 57—58°, boils at 141—143° under 17 mm. pressure, is very soluble in ether or in alcohol, and has an odour resembling that of hydrofurfuran derivatives. It is identical with the ester obtained from δ-chloro-α-acetyl-γ-valerolactone, and is therefore *ethyl 2-chloromethyl-5-methyl-2:3-dihydrofurfuran-4-carboxylate.* The first action is to produce an ester by opening the lactone-ring; $CO_2Et\cdot CH_2\cdot CO\cdot CH(CO_2Et)\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$ is formed, and in the tautomeric enolic form loses a molecule of water and gives



$\begin{matrix}CH_2\cdot CH(CH_2Cl)\\ CO_2Et\cdot C{:}C(CH_2\cdot CO_2Et)\end{matrix}{>}O$.

The second compound is formed from this by the addition of a molecule of water and elimination of a molecule of carbon dioxide and one of alcohol:



$$C_{12}H_{17}O_5Cl + H_2O = CO_2 + EtOH + O{<}\begin{matrix}CMe{=\!=\!=}C\cdot CO_2Et\\ CH(CH_2Cl)\cdot CH_2\end{matrix}$$

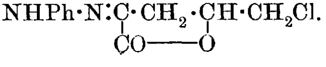
The acid obtained from this dihydrofurfuran ester melts at 108—109°

If the original keto-lactone is boiled with a dilute aqueous solution of potassium carbonate, carbon dioxide is evolved, and a substance having the formula $COMe\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ is formed; this is identical with the compound described by Traube and Lehmann (Abstr., 1901, i, 501).

By the action of benzenediazonium chloride at 0° on the sodium derivative of the keto-lactone, crystals of the compound

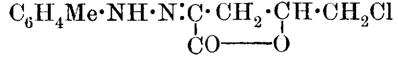
$$C_{11}H_{11}O_2N_2Cl$$

are formed which melt at 183—184°. The same compound is obtained by the action of benzenediazonium chloride on δ-chloro-α-benzoyl-γ-valerolactone, and its constitution is, therefore,



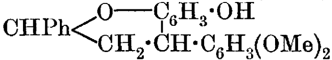
$$NHPh\cdot N{:}\underset{CO}{C}\cdot CH_2\cdot \underset{O}{CH}\cdot CH_2Cl.$$

If *p*-toluenediazonium chloride is used, the compound



$$\begin{array}{l} C_6H_4Me\cdot NH\cdot N{:}\underset{|}{C}\cdot CH_2\cdot \underset{|}{C}H\cdot CH_2Cl \\ \qquad\qquad\qquad\quad CO\text{——}O \end{array}$$

is produced, which crystallises in colourless needles from hot alcohol and melts at 210°. J. McC.

Quinonoid Benzopyranol Derivatives from 3:5-Dimethoxybenzoylacetophenone. I. CARL BULOW and GUSTAV RIESS (*Ber.*, 1903, **36**, 2292—2303).—The authors have previously shown (this vol., i, 101) that 3 : 5-dimethoxybenzoylacetophenone readily condenses with hydroxylamine and substituted hydrazines to form *iso*oxazoles and pyrazoles, and, in so doing, behaves partly as a ketonic and partly as an enolic compound, from which it was concluded that in the molecule of benzoylacetone the enolic group is adjacent to the phenyl and the ketonic group to the methyl (compare Bülow and Grotowsky, Abstr., 1902, i, 484; Bülow and Wagner, this vol., i, 647). When resorcinol is condensed with 3 : 5-dimethoxybenzoylacetophenone by heating in presence of glacial acetic acid, the enolic group in the molecule of the latter is next to the phenyl, since the product is *7-oxy-2-phenyl-4-(3′ : 5′)-dimethoxyphenyl-1 : 4-benzopyranol.* The alternative formulation of 3 : 5-dimethoxybenzoylacetophenone, where the ketonic group is next to the phenyl, is held to be untenable, since benzoresorcinol could not be isolated from the product of the condensation. The *hydrochloride*, $C_{23}H_{18}O_4,HCl,1\frac{1}{2}H_2O$, crystallises from alcohol containing hydrogen chloride in golden leaflets. The free *base*, $O{:}C_9OH_4Ph\cdot C_6H_3(OMe)_2$, forms minute, red needles, which soften at 75° and melt at 110°. It is not dissolved in dilute sodium hydroxide solution in the cold and probably has the quinonoid structure. The *picrate* decomposes at 220° and melts completely at 240—245°. The *platinichloride* forms orange-yellow needles. *4 : 7-Anhydro-7-oxy-2-phenyl-4-(3′ : 5′)-dimethoxyphenyl-1 : 4-benzopyranol sulphate* crystallises with $1\frac{1}{2}H_2O$ and, when dehydrated, melts at 220—230°. When 7-oxy-2-phenyl-4-(3′ : 5′)-dimethoxyphenyl-1 : 4-benzopyranol hydrochloride is reduced by zinc dust, it forms *7-hydroxy-2-phenyl-4-(3′ : 5′)-dimethoxyphenyl-1 : 4-dihydropyran,*  $CHPh\Big<\begin{array}{l} O\text{——}\overset{}{C_6H_3}\cdot OH \\ CH_2\cdot \overset{|}{C}H\cdot C_6H_3(OMe)_2 \end{array}$, which softens at 65° and melts completely at 110°. Its *acetyl* derivative softens at 85° and melts at 120—125°. From the benzopyranol, an oxime was prepared which softens at 50° and melts at 60—65°. By the action of potassium hydroxide on the benzopyranol hydrochloride, acetophenone, 3 : 5-dimethoxyacetophenone, resorcinol, and 3 : 5-dimethoxybenzoic acid are formed.

When sodium hydrogen sulphite is added to an alcoholic solution of a salt of the benzopyranol, the latter is decolorised, and when dilute acid is then added, the benzopyranol is precipitated. This indicates that the benzopyranol has the quinonoid structure.

A. McK.

Spacial Retardation. ZDENKO H. SKRAUP (*Monatsh.*, 1903, **24**, 311—334).—The paper is largely theoretical and deals with the influence of spacial retardation in the different varieties of cinchonine, in the molecules of which the groups, hydroxyl and vinyl, mutually retard one another.

Whilst cinchonine and *allo*cinchonine give reactions characteristic of hydroxylic substances, α- and β-*iso*cinchonines, on the other hand, do not. Just as cinchonine can be readily transformed into the isomeric cinchonicine, the three *iso*cinchonines can also be transformed into compounds similar to cinchonicine. Cinchonicine and the transformation product of *allo*cinchonine contain the keto-grouping and react with phenylhydrazine, in contradistinction to the transformation products of α- and β-*iso*cinchonines, which do not behave like ketonic substances. Hydrogen iodide gives one and the same additive product with all four bases, but the rate of formation of this product is much more rapid with cinchonine than with the others. Cinchonine readily unites with bromine, which attaches itself to carbon; *allo*cinchonine and α- and β-*iso*cinchonines, on the other hand, form perbromides, where the bromine is attached to nitrogen. Cinchonine and *allo*cinchonine are oxidised by potassium permanganate with approximately the same ease, whilst α- and β-*iso*cinchonines are attacked with some difficulty.

Eight stereoisomerides of cinchonine are theoretically possible (compare Skraup, this vol., ii, 67). The evidence for the constitution of the *iso*bases is described.

Experiments on the acetylation of cinchonine and *allo*cinchonine showed that the bases are acetylated at approximately equal rates.

α-*iso*Cinchonine, by aid of its hydrogen sulphate, was converted into the isomeric α-*iso*-ψ-cinchonicine, the *oxalate* of which crystallises with $3\frac{1}{2}H_2O$. The free base is precipitated from its hydrochloride by the addition of ammonia as an oil, which crystallises after a long time. The β-*iso*-ψ-cinchonicine was not obtained crystalline. The hydrochloride of the α-base was dissolved in absolute ethyl alcohol and mixed with an equivalent amount of alcoholic sodium ethoxide. The solution, so prepared, had $[\alpha]_D$ $+4{\cdot}9°$, where $p = 0{\cdot}625$ and d $20°/4° = 0{\cdot}7996$, whilst a similar solution of the β-base was practically inactive.

A. McK.

Alkaloids of Dicentra Formosa. GEORG HEYL (*Arch. Pharm.*, 1903, **241**, 313—320).—The roots were digested with 80 per cent. alcohol containing some acetic acid and the extract freed from alcohol, mixed with excess of ammonia, and extracted with ether. After evaporating off the ether, protopine separated (the yield being 3 per cent.), and when purified by crystallising its hydrochloride, it melted at 201—202°. The remaining *alkaloids* were separated by fractional crystallisation of the mixed hydrobromides from dilute alcohol. Two were obtained in small quantity; that from the less soluble hydrobromide melted at 168·5—169°, the other at 142·5°; they have some resemblance to homochelidonine and chelidonine respectively, but appear to be different from these. Along with the first, a small quantity of a greenish-yellow *substance* crystallises; this softens and decomposes from 186° onwards, and gives a blue fluorescence in alcoholic solution; it is perhaps identical with the colouring matter isolated by Schlotterbeck and Watkins from *Stylophorum diphyllum* (Abstr., 1902, ii, 101; i, 231).

C. F. B.

Action of High Temperatures on Alkaloids when these are Fused with Carbamide. I. Narcotine and Hydrastine. Heinrich Beckurts and Gustav Frerichs (*Arch. Pharm.*, 1903, **241**, 259—270).—Narcotine was heated over a bare flame with 2—3 times its weight of carbamide; as much as 50 grams of the alkaloid may be taken in one operation. The temperature rose to about 220°; much ammonia was evolved, and there was a smell of organic bases. The appearance of boiling was maintained for several minutes, the liquid allowed to cool somewhat, poured into cold water, and the solution extracted with ether. The product was meconin; no cotarnine could be detected. If a decidedly shorter or longer heating is given, the product is not wholly soluble in water; the insoluble part consists largely of unchanged narcotine with gnoscopine; these were separated by means of the insolubility of the latter in alcohol.

With hydrastine, the result was similar, meconin being formed.

Other alkaloids behave differently; for instance, narceine yields narceineimide, and papaverine is unchanged. The investigation is being continued.

It is noteworthy that meconin, when examined for nitrogen by the Dumas method, yield much inflammable gas; in one experiment, 0·3 gram gave 15 c.c. Its chloro- and bromo-derivatives behave similarly. C. F. B.

Sparteine. General Characters: Action of some Reducing Agents. Charles Moureu and Amand Valeur (*Compt. rend.*, 1903, **137**, 194—196).—Sparteine, obtained from the sulphate by adding alkali and extracting with ether, is a colourless, viscid liquid which boils at 188° (corr.) under 18·5 mm. pressure, and at 325° (corr.) in a current of dry hydrogen under 754 mm. pressure. It has a sp. gr. 1·034 at 0° and 1·0196 at 20°; $[\alpha]_D = -16·42°$ in alcoholic solution; $n_D = 1·5293$ at 19°. At 22°, 100 c.c. of water dissolve 0·304 gram, and it is easily soluble in the common organic solvents. It is readily volatile with steam. Analysis and cryoscopic determinations show that it has the formula $C_{15}H_{26}N_2$.

It is a strong base and can be exactly estimated by titration with alkali; towards litmus and phenolphthalein, it behaves as a monacidic base, and towards methyl-orange as a diacidic base. Its *platinichloride* has the formula $C_{15}H_{26}N_2,H_2PtCl_6,2H_2O$; its *picrate*,

$$C_{15}H_{26}N_2,2C_6H_3O_7N_3,$$

melts at 208°. These facts indicate that the two nitrogen atoms of sparteine are basic, and consequently that it is a diamine. From the investigations of Mills and of Bamberger it is certain that at least one of the aminic functions is tertiary, and since it does not give a nitroso-derivative or a benzoyl derivative, it must be assumed to be a ditertiary diamine. On treatment with hydriodic acid, it does not give methyl iodide, and therefore contains no methyl group attached to nitrogen. When subjected to the action of reducing agents (tin and hydrochloric acid, sodium and alcohol, sodium and amyl alcohol), it does not give any reduction products. It is not affected by permanganate. The latter observations show that it does not contain a double linking, and it seems highly probable that it contains two, or even three, closed chains. J. McC.

Ammonium Compounds. XIV. Action of Alkalis on Oxydihydro-bases. HERMAN DECKER [and, in part, OSCAR ELIASBERG and WAÇLAW WISLOÇKI] (*Ber.*, 1903, 36, 2568—2572. Compare this vol., i, 516).—The volatile hydro-base obtained by the action of alkalis on methyl quinolinium salts is 1-methyltetrahydroquinoline (kairoline). It appears that of every 3 molecules of the carbinol base, two become oxidised to the alkylquinolone and one reduced to the alkyltetrahydroquinoline.

The tetrahydro-base is most readily purified by the aid of the picrate, which melts at 144·5° and not at 122—125° as stated by Ladenburg (Abstr., 1895, i, 480).

Kairoline methiodide crystallises in large plates melting and decomposing at 173°, and with picric acid yields 1 : 1-*dimethylquinolinium picrate* melting at 124°. A table is given of the solubility of quinoline, 1-methylquinolinium, kairoline, and 1 : 1-dimethylquinolinium picrates in water, alcohol, and benzene.

Quinoline ethiodide, when decomposed with alkalis, yields quinoline and ethyltetrahydroquinoline, the *picrate* of which melts at 117—118°.

J. J. S.

2 : 4-Substituted-7-hydroxyquinolines. CARL BULOW and GOTTHOLD ISSLER (*Ber.*, 1903, 36, 2447—2459).—In condensation reactions, *m*-aminophenol acts sometimes as a phenol and sometimes as an amino-compound. It is now found that *m*-aminophenol condenses with 1 : 3-diketones to form 7-hydroxyquinoline derivatives; the amino-group is accordingly in this case more reactive than the hydroxyl, since, if the reverse were the case, the condensation products would be benzopyranol derivatives.

Anilides are formed as intermediate products, for example,

$$OH{\cdot}C_6H_4{\cdot}NH_2 + O{:}CMe{\cdot}CH_2{\cdot}COPh = H_2O + OH{\cdot}C_6H_4N{:}CMe{\cdot}CH_2{\cdot}COPh;$$

the ketonic group adjacent to the methyl group reacts with the amino-group of the aminophenol. The anilides part with water to form hydroxyquinoline compounds and, in consequence, the 1 : 3-diketones behave in the keto-enolic form, benzoylacetone, for instance, acting according to the structure $OH{\cdot}CPh{:}CH{\cdot}COMe$. Further, when the phenyl group is in the para-position to the quinoline nitrogen atom, the enolic hydroxyl must be adjacent to the phenyl group.

Benzoylacetone m-*hydroxyanilide*, $OH{\cdot}C_6H_4{\cdot}N{:}CMe{\cdot}CH{:}CPh{\cdot}OH$, prepared by dissolving *m*-aminophenol in glacial acetic acid and then adding benzoylacetone, melts at 160°. When boiled with water, it is resolved into its components. Its *semicarbazone* forms colourless needles melting at 124°. When benzoylacetone *m*-hydroxyanilide is carefully added to concentrated sulphuric acid, it forms 7-*hydroxy*-4-*phenyl*-2-*methylquinoline sulphate*, from which the free *base* is isolated by the addition of sodium acetate. The base forms yellow needles melting at 262°, and, in accordance with its phenolic character, dissolves readily in dilute sodium hydroxide solution. Its *chloride* becomes brightly yellow at 120° and decomposes at 280°; the *dichromate* forms red needles which begin to decompose at 175°; the *platinichloride* melts at 218—220°, the *picrate* at 208°. The *acid oxalate* contains $1H_2O$ and decomposes at 175°. The *ethoxy*-derivative, obtained by alkylating the base with ethyl bromide, forms quadratic needles melting at 91°. The *benzoate* melts at 144°.

4-*Phenyl*-2-*methylquinoline*, a yellowish-green fluorescent oil, boiling at 200—203° under 20 mm. pressure, was prepared by heating 7-hydroxy-4-phenyl-2-methylquinoline with zinc dust; its methiodide melts at 205°. When oxidised by potassium permanganate, the hydroxy-base is converted into 4-*phenyl*-2-*methylpyridine*-5 : 6-*dicarboxylic acid.* This accords with the regularities observed by v. Miller with the oxidation of quinoline derivatives (Abstr., 1890, 1324; 1891, 1094), the methyl group remaining intact. The *copper* salt was first isolated, and the acid prepared from it begins to evolve gas at 100°, and is totally decomposed at 150°. When heated, it is converted into 4-*phenyl*-2-*methylpyridine*, a colourless oil which boils at 280°. The *picrate* melts at 203°. A. McK.

Nitroquinolones and Nitrocarbostyrils. HERMAN DECKER and A. STAVROLOPOULOS (*J. pr. Chem.*, 1903, [ii], **68**, 100—103. Compare Abstr., 1901, i, 654; 1902, i, 494).—8-Nitro-1-methyl-2-quinolone, formed by oxidation of 8-nitroquinoline methiodide (Abstr., 1903, i, 278) with potassium ferricyanide, melts at 133—134°, and not at 124—125° as formerly stated (Abstr., 1901, i, 654).

2-*Chloro*-8-*nitroquinoline*, obtained by the action of phosphorus pentachloride on nitromethylquinolone, forms clusters of sickle-shaped crystals, melts at 152°, and is easily soluble in benzene or chloroform. When boiled with hydrochloric acid, it yields the hydrochloride of 8-nitrocarbostyril.

8-Nitro-1-ethyl-2-quinolone, obtained by the action of ethyl iodide on the sodium derivative of nitrocarbostyril formed from chloronitroquinoline, melts at 87° (m. p. 92°, Abstr., 1901, i, 654).

The action of phosphorus bromide on 8-nitromethylquinolone leads to the formation of a 2 : 8-*tribromoquinoline*, which crystallises in large plates and melts at 165°. When boiled with hydrochloric acid, it yields 8-*dibromocarbostyril*, which crystallises in needles and melts at 188°.

8-*Dinitro*-1-*methyl*-2-*quinolone*, formed from 8-nitro-1-methyl-2-quinolone, separates from alcohol in small, yellow crystals and melts at 208°. Further nitration leads to the formation of 8:6-trinitro-1-methyl-2-quinolone, which is identical with the trinitro-compound obtained by nitration of 6-nitro-1-methyl-2-quinolone. G. Y.

Thioacridone and Selenoacridone. ALBERT EDINGER and J. C. RITSEMA (*J. pr. Chem.*, 1903, [ii], **68**, 72—99. Compare Abstr., 1901, i, 753; 1902, i, 181).—5-*Ethylthiolacridol*, $C_{13}H_8N{\cdot}SEt$, prepared by treating thiolacridol and ethyl iodide with sodium ethoxide in alcoholic solution or by heating thioacridol with ethyl bromide at 90—100°, crystallises in yellow needles and melts at 65°; the *picrate* forms yellow needles and melts at 182—183°; the *platinichloride* forms brown needles.

5-o-*Nitrobenzylthiolacridol*, $C_{13}H_8N\cdot S\cdot C_7H_6\cdot NO_2$, prepared by the action of sodium ethoxide and *o*-nitrobenzyl chloride on thiolacridol in alcoholic solution, crystallises in light yellow leaflets and melts at 129—130°; the *picrate* forms yellow pyramids and melts at 190—191°; the *platinichloride* crystallises in small, yellow needles.

5-p-*Nitrobenzylthiolacridol* forms short, yellow crystals and melts at 152°; the *picrate* is a yellow, crystalline substance and melts at 204°; the *platinichloride* is a brown powder.

5-*Picrylthiolacridol*, $C_{13}H_8N\cdot S\cdot C_6H_2(NO_2)_3$, crystallises in long, red needles and melts at 233°.

5-o-p-*Dinitrobenzylthiolacridol*, $C_{13}H_8N\cdot S\cdot C_7H_5(NO_2)_2$, prepared by the action of sodium hydroxide on thiolacridol and *o-p*-dinitrobenzyl chloride in alcoholic solution, crystallises in whitish-yellow needles, melts at 290°, and is decomposed by warming with concentrated acids with formation of dinitrophenylmercaptan; the *picrate* forms yellow needles and melts and decomposes at 226°; the *platinichloride* is a yellow powder.

Acridyl sulphide (*acridylthiolacridol*), $C_{13}H_8N\cdot S\cdot C_{13}H_8N$, prepared by the action of 5-chloroacridine on thiolacridol in alcoholic solution or along with chloroacridine by the action of limited amounts of phosphorus pentachloride on thiolacridol, crystallises in long, yellow needles, melts at 267°, is soluble in chloroform, benzene, or xylene, but not in alcohol, ether, or acetone, is soluble in acids and reprecipitated on addition of alkalis, forms a *picrate* and a *platinichloride*, and is hydrolysed by alcoholic hydrochloric acid to acridone and thiolacridol.

Selenoacridone, prepared by the action of sodium hydrogen selenide or sodium selenide on 5-chloro- or bromo-acridine, crystallises in blackish-brown needles, melts at 238°, dissolves in alcohol or acetone to a reddish-violet, in alcoholic sodium hydroxide to a red solution, is soluble in chloroform or benzene, less so in light petroleum, and is insoluble in dilute acids. When boiled with alcohol, acetone, or alkalis, it is decomposed with formation of selenium and acridone.

5-*Benzylselenolacridol*, prepared by the action of sodium ethoxide and benzyl chloride on selenolacridol in alcoholic solution, crystallises in yellowish-white needles, melts at 110°, is soluble in the ordinary organic solvents, and is hydrolysed by boiling concentrated alcoholic hydrochloric acid with formation of acridone and benzyldiselenide. The *picrate*, $C_{20}H_{15}N\cdot Se\cdot C_6H_2(NO_2)_3\cdot OH$, crystallises in yellow needles and melts at 179°; the *platinichloride* forms a brown precipitate.

5-*Methylselenolacridol*, prepared by the action of methyl iodide and sodium ethoxide on selenolacridol in alcoholic solution or by heating methyl iodide with selenolacridol under pressure, crystallises in whitish-yellow needles, melts at 108°, is soluble in organic solvents, and is decomposed by acids with formation of acridone. The *picrate* crystallises in yellow needles and melts at 176°; the *platinichloride* forms a red precipitate.

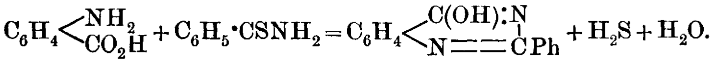
5-*Picrylselenolacridol*, prepared by the action of sodium hydroxide and picryl chloride on selenolacridol in alcoholic solution, crystallises in red needles, decomposes at 198°, is soluble in xylene, benzene, chloroform, or glacial acetic acid, but almost insoluble in acetone, alcohol, ether, or light petroleum, and is decomposed by acids. The *picrate* crystallises in yellow octahedra and melts at 166°; a platinichloride is not formed. 5-o-p-*Dinitrobenzylselenolacridol* crystallises in yellow prisms, melts at 273°, and is decomposed by concentrated acids. The *picrate* crystallises in yellow needles and melts at 218°; the *platinichloride* forms a brown powder. G. Y.

Some Reactions of the Di- and Tri-phenylmethane Groups. Eduard Vongerichten and Carl Bock (*Zeit. Farb. Text. Chem.*, 1903, **2**, 249—250).—The rosanilines, prepared from *o*-toluidine and diaminodiphenylmethane on the one hand, and aniline and diaminophenyltolylmethane on the other, are not identical. The authors find that diaminodiphenylmethane, when heated with excess of *o*-toluidine and *o*-toluidine hydrochloride, yields diaminophenyltolylmethane, but the phenyl group could not further be replaced by the tolyl to form diaminoditolylmethane. With triphenylmethane derivatives, however, complete interchange of phenyl and tolyl groups could be effected, triaminotritolylmethane giving, with a mixture of aniline and aniline hydrochloride, triaminotriphenylmethane, from which triaminotritolylmethane could be regenerated by the action of *o*-toluidine and its hydrochloride.

Diaminodiphenylmethane and diaminoditolylmethane, can, by oxidation of their acetyl derivatives, be converted into the corresponding ketones, which give diaminobenzohydrols on reduction with sodium amalgam (Wichelhaus, Abstr., 1889, 781). Those diaminobenzohydrols like tetramethyldiaminodiphenylcarbinol, when dissolved in acetic acid and then heated, become intensely coloured. When diaminodiphenylcarbinol is heated with an aqueous solution of aniline hydrochloride, the change represented by the equation $(C_6H_4NH_2)_2CHOH + PhNH_2 = (NH_2C_6H_4)_3CH + H_2O$ takes place. In a similar manner, triaminotritolylmethane is formed from diaminoditolylcarbinol and *o*-toluidine hydrochloride. There is no change when diaminodiphenylmethane is heated with a mixture of *m*-toluidine and *m*-toluidine hydrochloride. A. McK.

Formation of Heterocyclic Compounds from Hydrazine Derivatives. Robert Stollé (*J. pr. Chem.*, 1903, [ii], **68**, 130—147).—A review of the reactions by which heterocyclic compounds have been obtained from the acylhydrazides and their derivatives. G. Y.

Synthesis of 4-Hydroxy-2-phenylquinazoline. Bronislas Pawlewski (*Ber.*, 1903, **36**, 2384—2385).—Pheno-β-phenylhydroxymetadiazine [4-hydroxy-2-phenylquinazoline] (compare Bischler and Lang, Abstr., 1895, i, 250) may be directly synthesised by heating thiobenzamide with anthranilic acid at 160—162°:



$$C_6H_4<\begin{matrix}NH_2\\CO_2H\end{matrix} + C_6H_5{\cdot}CSNH_2 = C_6H_4<\begin{matrix}C(OH){:}N\\N{=\!=\!=}CPh\end{matrix} + H_2S + H_2O.$$

The properties of the product are identical with those of Bischler and Lang's compound. C. H. D.

Pyridazine Derivatives. III. Ethyl Dimethylpyridazinecarboxylate. CARL PAAL and CARL KOCH (*Ber.*, 1903, **36**, 2538—2539).—*Ethyl dimethylpyridazinecarboxylate*, $C_{12}H_{16}O_4N_2$, prepared by oxidising the dihydro-compound with nitrous acid, crystallises from light petroleum in long, white, feathery needles, melts at 22°, boils with slight decomposition at 200° under 22 mm. pressure, and under atmospheric pressure with considerable decomposition at 275°; it was previously prepared in an impure state by oxidation with nitric acid (Paal and Ubber, this vol., i, 290). T. M. L.

Products from the Hydrolysis of Diazo-ethers. HANS EULER (*Ber.*, 1903, **36**, 2503—2508).—Diazo-ethers are considered by Bamberger (Abstr., 1895, i, 215) to be "normal" ethers on account of the rapidity with which they couple up and on account of their hydrolysis to normal diazoxides. Hantzsch, on the other hand (this vol., i, 210), considers them to be *anti*diazo-compounds, since he finds that diazo-ethers are hydrolysed to *anti*- and not to *syn*-diazoxides. The author has studied the behaviour of the products from the hydrolysis of diazo-ethers towards α- and β-naphthols, and his results are in accordance with Bamberger's contention.

From comparative experiments as to the ease with which α- and β-naphthols respectively couple with potassium *p*-bromobenzene*iso*diazoxide, it is concluded that α-naphthol is as suitable as β-naphthol for the characterisation of normal and *iso*diazoxides, although the view has been advanced that α-naphthol could not be used to distinguish between the *syn*- and the *anti*-isomerides. Whilst potassium benzene*iso*diazoxide, in the presence of hydrolytic agents and α- or β-naphthol, shows, after several hours, no trace of coloration or precipitation, the products of hydrolysis of diazobenzenemethyl ether couple up very quickly with α- or β-naphthol. When 0·2 or 1·2*N* sodium hydroxide solution is used, the action is practically instantaneous, whilst with 30 per cent. alkali, the action takes place after about two minutes. Hence the products of hydrolysis undoubtedly behave like *syn*-(normal)-diazo-compounds. When *p*-bromodiazobenzenemethyl ether is employed, the products of hydrolysis again behave towards α- and β-naphthols like normal diazoxides. A. McK.

Formazyl Dyes. FRIEDRICH FICHTER and J. FRÖHLICH (*Zeit. Farb. Text. Chem.*, 1903, **2**, 251—253).—The formation of dyes from formazyl derivatives has been proved by Wislicenus (Abstr., 1893, i, 156) and by Fichter and Schiess (Abstr., 1900, i, 366), who prepared the three isomeric formazylbenzenesulphonic acids.

By the action of diazobenzene on a mixture of α-naphthol and benzylidinephenylhydrazone in alkaline solution, a mixture of formazylbenzene and benzeneazo-α-naphthol is formed with the former in excess. No formazyl formation was noted when β-naphthol was used.

By the action of diazobenzene on salicylaldehydephenylhydrazone, no azo-compound was formed; the *o-hydroxyformazylbenzene*,

$$OH\cdot C_6H_4\cdot C(N:NPh):N\cdot NHPh,$$

formed instead, separates from alcohol as a black, crystalline powder melting at 164—165° and dissolving in alkalis to a brown solution. It was further identified by its giving, when heated with glacial acetic acid and concentrated sulphuric acid, o-*hydroxyphenyl-a-benzotriazine*, which crystallises from alcohol in yellow needles melting at 167°.

Salicylaldehydephenylhydrazone combines with diazobenzene-*p*-sulphonic acid in alkaline solution to form *potassium* o-*hydroxyformazylbenzene*-p-*sulphonate*, $OH\cdot C_6H_4\cdot C(N{:}N\cdot C_6H_4\cdot SO_3K){:}N\cdot NHPh$, which crystallises from a mixture of alcohol and chloroform in dark, glistening needles and dissolves in alkali to a yellow solution, which turns red on the addition of acid.

Piperonalphenylhydrazone in alkaline solution combines with diazobenzene to form *methylene*-3 : 4-*dioxyformazylbenzene*,

$$CH_2O_2{:}C_6H_3\cdot C(N{:}NPh){:}N\cdot NHPh,$$

which crystallises from alcohol in dark red needles melting at 156°. Like *o*-hydroxyformazylbenzene, it suffers the triazine decomposition, giving *methylene*-3 : 4-*dioxyphenyl-a-benzotriazine*, which crystallises from alcohol in yellow needles melting at 154°. Piperonalphenylhydrazone combines, in alkaline solution, with diazobenzene-*p*-sulphonic acid to give *potassium methylene*-3 : 4-*dioxyformazylbenzene*-p-*sulphonate*, which crystallises from aqueous alcohol in dark red leaflets and forms a red solution with water.

By the action of nitroformaldehydehydrazone on potassium diazobenzene-*p*-sulphonate, *potassium nitroformazyl*-p-*sulphonate* was obtained; this crystallises from alcohol in red leaflets melting and decomposing at 213°. Its aqueous solution is reddish-yellow. Sodium *phenyl a-naphthylformazylbenzene*-p-*sulphonate* separates from alcohol as a dark powder.

Phenyl-β-naphthylformazylbenzene crystallises from benzene in dark green needles melting at 172°.

β-Naphthylphenylformazylbenzene separates from alcohol in dark red crystals melting at 150°.

p-Chlorobenzylidenephenylhydrazone and diazobenzene gave *chloroformazylbenzene*, $C_6H_4Cl\cdot C(N{:}NPh){:}N\cdot NHPh$, which crystallises from alcohol in red needles melting at 190°.

Potassium p-*chloroformazylbenzene*-p-*sulphonate* forms red needles. *Potassium phenyl-a-naphthyl*-p-*chloroformazylbenzene*-p-*sulphonate*,

$$C_6H_4Cl\cdot C(N{:}N\cdot C_{10}H_6\cdot SO_3K){:}N\cdot NHPh,$$

dissolves in alcohol to form a violet solution, from which dark red leaflets separate.

A. McK.

Preparation of Carbamide by the Oxidation of Albumin with Permanganate. Adolf Jolles (*Zeit. physiol. Chem.*, 1903, **38**, 396—398. Compare Abstr., 1901, i, 583).—The author refers Abderhalden (this vol., i, 588) to Lanzer's results (this vol., ii, 584), which confirm his own earlier work.

J. J. S.

Tryptic Fermentation of Gelatin. Th. Richard Krüger (*Zeit. physiol. Chem.*, 1903, **38**, 320—322).—Trypsin-glutinpeptone-*β*, obtained by Siegfried's method, has the composition $C_{19}H_{30}O_9N_6$. Molecular weight determinations point to the doubled formula, and the compound would then be a dibasic acid. It has $[\alpha]_D - 100{\cdot}8°$ at 20°, and it usually contains minute traces of sulphur. Other peptones are formed at the same time by the action of trypsin on gelatin. J. J. S.

Sodium Phenyl. Action of Sodium on Ketones.

Salomon Farby Acree (*Amer. Chem. J.*, 1903, 29, 588—609).—From his experiments with sodium phenylacetylene, Nef (Abstr., 1900, i, 20) had assumed that sodium phenyl is formed as an intermediate product by the action of sodium on bromobenzene.

Sodium phenyl, PhNa, formed when mercury diphenyl is dissolved in dry benzene or light petroleum and then acted on with sodium wire, is a light brown powder, very readily decomposable by moisture, and catches fire when exposed to the air. When ethyl bromide is gradually added to it in presence of light petroleum and the resulting product fractionated, ethylbenzene is formed as the main fraction, small amounts of benzene and ethylene being also present. Ethyl iodide behaves in an analogous manner. According to Nef's conceptions, the primary action in the latter case, for example, is the dissociation of the ethyl iodide into hydrogen iodide and alkylidene; the latter then acts on sodium phenyl to form the compound CHMePhNa, from which ethylbenzene results by the action of hydrogen iodide.

By the action of *iso*amyl iodide on sodium phenyl, benzene, *iso*amylene, and *iso*amylbenzene are formed. Benzyl chloride and sodium phenyl give diphenylmethane and stilbene. The action of sodium phenyl on bromobenzene is very vigorous, diphenyl being the main product.

Triphenylcarbinol in nearly quantitative yield is formed by the action of sodium phenyl on benzophenone. When benzoyl chloride is used, triphenylcarbinol is also produced, benzophenone being first formed and then acted on by the excess of sodium phenyl present. Sodium phenyl and benzil give a mixture of phenylbenzoin and triphenylcarbinol, which are also formed by the action of bromobenzene and sodium on benzil. Phenylbenzoin crystallises from light petroleum in radiating needles which melt at 87°. Dry carbon dioxide acts vigorously on sodium phenyl to form sodium benzoate. Sodium phenyl and ethyl chlorocarbonate give very little ethyl benzoate, since the latter acts on the excess of sodium phenyl present to form benzophenone, which then forms triphenylcarbinol.

Diphenyl-α-naphthylcarbinol is formed by interaction of benzophenone, α-bromonaphthalene, and sodium; when crystallised from ether, it melts at 135°. Diphenyl-*p*-tolylmethane, formed from benzophenone, *p*-bromotoluene, and sodium, melts at 74°.

By the action of sodium on benzophenone, a mixture of benzopinacone (m. p. 185—186°) and benzohydrol results, the latter being produced either by the action of water on the disodium compound of benzophenone or by the reduction of the benzophenone by nascent hydrogen. Benzilic acid is formed by the action of sodium and carbon dioxide on benzophenone. A. McK.