

## Organic Chemistry.

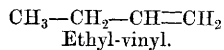
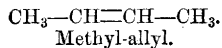
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**Preparation of Methyl-Allyl.** By H. GROSHEINTZ (*Bull. Soc. Chim.* [2], xxxix, 201—203).—By the action of zinc-methyl on allyl iodide, Wurtz (*ibid.*, 1867, viii, 265) obtained a butylene, which he called methyl-allyl. On repeating these experiments, however, the author has obtained a mixture of three isomeric butylenes, the bromides of which boil at 158°, 148°, and 168° respectively. The hydrocarbon whose bromide boils at 158° is formed in the largest quantity, whilst methyl-allyl, which ought to be identical with Wurtz's ethyl-vinyl, and whose bromide boils at 168°, is formed only in small quantities.\* The bromide boiling at 148° is isobutylene bromide. In this reaction a molecular change takes place, by which methyl-allyl is converted into an isomeric butylene. The author has also observed a fourth bromide, which is very stable, and distils at 175—195°; it appears to be allyl tribromide, but is obtained in such small quantities that it has not been completely investigated. L. T. O'S.

**Oxidation of the Valerylene**  $(\text{CH}_3)_2\text{CH.C}\equiv\text{CH}$ . By FLAVITZKY and KRILOFF (*Bull. Soc. Chim.* [2], xxxix, 214).—By the oxidation of this valerylene, acetone, acetic acid and isolactic acid have been obtained, the hydrocarbon being split up at the triple linking. By the action of sulphuric acid, sp. gr. 1.65, the same valerylene yielded, amongst other products not yet studied, a ketone having the constitution,  $(\text{CH}_3)_2\text{CH.CO.CH}_3$ . L. T. O'S.

**Tetramethylethene.** By A. PAWLOW (*Deut. Chem. Ges. Ber.*, xi, 513).—Tetramethylethene (b. p. 73°) obtained by the action of

\* Methyl-allyl and ethyl-vinyl are not identical, inasmuch as the boiling-points of their dibromides differ, according to Wurtz (*Bull. Soc. Chim.* [2], viii, 265), by about 10 degrees. Methyl-allyl, obtained by the action of zinc-methyl on allyl iodide, forms a dibromide boiling at 156—159°; ethyl-vinyl, obtained by the action of zinc-ethyl on vinyl bromide, boils at 165—166°. The two hydrocarbons are represented by the following constitutional formula:—



H. W.

alcoholic potash on dimethylisopropylcarbinyl iodide, unites directly with bromine, forming a solid compound,  $C_6H_{12}Br_2$ , which is soluble in ether, alcohol, and benzene. The ethereal solution deposits long, needle-shaped crystals, which melt with partial decomposition at  $140^\circ$ .  $C_6H_{12}.HI$  boils at  $140^\circ$ , and solidifies at  $-22^\circ$ .  $C_6H_{12}.HCl$  boils at  $112^\circ$ , and solidifies at  $-14^\circ$ . Tetramethylethene is completely oxidised to acetone by a 10 per cent. chromic acid solution; it is converted into dihexylene by the action of sulphuric acid at  $60^\circ$ .

The author considers it probable that pinacone is tetramethylethene glycol, since pinacone hydrate is formed by the action of baryta on the ether obtained by treating tetramethylethene bromide with silver nitrate.

W. C. W.

**The Order in which the Separation of the Elements of the Hydracids takes place in the Haloid Derivatives of the Olefines.** By H. ELTEKOFF (*Bull. Soc. Chim.* [2], xxxix, 210—212).—Markownikoff first enunciated the hypothesis that in the separation of hydracids, the hydrogen necessary for their formation is derived from the carbon-group adjoining that which is combined with the halogen, and this has since been shown to be the case by Butlerow, in his researches on isopropylic ether, and by the author, in the formation of ethyl valerate, whilst Saytzeff has since proved that when the carbon-atoms are in different states of hydrogenation, the hydrogen, as a rule, is separated from that carbon-atom which is least hydrogenated.

Reboul has proved that in the case of propylene bromide the elements of the hydracids separate themselves from the carbon-atoms directly linked to the halogens, which the author confirms in the case of isopropylethene bromide. The bromamylenes thus obtained consists of a mixture of two isomerides,  $(CH_3)_2.CH.CH=CHBr$  and  $(CH_3)_2.CH.CBr=CH_2$ , which lose another molecule of hydrobromic acid, and yield the same hydrocarbon isopropyl acetylene,

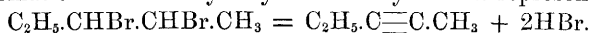


Similarly the two isomeric bromopropylenes yield the same allylenes. The author has also arrived at the conclusion that in those hydrocarbons derived from acetylene by the replacement of one atom of hydrogen by an alcohol-radicle, the latter remains intact in the hydrocarbon generated. Hydrocarbons derived from ethylene by the displacement of the alcohol-radicles by two hydrogen-atoms combined with the same carbon-atom, can lose only one molecule of an hydracid, whilst those of the formula  $R.CH=CH.R$  readily form hydrocarbons of the acetylene group. In order to confirm these hypotheses, the author has studied the chemical properties of the valerylene boiling at  $51^\circ$ , to which he assigns the constitution methylethyl-acetylene,



On oxidation with chromic mixture it yields propionic and acetic acids.

Its formation from methylethylethene may be thus represented—



L. T. O'S.  
2 r 2

**Action of the Halogens on Guanidine Salts.** By J. KAMENSKI (*Deut. Chem. Ges. Ber.*, xi, 619—620).—By the action of a solution of iodine in hydriodic acid on guanidine carbonate, the compound,



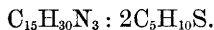
is obtained, crystallising in prisms of the colour of iodine. The corresponding bromine compound,  $\text{CN}_3\text{H}_5.\text{HBr}.\text{Br}_2$ , appears to be produced by the action of bromine (3 mols.) upon guanidine carbonate (1 mol.). It forms large red prisms, which readily lose bromine. If bromine be allowed to react on dry guanidine carbonate in the proportion of equal numbers of molecules, and the product be subsequently decomposed with water, the compound  $\text{CN}_3\text{H}_4\text{Br}$ , a monobromoguanidine, is obtained in small yellow needles, which are very difficultly soluble in cold water or in ether, but easily in alcohol. The corresponding chlorine compound,  $\text{CN}_3\text{H}_4\text{Cl}$ , has also been obtained.

C. F. C.

**Amylidenamine Silver Nitrate.** By W. G. MIXTER (*Am. J. Sci.* [3], xv, 205—207).—When a solution of silver nitrate in strong ammonia is mixed with an alcoholic solution of valeral-ammonia, and the mixture is allowed to evaporate spontaneously, crystals are deposited, having the composition  $\text{C}_{15}\text{H}_{33}\text{N}_4\text{O}_3\text{Ag}$ . The reactions of this body point to the structural formula,



The new substance is insoluble in water, ammonia, alcohol, and ether, but is readily dissolved by ammoniacal alcohol, from which it may be crystallised. By suspending it in ether, decomposing with sulphuretted hydrogen, filtering, and evaporating, a thick yellowish oil was obtained, having the odour of thiovaleral, and giving numbers, on analysis, pointing to a mixture in the proportion,



M. M. P. M.

**Oxidation of the Amyl Glycol**  $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$ . By FLAVITZKY (*Bull. Soc. Chim.* [2], xxix, 214—215).—The oxidation of this amyl glycol takes place at the carbon atoms united with the hydroxyl radicles, with formation of acetone and acetic acid. By the dehydration of the glycol  $(\text{CH}_3)_2\text{CH}.\text{CH}(\text{OH}).\text{CH}_2(\text{OH})$  there is formed, besides valeral, a ketone having the constitution—



Thus it may be inferred that primary secondary glycols yield by dehydration a mixture of aldehydes and ketones.

The amyl glycol  $(\text{CH}_3)_2\text{COH}.\text{CH}(\text{OH}).\text{CH}_3$  gives rise, by dehydration, to a compound,  $(\text{CH}_3)_2\text{CH}.\text{CO}.\text{CH}_3$ .

L. T. O'S.

**Reaction of some Polyatomic Alcohols.** By D. KLEIN (*Bull. Soc. Chim.* [2], xxxix, 195—197).—By mixing solutions of mannite and borax of known strength, in different proportions, liquids of different rotatory powers have been obtained, for which the author has constructed two curves: (1) in the case when to a constant volume of a solution of mannite increasing quantities of borax solutions are added, the total volume of the liquid varying in each case; and (2) when

increasing quantities of borax solution are added to a constant volume of mannite solution, the total volume being made up in each case to 50 c.c.

In these experiments the author observed that if less than  $\frac{1}{2}$  equivalent of borax is added to 1 equivalent of mannite, the solution is acid, but if  $\frac{1}{2}$  equivalent of borax is added to 1 equivalent of mannite, the solution remained neutral. At this point, there is an inflection in the curve representing the rotatory power. If alcohol is added to this solution, it yields a compound identical with that formed when equal equivalents of mannite and borax are mixed in solution. If more than  $\frac{1}{2}$  equivalent of borax be added for each equivalent of mannite, the solution becomes alkaline.

Similar reactions have been observed when aqueous solutions of borax are added to other polyatomic alcohols, such as glycerin, erythrite, levulose, dextrose,  $\alpha$ - and  $\beta$ -galactose, &c. L. T. O'S.

**Hydrate of Ether.** By C. TANRET (*Compt. rend.*, lxxvi, 765—767).—By allowing ether to evaporate from a surface of bibulous paper, the author obtains the hydrate,  $C_4H_{10}O \cdot 2H_2O$ , which appears to be of the nature of a cryohydrate, the solid having the temperature  $-3.5^\circ$ , which is the constant minimum obtained by mixing ether and ice. C. F. C.

**Formation of Dichloroacetic Ether from Chloral.** By A. CLAUS (*Deut. Chem. Ges. Ber.*, xi, 498—500).—Wallach has recently (*Ber.*, x, 2120) explained the action of potassium cyanide on chloral, by assuming that hydrocyanic acid in presence of chloral decomposes water, the free hydrogen of which replaces one atom of chlorine in the chloral, while the oxygen converts the aldehyde into acid.

The action of the potassium cyanide is supposed to be due to its being a cyanide, and not in virtue of its alkaline properties. The author differs from Wallach, as he considers that the potassium in the potassium cyanide plays an important part in the reaction, for potassium in potassium cyanide has generally a tendency to exchange cyanogen with the halogen, in an organic chloride, bromide, or iodide.

In the reaction with chloral, the easily oxidisable molecule, in presence of water or alcohol, furnishes disposable hydrogen, which on the one hand displaces the chlorine, and on the other by attraction for the cyanogen of the potassium cyanide, leaves the metal free to combine with the chlorine. W. C. W.

**Action of Potassium Cyanide on Dichloroacetic Ether.** By A. CLAUS and R. WEISS (*Deut. Chem. Ges. Ber.*, xi, 496—498).—When pure potassium cyanide acts on pure dichloroacetic ether, hydrocyanic acid is evolved, and the ether is saponified. On long-continued boiling, a complicated decomposition takes place, the mixture blackens, and ammonium carbonate, oxalic and acetic acids are formed.

The dicyanacetic acid described by Amato (*Annalen*, clxii, 389) is not formed in this reaction, and the authors consider that Amato must have used impure materials. W. C. W.

**Action of Sulphuryl Chloride on Acetoacetic Ether.** By F. ALLIHN (*Deut. Chem. Ges. Ber.*, xi, 567—570).—Ethylic *acetodichloracetate*,  $C_6H_5Cl_2O_3$ , described by Conrad (*Annalen*, clxxvi, 161), is obtained by the action of two molecules of sulphuryl chloride on one of acetoacetic ether, hydrochloric acid and sulphurous anhydride being evolved; but if equal molecules of sulphuryl chloride and of acetoacetic ether are taken, then *ethylic acetomonochloracetate*,  $C_6H_5ClO_3$ , or  $CH_3.CO.CHCl.COOC_2H_5$ , is formed. This latter substance is a colourless liquid, which boils at  $193-195^\circ$ , and has a sp. gr. of 1.19 at  $14^\circ$ . Ethylic acetomonochloracetate yields potassium monochloracetate on treatment with alcoholic potash-solution.

W. C. W.

**Potassium Cyanide and Ethyldibromosuccinate.** By A. CLAUS and F. CALLIESS (*Deut. Chem. Ges. Ber.*, xi, 496).—Succinic acid is formed by the action of potassium cyanide on ethyldibromosuccinate. The intermediate products of the reaction, viz., dicyano-succinic acid, and a tetrabasic acid derived from it, could not be isolated.

W. C. W.

**On Isomeric Caproic Acids.** By A. SAYTZEFF (*Deut. Chem. Ges. Ber.*, xi, 511—513).—*Diethylacetic acid* obtained from the product of the action of potassium cyanide on the iodide of di-ethyl carbinol, is a colourless liquid boiling at  $190^\circ$ . It has a pleasant odour, and is only slightly soluble in water. Its sp. gr. at  $18^\circ$  is 0.9196.

*Methylpropylacetic acid*, derived from the product of the action of potassium cyanide on amylene hydriodide, closely resembles the preceding acid. It boils at  $193^\circ$ , and its sp. gr. at  $18^\circ$  is 0.9279.

The sp. gr. of *ethylic di-ethylacetate* (b. p.  $151^\circ$ ) is 0.8686 at  $18^\circ$ , and that of *ethylic methylpropylacetate* (b. p.  $153^\circ$ ) is 0.867 at the same temperature.

The silver salts of these acids are deposited from hot saturated solution, on cooling, as needle-shaped crystals. *Silver di-ethylacetate* is less soluble in cold, but more soluble in hot water than its isomeride.

The barium salts are easily soluble in water and in alcohol. *Barium di-ethylacetate* is crystalline, but *barium methylpropylacetate* forms a thick syrup which dries to a gum-like mass. The solubility of *calcium di-ethylacetate* in water increases with the temperature. *Calcium methylpropylacetate* is less soluble in hot than in cold water. The lead salts are very soft and easily fusible.

The zinc salts dissolve in alcohol; they are more soluble in cold than in hot water. Ferric chloride forms a yellow precipitate with ammonium di-ethylacetate, insoluble in excess, whilst with the methylpropylacetate it produces a flesh-coloured precipitate soluble in excess of the reagent.

W. C. W.

**Lactic Fermentation.** By L. BOUTROUX (*Compt. rend.*, lxxxvi, 605—607).—The present communication is a continuation of a research published by Pasteur in 1867 (*Ann. Chim. Phys.* [3], lii, 404), and has been carried out under his direction.

A detailed description of the microscopical appearance of the lactic ferment is given. The cells are oval, having a breadth of .001 to .003 mm.; the length is about double this. These organisms develop

rapidly when placed in mixtures containing sugar and some nitrogenous matter, such as whey, yeast-water, infusion of malt, or infusion of hay. Inverted sugar or glucose answers best for their growth. A certain amount of acid does not prevent the development of the ferment, although it slightly retards it. The liquor can attain an acidity of 1.5 grams of lactic acid per 100 c.c. If chalk be added in such quantity that the acid becomes neutralised as it is formed, a much larger yield of lactic acid is obtained. If a vessel containing the sugar mixture is sown with the ferment, and the air is then exhausted or displaced by a current of carbonic anhydride free from dust, no fermentation takes place. The ferment is not killed, however, for on re-admitting the air, it again becomes active, and after two or three days forms a film on the surface. When a vessel containing a certain amount of air is sealed up, the growth takes place, but is soon stopped. In a closed flask with pure oxygen, it was found that this gas was entirely absorbed and replaced by carbonic anhydride, which occupied less than one-quarter the volume of the oxygen.

The ferment produces only lactic acid; no alcohol or volatile acid is formed. When the action is completed, the film of the lactic ferment sinks to the bottom of the vessel, but retains its vitality for many months. The formation of spores has not been proved; the cells are preserved without transformation. Besides solutions of sugar, the ferment flourishes in a mixture of yeast-water and alcohol, with or without the addition of acetic acid, or in a mixture of yeast-water and glycol; but then special acids are produced.

The author considers that the lactic ferment and *mycoderma aceti* are identical, but that their functions vary according to the composition of the mixture in which they grow.

R. C. W.

**Lactic Fermentation of Milk-sugar.** By C. RICHET (*Compt. rend.*, lxxxvi, 550—552).—Milk which has been kept at a temperature of 40° becomes acid, coagulates, and finally attains an acidity equal to 1.6 grams of lactic acid per 100 of milk, which amount it never exceeds. Moreover, hydrochloric and sulphuric acids, when added in such quantity as to give the milk an acidity equivalent to 1 gram of lactic acid per cent., prevent fermentation. But if instead of a mineral acid, gastric juice is added, the casein is coagulated and finally dissolved, and in less than twenty-four hours the milk contains a larger quantity of acid than it would otherwise have produced in a week. After four or five days an amount of acid corresponding to 4 grams of lactic acid per cent. was found in the liquid. This large increase is probably due to the dissolved casein increasing the fermentation.

When milk is coagulated with rennet and filtered, the whey never gives more than 1.6 grams of lactic acid, even after keeping for six months. The casein, free from lactose, ferments and produces lactic and butyric acids, besides other products of decomposition. If the albuminous substances in milk are coagulated, and it is then evaporated to dryness, and water added in such quantity as to make it up to the original volume, it will not undergo fermentation, even after the addition of pepsin. Whey ferments, although free from casein, because it contains nitrogenous substances in solution, lactoprotein, &c.

A solution of pure lactose will not ferment, nor will a solution of casein in gastric juice; but if these two liquids are mixed, fermentation takes place. A current of oxygen passed through the mixture greatly assists this fermentation.

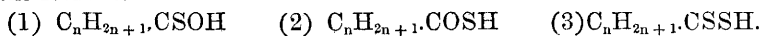
Phenol added in excess entirely stops fermentation, but if it be added in insufficient quantity, lactic fermentation is only retarded, whereas butyric fermentation is quite checked; a circumstance which may perhaps lead to the separation of these two ferments.

The gastric juice of fish has a similar action to that of mammals, but it requires a temperature of  $35^{\circ}$  to coagulate the casein.

There is no doubt that, in newly born animals, the rapid acidification of the milk plays a very important part in saving the necessity for a secretion of a large quantity of acid, and that the oxygen contained in the blood greatly assists this rapid fermentation. R. C. W.

**Conversion of Acetyl Cyanide into the corresponding Ketone-acid.** By J. CLAISEN and J. SHADWELL (*Deut. Chem. Ges. Ber.*, xi, 620—621).—By the addition of concentrated hydrochloric acid (2 mol.) to well cooled acetyl cyanide (1 mol.), the compound  $C_3H_5O_2N$  is obtained: isomeric, therefore, and probably identical with the amide of pyrroacemic acid. Heated with dilute hydrochloric acid, it is rapidly converted into acetylformic acid,  $CH_3.CO.COOH$ . This ketone-acid is a liquid boiling at  $155$ — $165^{\circ}$ , of sp. gr.  $1.2415$ , and yielding a well crystallised silver salt  $C_3H_3O_3.Ag$ : from the barium salt, by Finckh's method, uvitic acid is easily prepared; thus rendering it probable that the original acid is identical with pyrroacemic acid. C. F. C.

**Substitution of Oxygen for Sulphur in the Fatty Acids.** By A. DUPRÉ (*Compt. rend.*, lxxxvi, 665—668).—If one or two atoms of oxygen in the fatty acids be displaced by sulphur, three series of acids may be obtained: thus  $C_nH_{2n+1}.COOH$  being the general formula for the fatty acids, the substituted acids are represented by the formulæ—



Those of the first series the author calls *sulpho-acids*; their isomerides, the acids of the second series, which have been studied by Kekulé, Ulrich, &c., are the *thio-acids*; whilst the third series are called *thio-sulpho-acids*. The author has endeavoured to prepare acids belonging to the first and third series.

With a view to obtain thiosulphopropionic acid, propionitril was peated with an alcoholic solution of sodium hydrosulphide and sulphuretted hydrogen for several days, but it was found that water always took part in the reaction, so that the thiosulphopropionate was not produced. The product separated into two layers, the lower one, on cooling, solidifying to a crystalline mass of sodium sulphopropionate,  $C_2H_5.CSONa + H_2O$ . It is very soluble in water, less soluble in dilute alcohol, and only sparingly in absolute alcohol. Its aqueous solution possesses the following reactions:—Barium chloride gives a white precipitate; silver nitrate a yellowish-white precipitate, which rapidly decomposes; mercuric chloride a yellowish-white precipitate;



acetate of lead forms a white precipitate not decomposed in the cold, a character by which sulphopropionic acid may be distinguished from its isomeride, lead thiopropionate being decomposed in the cold. When sodium sulphopropionate is treated with  $\text{POCl}_3$ , sulphopropionyl chloride is formed, which proves that the sulphur replaces the oxygen in the group CO.

The author has obtained sodium sulpho-acetate.

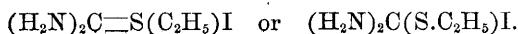
L. T. O'S.

**Glyceric Anhydride.** By N. SOKOLOFF (*Deut. Chem. Ges. Ber.*, xi, 679).—An aqueous solution of glyceric acid when evaporated at  $100^\circ$  and left at rest, deposits microscopic crystals of a compound which, by re-crystallisation from water, may be obtained in slender six-sided needles, having the composition  $\text{C}_3\text{H}_4\text{O}_3$ . This anhydride is insoluble in cold alcohol and in boiling ether; it is soluble in 647 parts of boiling water, by which, moreover, it is but very slowly converted into glyceric acid.

C. F. C.

**Sulphine-compounds of Thiocarbamide.** By A. BERNTHSEN and H. KLINGER (*Deut. Chem. Ges. Ber.*, xi, 492—495).—Methyl iodide slowly combines with thiocarbamide at the ordinary temperature forming *methiodide-thiocarbamide*,  $\text{CSN}_2\text{H}_4\cdot\text{CH}_3\text{I}$ . This substance crystallises in prisms (m. p.  $117^\circ$ ), soluble in alcohol and in water. It differs from  $\text{CSNH}_2\cdot\text{NH}\cdot\text{CH}_3\cdot\text{HI}$ , the iodide of methylthiocarbamide (m. p. below  $100^\circ$ ), in its melting point and its decomposition by silver oxide. Iodide of methylthiocarbamide is completely desulphurised by the action of moist silver oxide, methylcyanamide being formed. When, however, methiodide-thiocarbamide is treated with silver oxide, a strong base is formed (probably  $\text{CSN}_2\text{H}_4\cdot\text{CH}_3\text{OH}$ ), which gives characteristic precipitates with metallic salts. Methiodide-thiocarbamide is decomposed by mercuric oxide forming cyanamide, dicyandiamide, and methyl sulphide. Ethyl iodide readily combines with thiocarbamide at  $100^\circ$  to form ethiodide-thiocarbamide,  $\text{CSN}_2\text{H}_4\cdot\text{C}_2\text{H}_5\text{I}$ , first prepared by Claus.

These addition-products are decomposed by heat, hydrocyanic acid being evolved and a residue left which, by treatment with water, may be separated into a difficultly soluble amorphous substance and a compound which is readily soluble and crystallises in needles. The authors consider that these bodies have the constitution—



W. C. W.

**Hydrocarbon from Betulin.** By E. PATERNO and P. SPICA (*Gazzetta chimica italiana*, vii, 508—510).—As zeorin,  $\text{C}_{13}\text{H}_{22}\text{O}$  (*Gazz.*, vi, 113; this Journal, 1876, ii, 203), and betulin,  $\text{C}_{12}\text{H}_{20}\text{O}$ , both appear to be homologues of camphor,  $\text{C}_{10}\text{H}_{16}\text{O}$ , it was of interest to try the effect of dehydrating agents on them. From want of material, the experiment could not be tried with zeorin, but on distilling betulin with phosphoric anhydride, an oil was obtained, which by fractionation yielded a hydrocarbon, boiling at  $245\text{--}250^\circ$ , apparently identical with the compound boiling at  $243^\circ$  which Hausmann obtained by the dry distillation of betulin, but to which he assigned the formula,  $\text{C}_{36}\text{H}_{56}\text{O}$ .

The analyses of the hydrocarbon gave  $\text{C} = 89.23$ ;  $\text{H} = 10.74$ ,



agreeing with the formula,  $C_{11}H_{16}(C = 89.18 : H = 10.82)$ , rather than as might have been expected with  $C_{12}H_{18}$ , which is that required by the equation,  $C_{12}H_{20}O = C_{12}H_{18} + H_2O$ . C. E. G.

**Action of  $\alpha$ -Dinitrochlorobenzene on Urea, Azo-compounds, Aromatic Hydrocarbons, and Sodium Amalgam.** By C. WILLGERODT (*Deut. Chem. Ges. Ber.*, xi, 601—605).— $\alpha$ -Dinitrophenylaniline,  $C_6H_5.NH.C_6H_3(NO_2)_2$ , is formed by heating equal weights of  $\alpha$ -dinitrochlorobenzene and sulphocarbaniid with alcohol in sealed tubes, at  $130$ — $150^\circ$ . It crystallises in yellow needles, which do not melt at  $300^\circ$ , but decompose with explosion a little above that temperature.  $\alpha$ -Dinitrophenylbromaniline,  $C_6H_4Br.NH.C_6H_3(NO_2)_2$ , can be obtained in reddish-yellow crystals (m. p.  $152^\circ$ ) by heating a mixture of  $\alpha$ -dinitrochlorobenzene and dibromodiphenylcarbamide at  $170^\circ$  in sealed tubes. Bromaniline chloride is formed at the same time.  $\alpha$ -Dinitrophenylbromaniline is soluble in hot alcohol, ether, and acetic acid, but is insoluble in hydrochloric acid and water.

$\alpha$ -Dinitrochlorobenzene does not act on azo-compounds, nor does it combine with anthracene. When added to alcoholic solutions of naphthalene and phenanthrene, it unites directly with the hydrocarbons, to form addition-products. The naphthalene-compound forms needle-shaped crystals (m. p.  $78^\circ$ ), which are insoluble in ether, alcohol, and glacial acetic acid. The phenanthrene-compound crystallises in orange-coloured needles, which melt at  $44^\circ$ .

Sodium amalgam converts  $\alpha$ -dinitrochlorobenzene into a dark brown substance. W. C. W.

**Chlorocymene from Thymol and nearly related Bodies.** By E. v. GERICHTEN (*Deut. Chem. Ges. Ber.*, xi, 364—369).—When chlorocymene obtained directly from cymene is treated with nitric acid of sp. gr. 1.24, there separates out after five hours' boiling a mass of crystalline needles, consisting of chlorotoluic acid, m. p.  $195^\circ$ . If, however, the chlorocymene obtained from thymol (b. p.  $209^\circ$ ) is treated in a similar manner, crystals are deposited on cooling, after 14 days boiling, which have a different composition. These crystals were dissolved in caustic potash, the filtered solution precipitated with hydrochloric acid, and the acid thus obtained purified by means of the barium salt. It crystallises from dilute alcohol in beautiful long needles (m. p.  $122^\circ$ ), the analysis of which corresponded with either of the two following formulæ:— $C_6H_3Cl(CH_3).CH_2.CH_2.COOH$ , paramethyl-ortho-chloro-hydro-cinnamic acid; or  $C_6H_3Cl(C_2H_7).COOH$ , chlorinated isomeride of cuminic acid, and not with that of chlorotoluic acid, as formerly supposed (this Journal, p. 49). The barium salt crystallises in pearly plates, with three molecules of water.

The following represents the constitution of the two chlorocymenes, and of the acids which they yield on oxidation:—

Chlorocymene from cymene,  $(C_3H_7 : Cl : CH_3 = 1 : 3 : 4)$ , gives chlorotoluic acid  $COOH : Cl : CH_3 = 1 : 3 : 4$ .

Chlorocymene from thymol,  $(C_3H_7 : Cl : CH_3 = 1 : 2 : 4)$ , gives an isomeride of chlorocuminic acid,  $(C_3H_7 : Cl : COOH = 1 : 2 : 4)$ , or methyl-chloro-hydro-cinnamic acid  $(CH_2.CH_2.COOH : Cl : CH_3 = 1 : 2 : 4)$ .

Which of the last two formulæ is correct is not yet decided. By treatment with sodium amalgam, either a cuminic acid with normal propyl, or a paramethyl-hydro-cinnamic acid would be produced; whilst by oxidation with permanganate, either the second possible chlorotoluic acid,  $\text{C}_6\text{H}_3\text{Cl}(\text{CH}_3).\text{COOH}$ , or  $\text{C}_6\text{H}_3\text{Cl}(\text{COOH}).\text{C}_2\text{H}_4.\text{COOH}$ , or  $\text{C}_6\text{H}_3\text{Cl}(\text{COOH})_2$  would result. The author intends preparing the analogous bromine derivative of cymene from thymol, and with it to carry out the above reactions.

Morse and Remsen (*Ber.*, xi, 224; and p. 405 of this volume) have obtained results with para-methyl-ethyl benzene, similar to those described above with para-methyl-propyl-benzene. They treated para-ethyl-toluene with bromine, and oxidised the resulting monobromoderivative, with formation of bromoparatoluic acid (m. p.  $204^\circ$ ). In order to explain this fact, they make use of the supposition first proposed by Remsen, that if a negative atom, as Cl, &c., enter a benzene nucleus in the ortho-position in reference to a side-chain already present, it protects the latter from the influence of oxidising agents; but if a second side-chain be also present in another position, this will be converted by oxidising agents into carboxyl. As, however, this is merely an hypothesis, which has not yet been experimentally proved, the author thinks that Morse and Remsen are not justified in concluding, on the strength of it, that the bromine in brom-para-ethyl-toluene and brom-paratoluic acid is in the ortho-position. Nevertheless the results detailed above with regard to the products of oxidation of the two chlorocymenes, are an important illustration of Ramsen's hypothesis as to the influence of negative atoms in protecting ortho side-chains from oxidation.

The author believes that the chlorotoluic acid (m. p.  $185^\circ$ ) prepared by Kekulé and Fleischer from the chlorocymene from carvacrol, is identical with that (m. p.  $195^\circ$ ) obtained by himself directly from cymene, and that the difference in melting point is due to an error in Kekulé and Fleischer's determination. T. C.

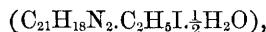
**Method for distinguishing between Orthodiamines and their Isomerides.** By A. LADENBURG (*Deut. Chem. Ges. Ber.*, xi, 600).—The hydrochlorides of orthodiamines, when heated with benzaldehyde at  $100$ – $120^\circ$  for a few minutes, evolve hydrochloric acid. Meta- and para-diamines do not exhibit this reaction. W. C. W.

**Aldehydines, a New Class of Bases.** By A. LADENBURG (*Deut. Chem. Ges. Ber.*, 590–600).—Aldehydine is the name proposed for the class of compounds formed by the union of 1 molecule of an orthodiamine with 2 molecules of aldehyde, the combination being attended by the loss of 1 molecule of water. Meta- and para-diamines do not form stable compounds with aldehydes.

*Tolubenzaldehydine*,  $\text{C}_{21}\text{H}_{18}\text{N}_2$ , is prepared by heating benzaldehyde with orthotoluyldiamine at  $140^\circ$ , and may also be obtained by heating the hydrochloride of the base with benzaldehyde, first at  $100^\circ$ , and then at  $130^\circ$ , until hydrochloric acid ceases to be evolved. The crude product is dissolved in hot dilute hydrochloric acid, and the crystals which separate out on cooling are decomposed by ammonia. The free

base is soluble in alcohol, acetone, and acids; it is deposited from an alcoholic solution, in transparent, monoclinic prisms, which melt at  $195.5^{\circ}$ . The base can be sublimed in small quantities, without decomposition. The hydrochloride,  $C_{21}H_{18}N_2 \cdot HCl \cdot \frac{1}{2}H_2O$ , is but slightly soluble in strong hydrochloric acid; it separates out in long, needle-shaped crystals from a solution in the hot dilute acid. The acetate and sulphate could not be obtained in the pure state.

*Tolubenzaldehydine Ethiodide*.—Two kinds of crystals are produced by the union of ethyl iodide with the aldehydine, viz., thick prisms or tables, and long needles, both of which are soluble in water and in alcohol, and possess the same composition,



and melting point ( $180-181^{\circ}$ ). An alcoholic solution of iodine converts this compound into  $C_{23}H_{23}N_2I_3$ , which crystallises in brown plates (m. p.  $123^{\circ}$ ). By the action of silver oxide on tolubenzaldehydine ethiodide an oily liquid is formed, the hydrochloric acid solution of which gives, with platinum chloride, a yellow crystalline precipitate of tolubenzaldehydine ethyl-platinochloride,  $(C_{23}H_{23}N_2Cl)_2 \cdot PtCl_4$ .

*Tolubenzaldehydine methiodide* forms white, needle-shaped crystals, which melt at  $209^{\circ}$ , with decomposition. On oxidation with potassium permanganate, tolubenzaldehydine yields an acid, melting at  $253.5-254.5^{\circ}$ , which is probably dibenzylamidobenzoic acid,  $C_{21}H_{14}N_2O_2$ .

The preparation of *tolufurfuraldehydine* resembles that of the preceding aldehydine. The pure base crystallises in white, silky prisms (m. p.  $115-116^{\circ}$ ) soluble in alcohol, ether, benzene, toluene, and in acids. The nitrate,  $C_{17}H_{14}N_2O_2 \cdot HNO_3$ , is precipitated on the addition of dilute nitric acid to a solution of the base, the chloride forms a crystalline double salt with platinum chloride, and the sulphate is deposited from an alcoholic solution in prismatic crystals.

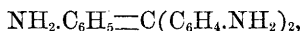
*Compounds of Orthotolylendiamine with Salicyl Aldehyde*.—A substance having the formula,  $C_{26}H_{22}N_2O_3$ , appears to be formed on heating 1 molecule of orthotolylendiamine with 2 molecules of salicyl aldehyde at  $110^{\circ}$ ,  $C_7H_{10}N_2 + 3C_7H_6O_2 = C_{26}H_{22}N_2O_3 + 3H_2O$ . It is converted by long continued boiling with hydrochloric acid into an amorphous body; this is soluble in potash-solution, forming a blue fluorescent liquid, from which it is reprecipitated by carbon dioxide.

A substance to which the name *azurine* has been given, is obtained by heating the diamine with twice its weight of the aldehyde at  $135^{\circ}$ , and extracting the product with hot dilute hydrochloric acid. The acid solution is filtered, and the white amorphous precipitate, thrown down on adding strong hydrochloric acid to the filtrate, is dissolved in alcoholic potash, and shaken up with ether. The ethereal solution is evaporated to dryness, and the residue dissolved in water, precipitated by carbon dioxide, and recrystallised from amyl alcohol. Azurine is characterised by the blue fluorescence of its solutions, and has the composition,  $C_{35}H_{32}N_4O_3$ ;  $2C_7H_{10}N_2 + 3C_7H_6O_2 = C_{35}H_{32}N_4O_3 + 3H_2O$ . It forms colourless, tabular crystals (m. p.  $250.5^{\circ}$ ), soluble in amyl alcohol and acetone.

*Dibenzylidenparaphenyldiamine*,  $C_{20}H_{16}N_2$ , prepared by heating 1 molecule of paraphenyldiamine with 2 molecules of aldehyde at

120°, and extracting the crude product with alcohol, crystallises in scales, which melt at 133—140°. It is soluble in alcohol, petroleum-ether, and acids, but it does not form salts, nor does it form a definite compound with methyl iodide. W. C. W.

**Rosaniline.** By E. FISCHER and O. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 612—613).—The constitutional formula recently proposed by the authors (*Ber.*, xi, 191) for pararosaniline, viz.,



was based upon the direct conversion into rosaniline of the hydrocarbon diphenylphenylenemethane,  $\text{C}_{19}\text{H}_{14}$ , by Hemilian (*Ber.*, vii, 1208). On repeating his researches, however, they find that the product described by him (m. p. 138°) was apparently a mixture of triphenylmethane and the pure hydrocarbon,  $\text{C}_{19}\text{H}_{14}$ , which they have obtained crystallised in colourless needles (m. p. 145—146°); the latter is most probably identical with the diphenylphenylmethane recently prepared by Hemilian from fluorene alcohol. From neither of these have they succeeded in obtaining leucaniline: hence the above formula for para-roosaniline can no longer be maintained. C. F. C.

**Ethyl-derivatives of Phenylhydrazine.** By W. EHRHARDT and E. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 613—615).—By the action of ethyl bromide upon phenylhydrazine, there is formed in addition to the ammoniacal compound,  $\text{C}_6\text{H}_5.\text{N}_2\text{H}_2.(\text{C}_2\text{H}_5)_2\text{Br}$ , a mixture of volatile bases, from which the authors have isolated the following compounds:—1. A tertiary hydrazine base, which has not been further investigated. 2. *Diethyl-diphenyltetrazone*,  $(\text{C}_2\text{H}_5)_2\text{N—N}=(\text{C}_6\text{H}_5)_2$ . 3. *Azophenylethyl*,  $\text{C}_6\text{H}_5.\text{N}=\text{N}.\text{C}_2\text{H}_5$ . This compound, the simplest representative of the mixed azo-bodies, is a yellow oil, which may be distilled unchanged. It is dissolved by hydrochloric acid, and the solution is decomposed on boiling; by the action of reducing agents on its alcoholic solution it is converted into the hydrazine base  $\text{C}_6\text{H}_5.\text{NH.NH}.\text{C}_2\text{H}_5$ . This distils unchanged, and forms easily soluble salts. C. F. C.

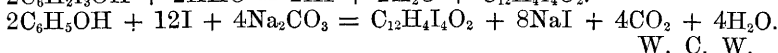
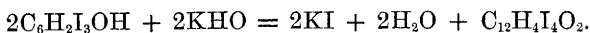
**Action of Nitrous Acid on Benzene-sulphinic Acid.** By W. KOENIGS (*Deut. Chem. Ges. Ber.*, 615—619).—By the action of nitrous acid (1 mol.) upon benzenesulphinic acid (2 mols.), the author has obtained the compound  $(\text{C}_6\text{H}_5.\text{SO}_2)_2.\text{HNO}$ , crystallising from its solution in alcohol in large, colourless prisms. It is almost insoluble in water, but soluble in alcohol and in ether, and somewhat less so in benzene and in chloroform. This body appears to be a mixed anhydride of nitrous acid and the sulphinic acid, into which it is resolved by the action of alkaline solutions. Boiled with water and aniline hydrochloride, it yields phenol. If this body be added in slight excess to a solution of potassium or barium hydroxide, and, after filtration, decomposed with aniline hydrochloride, a mixture of diazoamidobenzene and diazobenzene-benzene sulphinic acid is precipitated. The compound  $(\text{C}_6\text{H}_5.\text{SO}_2)_2.\text{HNO}$ , when heated with sulphuric acid, appears to yield hydroxylamine. This fact indicates the possibility of

its synthesis from benzene sulphochloride and hydroxylamine. By further treatment of its alcoholic solution with nitrous acid, it is converted into the compound  $C_{18}H_{15}NS_3O_7 = (C_6H_5SO_2)_3NO$ , a crystalline body, melting at  $98^\circ$ , and insoluble in alkalis. C. F. C.

**Iodated Derivatives of Phenols.** By H. KÄMMERER and E. BENZINGER (*Deut. Chem. Ges. Ber.*, xi, 557—561).—The addition of a solution of iodine in iodide of potassium to a hot dilute alkaline solution of phenol produces a red precipitate; in a similar solution of thymol a pale-violet precipitate; and in a solution of commercial creosote it produces first a greenish-brown fluorescent coloration, and finally a bulky brown precipitate.

The phenol derivative is prepared by adding excess of iodine (70—75 grams dissolved in 600 c.c. of water, containing 45 grams of potassium iodide) to a boiling solution of 300 grams of soda-crystals and 10 grams of phenol in 1 litre of water. After removing the excess of iodine, by adding 30 grams of soda-crystals to the boiling mixture, the reddish-brown precipitate is collected on a filter. Alcohol extracts from the filtrate, which should be colourless, a white crystalline compound (m. p. about  $150^\circ$ ), probably di-iodo-diphenylhydroquinone  $(HO)I_2C_6 + C_6H_3I(OH)$ . This body is at once converted into the insoluble red compound, by boiling with iodine and sodium carbonate.

The red substance is identical in its properties with a compound obtained by the decomposition of tri-iodophenol and tri-iodosalicylic acid, to which the formula  $C_{12}H_4I_4O_2$  was assigned by Lautemann (*Annalen*, cxx, 137) and Kekulé (*ibid.*, cxxxi, 221). The authors, however, regard it as *tetra-iododiphenylenequinone*  $C_{12}H_4I_4O_2$ , since it is converted into the hydroquinone  $C_{12}H_6I_4O_2$  by the action of sulphurous acid; its formation from tri-iodophenol and from phenol is explained by the following equations:—



W. C. W.

**Etherification of Phenols.** By MENSCHUTKIN (*Deut. Chem. Ges. Ber.*, xi, 679).—The etherification of phenols resembles that of tertiary alcohols. The following are the initial velocities and limits of etherification as determined for the following phenols:—

	Initial velocity.	Limits.
Phenol .....	1.45	8.61
Paracresol .....	1.40	9.54
Thymol .....	0.55	9.18
Naphthol .....	—	6.16

C. F. C.

**Thymol Derivatives.** By L. BARTH (*Deut. Chem. Ges. Ber.*, xi, 567).—Four acids are formed by fusing thymol with potassium hydroxide, viz.:—(1) oxybenzoic acid; (2) Burkhardt's oxyterephthalic acid; (3) an acid forming needle-shaped crystals (m. p.  $143^\circ$ ), which has the composition  $C_{10}H_{12}O_3$ , and which it is proposed to call *thymolowy-*

*cinnamic acid*; (4) a bibasic acid,  $C_{10}H_{10}O_3$ , which is difficult to obtain in the pure state. It is easily soluble in water, and the aqueous solution precipitates lead salts, and gives an intense red coloration with ferric chloride. The author proposes to call this substance *thymolic acid*.  
W. C. W.

**Mononitropyrocatechin.** By R. BENEDIKT (*Deut. Chem. Ges. Ber.*, xi, 362—363).—This compound is produced by dissolving 4 grams of pyrocatechin and 20 grams of potassium nitrite in 150 c.c. of water, and adding dilute sulphuric acid until effervescence ceases. The dark-brown red liquid obtained is exhausted with an equal volume of ether, and the residue left on distilling off the latter recrystallised several times from hot benzene.

*Mononitropyrocatechin*,  $C_6H_3(NO_2)(OH)_2$ , crystallises in small yellow silky needles, which dissolve easily in water, alcohol, and ether, but are very difficultly soluble in benzene. It melts at  $157^\circ$  and dissolves in caustic potash with a beautiful purple colour.

*Barium salt*,  $C_6H_3(NO_2)_2O_2Ba + 3H_2O$ , crystallises in dark-red plates, with metallic lustre. It is very difficultly soluble even in boiling water. On drying at  $130^\circ$ , it loses its water of crystallisation and becomes dark green.

*Mono-amido-pyrocatechin*,  $C_6H_3(NH_2)(OH)_2$ , is produced by the action of reducing agents on the nitro-compound. The hydrochloride crystallises in long dark needles. On attempting to obtain the free base from this salt by treating it with caustic or carbonated alkalis, it oxidises immediately on contact with the air, and dissolves with a dark violet colour.

A second nitropyrocatechin has been obtained in small quantity, but has not yet been completely investigated. It distils with steam, is very difficultly soluble in water, and forms yellow drops which, after a time, solidify to a crystalline mass.  
T. C.

**A Quinone Derivative occurring in *Agaricus Atrotomentosus*.** By W. THÖRNER (*Deut. Chem. Ges. Ber.*, xi, 533—535).—On treating *Agaricus atrotomentosus* with ether, a wine-red solution is obtained, which on evaporation leaves a dark-brown crystalline mass, soluble in solutions of caustic alkalis. By dissolving the precipitate, which is produced on adding hydrochloric acid to this alkaline solution, in boiling glacial acetic acid,  $\alpha$ -dioxiquinone,  $C_{11}H_6O_2(OH)_2$ , is obtained in the pure state, in the form of dark-brown shining plates (m. p. above  $360^\circ$ ). It is insoluble in water, benzene, petroleum-ether, chloroform, and carbon bisulphide, and dissolves with difficulty in boiling alcohol and in glacial acetic acid, forming red solutions. The substance dissolves in alkalis, forming a yellowish-green liquid, which becomes colourless when boiled with zinc dust. Oxidation takes place on exposure to the air, and the solution assumes its original colour. The addition of ammonia to the red alcoholic solution first changes the colour to violet, which passes into dark blue, green, and finally yellow. The acetate,  $C_{11}H_6O_2(C_2H_3O_2)_2$ , forms reddish-yellow crystals, which melt at  $238$ — $240^\circ$ .

*Agaricus atrotomentosus*, *Ag. bulbosus*, and *Ag. integer* contain bodies



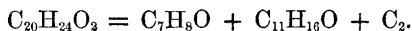
which form crystalline double salts with platinum chloride. The last-mentioned fungus also contains considerable quantities of mannite.

W. C. W.

**Aurin.** By E. and O. FISCHER (*Deut. Chem. Ges. Ber.*, xi, 473).—Triphenylmethane is formed by the action of alcohol on the diazo-compound of leucaniline prepared from pure aurin. This confirms the authors' view of the constitution of aurin, viz., that it has the formula  $C_{19}H_{14}O_3$ , and is a derivative of triphenylmethane.

W. C. W.

**Action of Boron Fluoride on Anethol.**—**Properties of Hydroboric Fluoride.** By F. LANDOLPH (*Compt. rend.*, lxxxvi, 601—604).—Anethol is instantaneously polymerised by fluoride of boron at the ordinary temperature, but at the boiling heat the action is different. In this way the author obtained anisol,  $C_7H_8O$ , and another substance,  $C_{11}H_{16}O$ , boiling at  $225-228^\circ$ , having a powerful odour, resembling that of camphor. *Hydroboric fluoride*,  $BF_3 \cdot 3HFl$ , is formed at the same time, and was easily isolated, distilling at about  $130^\circ$ , although no constant boiling point could be observed: its vapour-density was found to be 4.72, that calculated for 2 volumes being 4.42. The splitting up of anethol by the action of fluoride of boron is represented by the equation:—



The author's former communications on anethol are referred to in *Compt. rend.*, 1875, 12 Juillet; 1876, 17 Janvier, and 10 Avril; and this Journal, 1876, i, 246, 705, ii, 79.

R. R.

**Melilotol.** By T. L. PHIPSON (*Compt. rend.*, lxxxvi, 830—831).—Melilotol is an oily product found together with coumarin in the *Melilotus officinalis*, and may be extracted by distilling the plant (when in flower) with water, agitating the aqueous distillate with ether, and allowing the ethereal solution to evaporate spontaneously. It has an agreeable odour, is but very slightly soluble in water, very soluble in alcohol and ether, and when boiled with a concentrated solution of potassium hydroxide, yields *melilotic acid*,  $C_9H_{10}O_3$ , which is also found in the plant. The formula of melilotol the author states to be  $C_9H_8O_2$ . He believes it to be analogous to salicylic aldehyde, and that to it the agreeable odour of the *M. officinalis* is due. Coumarin,  $C_9H_6O_2$ , when treated with sodium amalgam in presence of water, gives melilotic acid, the reaction being:—



the melilotol, as it is produced uniting with the elements of water, to form melilotic acid.

C. E. G.

**Salicylic Acid.** By J. WILLIAMS (*Pharm. J. Trans.* [3], viii, 785—786).—The author, on comparing the physical and chemical properties of the natural and artificial salicylic acid, found that they differed, owing to the presence in the artificial acid of an impurity which he calls cresyl-salicylic acid. When purified, the natural and artificial acids exhibit identical properties. The purification is



effected by dissolving the acid in boiling water, and neutralising it with calcium carbonate. On cooling, calcium salicylate crystallises out, and is purified by repeated crystallisation from hot water. When this is decomposed with hydrochloric acid, and the precipitated salicylic acid is recrystallised from hot water, and finally from dilute alcohol, it is obtained in large white crystals similar to those of the natural acid.

Cresyl-salicylic acid is obtained from the uncrystallisable portion of the mother-liquor from the calcium salicylate, by decomposition with hydrochloric acid, but the author has not completed the investigation of this body.

L. T. O'S.

**Protocatechuic Series of Compounds.** By F. TIEMANN (*Deut. Chem. Ges. Ber.*, xi, 659—675).—The relations existing between the compounds containing the common group  $\text{C}_6\text{H}_3\begin{matrix} \text{C}\equiv \\ \diagup \text{O} \diagdown \\ \text{O} \end{matrix}$ , and derivable

therefore from protocatechuic acid, may be classified in four parallel series, viz. (1.) The *protocatechuic* acid series proper, the members of which contain a single carbon atom,  $\text{—C}\equiv$ , in the side chain. (2.) The  *$\alpha$ -homoprotocatechuic* series, of which the characteristic group is the side chain containing  $\text{—CH}_2\text{—C}\equiv$ . (3.) The *hydrocaffeic* series of bodies containing in the side chain the group  $\text{—CH}_2\text{—CH}_2\text{—C}\equiv$ . (4.) The *caffaic*, with the side chain group  $\text{—CH=CH—C}\equiv$ . Tables of the acids, alcohols, aldehydes, &c., of these series are given, with the melting points, as far as they are known, from an inspection of which it is evident that the higher homologues in the several series melt at a lower temperature than the lower; also that the melting points of members of the caffeic is uniformly higher than those of corresponding members of the hydrocaffeic series; and that of those acids which contain a single methoxyl group, those in which the latter group occupies the para-position in relation to the side chain, melt at a higher temperature than those in which the meta relation obtains. To each of the acids of the above series corresponds an aldehyde, alcohol, and a body resulting from the replacement of carboxyl by methyl.

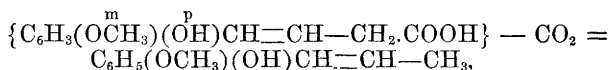
**Constitution of Eugenol.**—The question of the constitution of eugenol resolves itself into that of its side chain, the group  $\text{C}_3\text{H}_5$ . From the formation of acetic acid in the oxidation of the oil, Erlenmeyer inferred the presence of the group  $\text{CH}_3\text{—C}$ , and hence considered it as having the constitution  $\text{—CH=CH—CH}_3$ . He, however, has since shown (*Ber.*, ix, 273) that acetic acid is a product of the oxidation of the oxybenzoic acids, and that the above conclusion is not warranted. On this ground, together with the fact that the formation of acet( $\alpha$ )-homovanillic acid from acetoeugenol is irreconcilable with this view, it is rejected by him, and the formula  $\text{—CH}_2\text{—CH=C}$ , proposed for the side group. To this the author takes objection, maintaining the original formula on the following grounds:—Eugenol, coniferyl alcohol, and ferulic acid all yield vanillin as a product of limited oxidation, apparently in the same way that cinnamic acid and anethol yield benzaldehyde and anisaldehyde respectively, a result which indi-

cates an analogous constitution of the side chains. These reactions, as well as the formation of veratroyl-carbonic acid from methyl-eugenol, are explained with difficulty on Erlenmeyer's hypothesis.

The following series of reactions (in which R = the  $C_3H_5$  group), explaining the derivation of vanillin, and similarly of  $\alpha$ -homovanillin, are fully discussed by the author:—

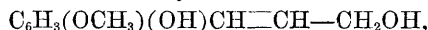
- (1)  $R.CH=CH.CH_3 + H_2O = R.CH(OH).CH_2.CH_3$
- (2)  $R.CH(OH).CH_2.CH_3 + O = R.CO.CH_2.CH_3 + H_2O$
- (3)  $R.CO.CH_2.CH_3 + H_2O = R.CO.H + CH_3.CH_2.OH.$

The author hopes to verify this view of the constitution of eugenol by effecting the following reaction:—



analogous to that of the conversion of phenylcrotonic acid into anethol (Perkin, *Journ. Chem. Soc.*, 1877, i, 412), but has not as yet obtained the acids in sufficient quantity.

*Constitution of Coniferyl Alcohol.*—The author in reply to certain objections urged by Erlenmeyer (*Ber.*, x, 630), discusses the formula proposed by himself for coniferyl alcohol,



in relation to its decomposition:—

(1.) By chromic acid, with formation of acetic acid and ethaldehyde. This might be supposed to be due to the union of the  $CH=CH$  group with water to form ethaldehyde, but the author does not consider this to be the case. He has, however, shown experimentally that acetic acid is not formed as a product of the reaction of the benzene nucleus with the elements of water, and concludes, therefore, that the reaction in question must be confined to the side chain.

Coniferyl alcohol, when boiled with dilute sulphuric acid, yields a small quantity of vanillin, from which reaction, bearing in mind the ease with which mixed aromatic and fatty ketones are decomposed, with formation of aromatic aldehydes, the presence of the  $-CO.CH_2.CH_3$  group might be inferred: on the other hand, the minuteness of the quantity of vanillin produced, the analogy of coniferyl to cinnamyl alcohol, and the tendency of the former to polymerisation, favour the original hypothesis. The formation of vanillin is explained by the hydration of coniferyl alcohol to form the compound

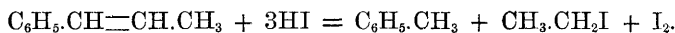


which is resolved into vanillin and ethyl alcohol in the same way that lactic acid splits up into ethaldehyde and formic acid.

(2.) By fuming hydriodic acid, with formation of methyl and ethyl iodides. The production of the latter compound is referred to the decomposition of the side chain. That this is its actual origin is rendered probable by the observation of Hlasiwetz (*Annalen*, cxlii, 227) of the conversion of caffeic acid,  $C_6H_3(OH)_2.CH=CH.COOH$ , into homopyrocatechin,  $C_6H_3(OH)_2.CH_3$ , by the action of hydriodic acid.

Nevertheless, Erlenmeyer failed to obtain ethyl iodide from cinnamyl alcohol by a similar reaction: but the author on repeating the experiment, has obtained results which are reconcilable with the original formula for coniferyl alcohol.

*Action of Hydriodic Acid upon Cinnamyl Alcohol.*—By the action of fuming hydriodic acid (25 parts) upon cinnamyl alcohol (10 parts) at 180—200°, in sealed tubes, the author has obtained a mixture of toluene and phenylpropylene. The first stage of the reaction probably consists in the formation of the latter body, which is decomposed by the prolonged action of the hydriodic acid according to the equation:—



From this it is a direct inference, that coniferyl alcohol would yield, when similarly treated with hydriodic acid, a dioxyphenylpropylene,  $\text{C}_6\text{H}_3(\text{OH})_2.\text{CH}=\text{CH}.\text{CH}_3$ , and a dioxytoluene (homopyrocatechin). The author appears to have identified the latter body amongst the products of this reaction, but the dioxyphenylpropylene is so very unstable that it could not be isolated, the chief product being an almost insoluble resinous substance containing considerable quantities of iodine.

C. F. C.

**Diaceto( $\alpha$ )homoprotocatechuic Acid.** By NAGAJOSI NAGAI (*Deut. Chem. Ges. Ber.*, xi, 658).—This acid is easily prepared by the action of acetic anhydride, at its boiling temperature, upon  $\alpha$ -homoprotocatechuic acid. It occurs in the form of minute crystals which melt at 89—90°, and are soluble in water, alcohol, and ether. It does not give any reaction with ferric chloride.

C. F. C.

**Synthesis of Caffeic Acid, and Derivatives of Caffeic and Hydrocaffeic Acids.** By F. TIEMANN and NAGAJOSI NAGAI (*Deut. Chem. Ges. Ber.*, xi, 646—657).—The direct and collateral results of this research are given under the successive compounds investigated:—

*Acetovanillin*,  $\text{C}_6\text{H}_3(\text{COH})(\text{O}.\overset{\text{m}}{\text{CH}_3})(\text{O}.\overset{\text{p}}{\text{C}_2\text{H}_3\text{O}})$ , is best prepared by allowing the sodium-compound of vanillin to remain in contact with an ethereal solution of acetic anhydride for some hours. It forms large flat needles which melt at 77°; it is easily soluble in alcohol and ether, but only sparingly in water.

*Acetoferulic acid*,  $\text{C}_6\text{H}_3(\text{CH}=\text{CH}.\text{COOH})(\text{O}.\overset{\text{m}}{\text{CH}_3})(\text{O}.\overset{\text{p}}{\text{C}_2\text{H}_3\text{O}})$ , is formed by heating either vanillin or the preceding compound with anhydrous sodium acetate and acetic anhydride. It crystallises in slender needles melting at 196—197°: it is readily soluble in alcohol and in ether, but with difficulty in water.

*Ferulic acid*,  $\text{C}_6\text{H}_3(\text{CH}=\text{CH}.\text{COOH})(\text{O}.\overset{\text{m}}{\text{CH}_3})(\text{O}.\overset{\text{p}}{\text{H}})$ , results from the decomposition of the preceding compound by sodium hydrate. This synthetic acid crystallises from boiling water in brittle prisms of high refractive power which melt at 168—169°. The authors have isolated ferulic acid from assafoetida according to the method of Hlasi-

wetz and Barth, and find that it also melts at 168—169°, and not at 153° as stated by them. In order, finally, to establish the identity of these products, (1) the latter was heated with acetic anhydride, and found to yield a body identical in all respects with the acetoferulic acid described above, and (2) the acetoferulic acid thus prepared from the “natural” acid was oxidised by potassium permanganate in acetic acid solution, and found to yield acetovanillin and acetovanillic acid.

In ferulic acid the hydrogen both of the carboxyl group and of the phenolic hydroxyl is capable of being replaced by metals, so that it yields two classes of salts, of which the primary ammonium and secondary potassium salts have been obtained by Hlasiwetz. Ferulic acid is a hydroxyl-methoxyl-cinnamic acid, and can readily take up two hydrogen atoms, forming hydroferulic acid.

*Hydroferulic acid*,  $C_6H_3(CH_2.CH_2.COOH)(OCH_3)^m(OH)^p$ , is easily obtained by the action of reducing agents upon ferulic acid. It crystallises from its aqueous solution in microscopic plates (m. p. 89—90°) which are very easily soluble in alcohol, ether, and hot water. Like the preceding it forms two classes of salts.

*Dimethylcaffeic acid*,  $C_6H_3(CH=CH.COOH)(OCH_3)^m(OCH_3)^p$ , or *methylferulic acid*, was prepared by the authors by two parallel methods, namely, by replacing the two hydroxyl groups of caffeic or dioxy-cinnamic acid, and the single hydroxyl group of ferulic acid by methoxyl, by heating them with potash and methyl iodide, in methyl alcohol solution; the acids thus obtained are identical in every respect, thus establishing beyond doubt the constitutional relations of the three acids. Dimethylcaffeic acid crystallises in needles which melt at 180—181°. It is a monobasic acid. The salts which it forms with the metals of the alkalis and alkaline earths are readily soluble.

*Hydrodimethylcaffeic acid*,  $C_6H_3(CH_2.CH_2.COOH)(OCH_3)^m(OCH_3)^p$ , was obtained by reduction from dimethylcaffeic acid prepared both from ferulic acid and from caffeic acid: the products were identical. This acid crystallises from its aqueous solution in slender needles which melt at 96—97° to an oil which solidifies at 60°.

*Isoferulic acid*,  $C_6H_3(CH=CH.COOH)(OH)^m(OCH_3)^p$ , is formed by heating caffeic acid with methyl iodide and potassium hydrate in insufficient quantity for the complete replacement of its hydroxyl. The methyl ethers of isoferulic and dimethylcaffeic acids are thus obtained: they are easily separated, and the isoferulic acid may be isolated, after saponification, in the form of crystals which melt at 211—212°. It forms two classes of salts.

*Hydroisoferulic acid*,  $C_6H_3(CH_2.CH_2.COOH)(OH)^m(OCH_3)^p$ , is readily formed from the preceding acid by reduction. The pure acid forms slender colourless needles which melt at 146° to an oil which solidifies at 130°.

*Synthesis of Caffeic Acid*.—By means of the action of sodium acetate and acetic anhydride on protocatechuic aldehyde, the authors have converted the latter into a diacetocaffeic acid, identical in all respects

with that obtained by the action of acetic anhydride on caffeic acid : thus finally establishing the constitution of the latter acid.

The *diacetocaffeic acid*,  $C_6H_3(CH.CH.COOH)(OC_2H_3O^m)^2$ , crystallises in slender needles which melt at  $190-191^\circ$ . It is readily converted into caffeic acid by heating it with a solution of potassium hydrate.

C. F. C.

**The Tannin of *Ilex Paraguayensis*.** By P. N. ARATA (*Gazzetta chimica italiana*, vii, 520—530).—The tannin from Maté or Paraguay tea has hitherto been considered as identical with the caffeotannic acid from coffee, but on making a careful comparison of the two the author finds there is, in many respects, a difference between them.

I. The tannin in both cases was extracted by means of dilute alcohol, and the solution, after the addition of a little subacetate of lead and filtration, was precipitated by lead acetate. This precipitate was decomposed by sulphuretted hydrogen, the solution evaporated at  $100^\circ$ , and again dissolved and precipitated by lead acetate, &c., the operation being repeated several times.

II. The chief differences in the behaviour of the two tannins with reagents were as follows:—

	Caffeotannic acid.	Ilex tannin.
Acetate of lead ..	Bright yellow pp.	Greenish-yellow pp.
Baryta water ....	Yellow pp.	Green pp.
Gelatin solution..	Slight pp.	Abundant pp.

III. By dry distillation, caffeotannic acid gives pyrocatechin, and ilex tannin also gives a distillate having the reactions of pyrocatechin, but the crystals obtained from it are very soluble in ether, and only slightly soluble in water, whilst pyrocatechin is very soluble.

IV and V. The solubility of the two tannins in alcohol differs, the ilex tannin being much less soluble. The analytical results obtained by the author for the ilex tannin also differ from those obtained by Rochleder and by Payen for caffeotannic acid; as the carbon in the three analyses given, however, is 40.49, 50.24, and 48.30 respectively, the evidence of a difference in composition can scarcely be considered as conclusive, although they are all considerably below that obtained from caffeotannic acid (C = 56.35).

VI. Heated with a strong solution of potassium hydroxide, as in the preparation of caffeic acid from caffeotannic acid, ilex tannin yields a similar compound, but differing from caffeic acid in its reactions. The two tannins, after fusion with potassium hydrate, neutralisation with acid, and extraction with ether in the usual way, both gave crystalline products; these, however, differed somewhat, the protocatechuic acid from caffeotannic acid giving a white precipitate with silver nitrate, and a red colour with mercurous nitrate, whilst the product from the ilex tannin gave no precipitate with silver nitrate, and a yellowish colour with the mercurous salt.

VII. The ilex tannin appears to be a glucoside as, after being boiled with an acid or an alkali, the solution reduces Fehling's test: this

sugar is uncrystallisable. The author believes the tannin, when free from sugar, to be like gallotannic acid (digallic acid), a polyacid ether, or rather a mixture of polyacid ethers. C. E. G.

**Oxytoluic and Oxyphthalic Acids.** By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, xi, 374—381).—Each of the four xylenols recently described by the author yields, on fusion with potassic hydrate, an oxytoluic and an oxyphthalic acid. The present communication refers to those obtained from the liquid (1 : 3 : 4) metaxyleneol. The fused mass obtained in the above manner from (1 : 3 : 4) xyleneol was dissolved in water, saturated with hydrochloric acid, and exhausted with ether: the acids were removed from the ethereal solution by caustic soda, and precipitated from the alkaline solution by hydrochloric acid in crystalline flocks. They were separated by distillation in steam, when the oxytoluic acid passed over in the distillate, leaving the oxyphthalic acid behind. The former was purified by recrystallisation.

*Oxytoluic acid*,  $C_6H_3(CH_3)(COOH)(OH)$ .—It is easily soluble in alcohol, ether, and hot water, but only slightly in the cold. It crystallises from petroleum ether in long needles (m. p.  $149^\circ$ ). The aqueous solution of the acid or of its salts gives a deep violet-blue coloration with ferric chloride.

*Barium salt*  $(C_6H_7O_3)_2Ba \cdot 2H_2O$ , is easily soluble in water, and crystallises in large arborescent groups of plates with silvery lustre.

*Normal copper salt* decomposes easily.

The formation of the acid from (1 : 3 : 4) metaxyleneol shows that only the two following formulæ are possible, viz.:— $CH_3 : COOH : OH = (1 : 3 : 4)$ , or  $(1 : 3 : 5)$ .

The acid when heated with strong hydrochloric acid at  $180$ — $185^\circ$ , in sealed tubes was easily split up into carbonic anhydride and a cresol, which, after purification, distilled at  $200^\circ$ , and crystallised in large rhombic plates, melting at  $35^\circ$ . This cresol, on fusing with caustic potash, was oxidised to para-oxybenzoic acid (m. p.  $210^\circ$ ). This fact, together with its other properties, proves that it was paracresol, and therefore that the oxytoluic acid (m. p.  $149^\circ$ ) is represented by the first of the above formulæ. It is consequently identical with that obtained by Engelhardt and Latschinoff (*Zeitschr. f. Chem.* (1869), 622) from paracresol, and by fusing crude potassium xylolsulphate with potash. Fittica has also arrived at a similar constitution for this body (*Ber.*, vii, 928). Not para-, but ortho-cresol appears to be obtained, however, when the calcium salt of this oxytoluic acid is distilled with excess of lime. The product is an oil which solidifies to a crystalline mass melting at about  $15^\circ$ , and when oxidised by fusion with potash, yields salicylic acid, and not a trace of paraoxybenzoic acid.

The *Oxyisophthalic acid*,  $C_6H_3(OH)(COOH)_2$ , obtained together with the oxytoluic acid as above described, crystallises from its hot aqueous solution in colourless needles, and from hot dilute alcohol in small prisms. 160 parts water at  $100^\circ$  dissolve one part of the acid. It is easily soluble in alcohol, less so in ether, and not at all in chloroform. Very dilute solutions of the acid or its salts give a cherry-red color-

tion with ferric chloride, which is not destroyed by boiling or hydrochloric acid. It melts at  $284^{\circ}$  (corrected), is decomposed at  $295^{\circ}$ , and sublimes slightly at  $220^{\circ}$ .

The *sodium salt* crystallises very easily from water in long, flat needles, containing water of crystallisation, which it loses slowly and partially in dry air at the ordinary temperature, and completely at a gentle heat.

The *barium salt* crystallises in small needles.

The cadmium, cobalt, copper, and neutral and acid silver salts were also prepared.

The *dimethyl ether* crystallises from dilute methyl alcohol in large flat needles, m. p.  $96^{\circ}$ .

The *diethyl ether* crystallises from the warm aqueous solution in needles, m. p.  $52^{\circ}$ .

The *amide*,  $\text{C}_6\text{H}_3(\text{OH})(\text{CO.NH}_2)_2$  (m. p.  $250^{\circ}$ ), separates from hot alcohol in minute rhombic plates, which are difficultly soluble in hot alcohol, and almost insoluble in cold alcohol or in water.

The constitution of oxyisophthalic acid follows from that of liquid metaxylenol, *i.e.*, its side chains are in the positions 1 : 3 : 4. By treatment with strong hydrochloric acid at  $180^{\circ}$ , it forms a colouring-matter similar to aurin, which crystallises from alcohol in needles having a green metallic lustre, and giving with alkalis a red coloration.

This oxyisophthalic is doubtless identical with the orthophenoldicarboxylic acid obtained by Ost (*J. pr. Chem.* [2], xiv, 103) from salicylic and carbonic acids, also with the  $\alpha$ -oxyisophthalic acid produced by Tiemann and Reimer (*Ber.*, x, 1571) on oxidising para-aldehydo-salicylic and ortho-aldehydo-paraoxybenzoic acids, which proves therefore that the constitution of the two latter bodies is 1 : 3 : 4.

Paraxylenol, on fusion with caustic potash, yields an oxytoluic acid (m. p.  $174^{\circ}$ ) and an oxyterephthalic acid, already described by Burkhardt; whilst (1 : 2 : 4) orthoxylenol, under similar circumstances, gives an oxytoluic acid (m. p.  $198^{\circ}$ ) and an oxyphthalic acid, which is not identical with that obtained by Baeyer. The author is still investigating the nature of these products. T. C.

**Oxytoluic and Oxyphthalic Acids.** By O. JACOBSEN (*Deut. Chem. Ges. Ber.*, xi, 570—574).—By long-continued fusion with caustic potash, paraxylenol yields Burkhardt's oxyterephthalic acid (*Ber.*, x, 144) and an oxytoluic acid (m. p.  $177^{\circ}$ ) identical with that obtained by Engelhardt and Latchinoff (*Zeitschr. f. Chem.*, 1869, 623), and by Oppenheim and Pfaff (*Ber.*, viii, 889) from metacresol. The same oxytoluic acid is formed by the oxidation of metahomosalicyligenic acid. This acid must be  $\text{CH}_3 : \text{OH} : \text{COOH} = 1 : 3 : 4$ ; since it is formed both by the introduction of the carboxyl group into metacresol, and by the oxidation of one of the methyl groups in paraxylenol. By heating with hydrochloric acid at  $170^{\circ}$ , oxytoluic acid is decomposed into metacresol and carbon dioxide.

Thymol is decomposed by fusion with caustic potash into acetic, oxytoluic, and oxyterephthalic acids. Carvacrol treated in this way

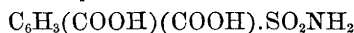


gives no acetic acid, but oxyterephthalic acid and an iso-oxy-cinnamic acid. This is a crystalline body (m. p.  $93^{\circ}$ ), which volatilises in a current of steam, and gives a reddish-violet coloration with ferric chloride.

The author thinks it probable that in this acid the groups OH, COOH, and CH<sub>3</sub> have the position 1 : 3 : 4, whilst in *metahomoparaoxybenzoic acid* they are 1 : 4 : 3.

W. C. W.

**A New Mode of Formation of  $\alpha$ -Oxyisophthalic Acid ( $\alpha$ -Phenol-dicarboxylic Acid).** By M. W. ILES and I. REMSEN (*Deut. Chem. Ges. Ber.*, xi, 579—582).—Sulphamin-isophthalic acid, obtained by oxidising para-sulphamine-toluic acid with potassium permanganate, yields when fused with potash,  $\alpha$ -phenol dicarboxylic acid, which has been described by Ost (*J. pr. Chem.*, xiv, 93, and xv, 301) and by Tiemann and Reimer (*Ber.*, x, 1571). Since  $\alpha$ -phenol dicarboxylic acid has the constitution C<sub>6</sub>H<sub>3</sub>(COOH)(COOH).OH (1 : 3 : 4), it follows that sulphamin-isophthalic acid is



(1 : 3 : 4), and parasulphamintoluic acid C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)(COOH).SO<sub>2</sub>NH<sub>2</sub> (1 : 3 : 6), and consequently the position of the side chains, CH<sub>3</sub>, CH<sub>3</sub>, and NH<sub>2</sub>SO<sub>2</sub>, in the xylenesulphamide, which melts at 95—96°, must be (1 : 3 : 6), as previously stated by the authors (*Ber.*, x, 1042), and not (1 : 3 : 2) as contested by Jacobsen (*ibid.*, xi, 17).

W. C. W.

**Behaviour of Benzoic Acid in the Organism of Birds.** By M. JAFFE (*Deut. Chem. Ges. Ber.*, x, 1925—1930).—The author confirms Shepard's result, that no hippuric acid is produced by the decomposition of benzoic acid administered to birds. The main product of the decomposition is a new body, for which the name of *ornithuric acid* is suggested. The new acid is extracted from the excrement of birds, to which benzoic acid has been administered, by boiling with alcohol, evaporating, extracting fat, &c., with ether, acidulating with sulphuric acid, and again shaking up with ether: the dark-coloured mass, which separates on cooling the ethereal liquid, is purified by a tedious process. Ornithuric acid crystallises in very small, colourless needles, insoluble in ether, soluble with difficulty in water, somewhat soluble in acetic ether, soluble in hot alcohol; the crystals melt at about 182°. The formula assigned to the acid is C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>. By the action of boiling hydrochloric acid, ornithuric acid yields benzoic acid.

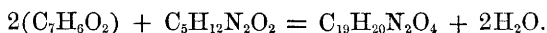
In the purification of ornithuric acid, a new base was obtained. This substance could not be perfectly purified, but from a study of its compounds with acids, it is shown to have the formula C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>. The base is a crystalline substance, with a burning taste and unpleasant odour; easily soluble in water and alcohol, yielding a strongly alkaline liquid; insoluble in ether.

Two series of crystalline salts were obtained; the following have been prepared: C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>.1½HCl: C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>.HCl: 2C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>.1½Ox.

The second and third were prepared from the first, which was itself obtained by boiling ornithuric acid with hydrochloric acid, filtering from separated benzoic acid, concentrating and treating with alcohol.

The formation of ornithuric acid is analogous to that of hippuric

acid, this compound being derived from 2 molecules of benzoic acid, and one of the base  $C_5H_{12}N_2O_2$ , with elimination of 2 molecules of water :



M. M. P. M.

**Ornithuric Acid and its Derivatives.** By M. JAFFE (*Deut. Chem. Ges. Ber.*, xi, 406—409).—Calcium and barium ornithurate are described:  $Ca(C_{19}H_{19}N_2O_4)_2$ , and  $Ba(C_{19}H_{19}N_2O_4)_2$ , respectively. The former is a crystalline salt, very slightly soluble in water, hot or cold, insoluble in alcohol and in ether. The latter forms a snow-white mass, easily soluble in water and in alcohol, insoluble in ether. The composition of these two salts shows that ornithuric acid is a monobasic acid, whilst the sparing solubility of the calcium salt and the ready solubility of the barium salt are very characteristic. For the base,  $C_5H_{12}N_2O_2$ , previously obtained by the author from birds' excrement, the name of *ornithine* is suggested.

By boiling ornithuric acid with hydrochloric acid until the whole is just dissolved, a product is obtained which the author calls *monobenzoylornithine*,  $C_{12}H_{16}N_2O_3$ , or  $C_5H_5O_2.NH_2.NHC_7H_5O$ . This body crystallises in hard, colourless needles, melting at  $225-230^\circ$ , easily soluble in water, but insoluble in alcohol and in ether.

Monobenzoylornithine forms easily soluble salts with mineral acids, by long-continued boiling with hydrochloric acid, it is decomposed into benzoic acid and ornithine. The formula formerly given for ornithine is confirmed by the preparation and analysis of the nitrate, which is a salt analogous in general properties to the chlorhydrate, crystallising in broad colourless plates. The author is inclined to regard this base as a diamido-derivative of a fatty acid, probably a diamidovaleric acid,  $C_5H_8(NH_2)_2O_2$ .  
M. M. P. M.

**Action of Chlorine on Metachloracetanilide.** By F. BEILSTEIN (*Deut. Chem. Ges. Ber.*, xi, 680).—The product of the above reaction is the compound  $C_6Cl_5.OH.Cl_2$ , which forms large crystals (m. p.  $68.5-70^\circ$ ), soluble in alcohol, benzene, and carbon bisulphide.

C. F. C.

**Action of Phosphorus Pentasulphide on Acid Amides.** By A. BERNTHSEN (*Deut. Chem. Ges. Ber.*, xi, 503).—Thiamides can be conveniently prepared by the action of phosphorus pentasulphide on amides. *Benzothianilide* is obtained by gently warming a mixture of the pentasulphide with twice its weight of benzanilid. The syrupy mass is extracted with alcohol, caustic soda is added, and the solution is poured into water. On the addition of hydrochloric acid, the benzothianilide is precipitated. In a similar way, *phenyl acetothiamide* can be prepared from phenylacetamide.  
W. C. W.

**Remarks on Bernthsen's Paper "On the Action of Phosphorus Pentasulphide on Acid Amides."** By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, xi, 504—507).—This is merely a reply to Bernthsen's complaint, that Hofmann was encroaching on his subject, and does not possess any scientific interest.  
W. C. W.

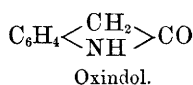
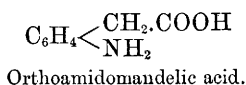
**A New Chloride of Camphor (Preliminary Notice).** By F. V. SPITZER (*Deut. Chem. Ges. Ber.*, xi, 363—364).—When finely-divided camphor is added gradually to phosphorus pentachloride, the whole being kept cool, a nearly pure dichloride of camphor is produced. It melts at 150—155°, whilst the isomeric dichloride obtained by Pfaundler melts at 70°. The author is making a complete investigation of this new substance. T. C.

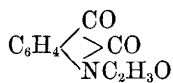
**Action of Boron Fluoride on Camphor.** By F. LANDOLPH (*Compt. rend.*, lxxxvi, 539—541).—Camphor, heated to its melting point, absorbs boron fluoride, and combines with it in equivalent proportion, forming a compound which crystallises in slender prismatic needles melting at about 70°. When this was heated in a sealed tube for 24 hours at 250°, boric acid was produced, besides liquid and gaseous products, the chief of which were:—Cymene and its polymerides; hydrocarbons belonging to the acetylene series  $C_nH_{2n-2}$ ; carbonic oxide; ethylene; and propylene. These results the author considers to point to the constitutional formula,  $C_5H_4.H_2.CO(CH_3)(C_3H_7)$ , for camphor, from which it appears that the generating hydrocarbon of camphor must be hexylene,  $C_6H_{10}$ ; and consequently there is a possibility of forming camphor synthetically from hexylene. R. R.

**Isatin and its Derivatives.** By W. SUIDA (*Deut. Chem. Ges. Ber.*, xi, 584—587).—*Acetylisin* prepared by heating isatin with twice its weight of acetic anhydride for 3—4 hours, crystallises in yellow prismatic needles, which melt at 141°. It dissolves readily in benzene and in alcohol, and splits up into isatin and acetic acid on boiling with water, or more easily with hydrochloric acid.

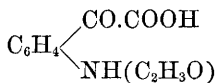
A dilute solution of potassium hydrate dissolves acetylisin, and dilute sulphuric acid precipitates acetylisinic acid from this solution. Acetylisinic acid,  $C_{10}H_9O_4N$ , is a white crystalline substance (m. p. 160°), soluble in alcohol, ether, and benzene. It forms isatin when boiled with hydrochloric acid. By the action of sodium amalgam on an acetic acid solution of acetylisinic acid, *acetylhydrindic acid*,  $C_{10}H_{11}NO_4$ , is produced. This substance forms colourless, needle-shaped crystals (m. p. 142°), which dissolve freely in water, alcohol, chloroform, and glacial acetic acid, but are insoluble in petroleum ether. This acid does not yield isatin on boiling with hydrochloric acid. Reducing agents (hydriodic acid or sodium amalgam) split up acetylhydrindic acid, forming acetic acid and oxindol.

Since acetylhydrindic acid is formed from acetylisinic acid, by the direct addition of two atoms of hydrogen, it cannot be an aldehyde, but must be identical with acetyl-orthoamidomandelic acid, and therefore bears the same relation to di-oxindol that acetylisinic acid does to isatin. The constitution of these bodies may be represented by the following formulæ:—

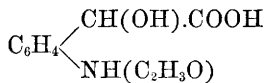




Acetylisatin.



Acetylisatic acid.

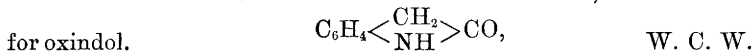


Acetylhydric acid.

Acetyloxindol begins to sublime at  $100^\circ$ , and melts at  $130^\circ$ . By adding sulphuric acid to a solution of this compound in sodium hydrate, a new crystalline body is obtained, which will form the subject of further research. W. C. W.

**Synthesis of Oxindol.** By A. BAEYER (*Deut. Chem. Ges. Ber.*, xi, 582—584).—The product of the action of tin and hydrochloric acid on a mixture of isomeric nitrophenylacetic acids, is neutralised with marble, and boiled with precipitated barium carbonate. The para- and meta-amido acids form barium salts, but the ortho-acid remains in solution in the form of an anhydride, and can be extracted with ether. This anhydride of orthoamidophenylacetic acid is identical with oxindol. It yields indol on heating with zinc dust.

This result confirms the correctness of the formula,



**Methyl Derivatives of  $\alpha$ -Naphthylamine.** By L. LANDSHOFF (*Deut. Chem. Ges. Ber.*, xi, 631—646).—It has already been shown (*Ber.*, x, 594 and 1582) that by the action of methyl chloride on aniline and toluidine, methyl substitution products of the respective bases are obtained. Its reaction with naphthylamine is somewhat different in character. By passing methyl chloride into naphthylamine at the temperature of  $150$ — $180^\circ$ , the author obtained, in addition to a methyl derivative, dinaphthylamine; the latter results from the action of naphthylamine on the naphthylamine hydrochloride which is formed in the course of the reaction. In order to identify this compound, a comparison was made between it and dinaphthylamine prepared directly from naphthylamine and naphthylamine hydrochloride, by converting them both into nitrosodinaphthylamine,  $(\text{C}_{10}\text{H}_7)_2(\text{NO})\text{N}$ . In both cases the nitroso compound was obtained as a yellow crystalline powder, melting at  $260$ — $262^\circ$ , with decomposition. Monomethylnaphthylamine,  $\text{C}_{10}\text{H}_7(\text{CH}_3)\text{HN}$  (b. p.  $293^\circ$ ), was also isolated from the product of the reaction: the acetyl derivative of this compound,  $\text{C}_{10}\text{H}_7(\text{CH}_3)(\text{C}_2\text{H}_5\text{O})\text{N}$ , crystallises in small white prisms, melting at  $90$ — $91^\circ$ , easily soluble in alcohol and ether, but with difficulty in water. By the action of methyl iodide (2 mols.) upon naphthylamine (1 mol.) dissolved in methyl alcohol, in sealed tubes at  $100^\circ$ , dimethylnaphthylamine,  $\text{C}_{10}\text{H}_7(\text{CH}_3)_2\text{N}$ , is obtained as a bright yellow oil, with a green fluorescence, boiling at  $267^\circ$ .

By heating this compound with methyl iodide for some days at  $100^\circ$ , in sealed tubes, trimethylnaphthylammonium iodide,  $\text{C}_{10}\text{H}_7(\text{CH}_3)_3\text{I}$ , is formed. This body crystallises in large, yellow needles, which are soluble in water, yielding a green solution. At  $164^\circ$  it is resolved into methyl iodide and dimethylnaphthylamine. The corresponding hydroxide, obtained by the action of silver oxide, is a powerful base, forming well crystallised salts. C. F. C.

**Formation of Xanthine Derivatives by the Action of Pancreas Ferment on Albumin.** By G. SALOMON (*Deut. Chem. Ges. Ber.*, xi, 574—576).—Hypoxanthine is formed by the action of pancreas ferment on pure blood fibrin. It is also produced in much smaller quantities, in the absence of pancreas ferment, by simple decay. Schützenberger (*Bull. Soc. Chim.*, 1874) has shown that in the decomposition of the albuminous constituents of yeast, leucine, tyrosine, xanthine, hypoxanthine, guanine, and carnine are formed.

W. C. W.

**Sulphate of Quinidine.** By J. E. DE VRIJ (*Pharm. J. Trans.* [3], viii, 745).—Pure sulphate of quinidine contains 2 molecules of water,  $2(\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2) \cdot \text{SO}_4\text{H}_2 + 2\text{H}_2\text{O}$ , as A. C. Ondemans has shown from the analysis of three different samples. The commercial sulphate, as Petit states, is, however, practically anhydrous, a sample analysed by the author containing only 0.35 per cent. water.\*

The purity of quinidine may be tested as follows:—By adding potassium iodide to a solution of the pure sulphate in 50 parts of water, a sandy crystalline precipitate is formed; and if, after leaving the liquid for some time, then filtering and adding ammonia, it remains clear, the salt may be regarded as pure; if the precipitate is resinous instead of sandy, cinchonine or cinchonidine, or perhaps both, are present; and if, after filtering and adding ammonia, only a slight turbidity is formed, the salt contains only traces of other cinchona alkaloids, and is commercially pure.

L. T. O'S.

**Quinine.** By F. A. FLÜCKIGER (*Pharm. J. Trans.* [3], viii, 885—886).—The action of light on quinine salts has been previously studied; and in order to ascertain whether the free base undergoes any change in sunlight, a clear solution of 1 part of quinine in 2,000 of water was exposed to direct sunshine in July and August, when it assumed a yellowish or brownish coloration, from which, after a few days, a flocculent brown precipitate separated, only a very small trace of alkaloid being left in solution. The change takes place when quinine dissolved in water previously freed from air by boiling, is exposed to sunlight, also on exposing a solution of quinine to the direct rays of the sun in an atmosphere of hydrogen. The author therefore considers that this substance, which he calls *quiniretin*, must have the same composition as quinine. It has no alkaline reaction, nor does it neutralise acids, in which it is freely soluble; it has a very bitter taste, and is insoluble in alcohol, ether, and water. The hydrochloric acid solution is precipitated by ammonia, but not by tannin. Nessler's solution produces a precipitate. It is dissolved by chlorine-water, the solution yielding a green precipitate when treated with ammonia. Dry quinine is not so readily transformed as when it is dissolved in water or alcohol. The other cinchona alkaloids being more sparingly soluble in water, are not so easily changed. Solutions of quinic acid, concentrated or dilute, are scarcely affected by exposure. Aqueous solutions of morphine or strychnine are only slightly coloured, whilst codeine and brucine are coloured very much. It seems that the solubility of the alkaloid plays a prominent part in the transformation, but the subject requires further investigation.

L. T. O'S.

**Veratrum Alkaloids.** By A. TOBIEN (*Pharm. J. Trans.* [3], viii, 808—810).—After a historical sketch and a detailed account of the extraction of the alkaloids from *V. lobelianum*, which contains principally a mixture of jervine and veratroidine, the author gives the following properties and reactions:—

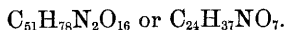
1. Jervine obtained from the nitrate by treatment with sodium carbonate solution, and subsequent crystallisation from alcohol, forms colourless needles, having the formula  $C_{13}H_{23}NO_4$ , or more closely,  $C_{27}H_{47}N_2O_8$ , but the latter cannot be correct, since the total number of nitrogen and hydrogen atoms is not an even number. It is a monacid base, insoluble in petroleum spirit, sparingly soluble in water, alkaline carbonates, and ether, more so in amyl alcohol and benzene, and freely soluble in alcohol. It is dissolved by sulphuric acid, with a yellow colour, which gradually changes to green. Hydrochloride of jervine, when heated with nitric acid, gives a rose colour, but a mixture of the concentrated acids has no effect on the free base.

2. Veratroidine is obtained from a solution in chloroform as a yellow amorphous mass, which, when treated with sulphuric acid, gives first a yellow solution, which changes to light brown, and finally to raspberry red. Concentrated hydrochloric acid gives a yellowish, rose-red coloration, which, on addition of sulphuric acid and heating, changes to brown-red.

Concentrated nitric acid dissolves veratroidine with a light yellow colour, and on treatment with sulphuric acid and heating, it changes into an orange, and finally a lemon-yellow.

The presence of veratrine will modify these reactions, but it can easily be detected by the permanent red coloration produced by heating a solution of the alkaloid in concentrated hydrochloric acid, which dissolves it in the cold without colour.

The ultimate analysis of veratroidine indicates the formula,



In its physiological action it resembles veratrine. Veratrine when treated with sulphuric acid and sugar, gives a green colour.

The composition of the veratrum alkaloids are, according to Weigelin and Tobien, as follows:—

Veratrine .....	$C_{52}H_{86}N_2O_{15}$ , W.
Veratroidine.....	$C_{51}H_{76}N_2O_{16}$ or $C_{24}H_{37}NO_7$ , T.
Sabatrine .....	$C_{51}H_{86}N_2O_{17}$ , W.
Sabadilline .....	$C_{41}H_{66}N_2O_{13}$ , W.
Jervine .....	$C_{27}H_{47}N_2O_8$ , T. ?

L. T. O'S.

**Alkaloid of Duboisia Myoporoides.** By A. W. GERRARD (*Pharm. J. Trans.* [3], viii, 787—790).—This alkaloid is obtained by mixing an aqueous extract of the bark with an equal volume of water, and adding alcohol until no further precipitation takes place. The solution is filtered, and the alcohol distilled off; the residue is then diluted with water, treated with a slight excess of ammonia, and shaken with chloroform, which dissolves the alkaloid. The solution in chloroform is evaporated, and the residue dissolved in dilute sulphuric



acid, and neutralised with ammonia, when oily drops separate out, from which the alkaloid is extracted by ether.

It is thus obtained as a yellow viscous mass, soluble in alcohol, chloroform, ether, benzene, and carbon bisulphide, but only sparingly soluble in water, to which it imparts an alkaline reaction. In its physiological, and also in some of its chemical actions, it resembles atropine.

With tannic acid and Nessler's solution it gives white precipitates, the former being soluble in hydrochloric acid; alkalis give white precipitates, soluble in excess; chlorides of platinum and gold produce yellow precipitates. Mercuric chloride precipitates concentrated solutions of the alkaloid. Concentrated nitric acid gives with duboisine a slight brown coloration; but no reaction with atropine. Concentrated sulphuric acid in the cold has no action on atropine, but on heating, it darkens in colour, and evolves an aromatic odour, which is increased by the addition of potassium dichromate, chromic oxide being precipitated. Duboisine treated in a similar manner gives, in the cold, a reddish-brown colour, and on heating, an odour of butyric acid, whilst chromate of potash is not reduced.

When boiled with baryta-water, atropine evolves an odour, which, according to the author, resembles oil of gaultheria, but according to others, of hawthorn, whereas duboisine evolves an odour of butyric acid. The free alkaloid is more soluble in water than atropine. The sulphate and hydrobromide are the only salts which crystallise. Its physiological actions resemble those of atropine. It dilates the pupil of the eye; causes dryness of the mouth, and thirst; it effectually prevents the action of muscarine on the heart, and after the lapse of some time produces tetanus.

The author proposes that it should be called duboisine, if after further research it should be found not to be identical with atropine.

L. T. O'S.

**Products of Oxidation of Cholic Acid from Ox-bile and of the Acids derived from Cholesterine.** By P. LATSCHINOFF (*Bull. Soc. Chim.* [2], xxxix, 212—213).—The author's results tend to prove that cholic and cholesteric acids are analogous, differing merely in their state of hydration. The products of oxidation of cholic acid and cholesteric acid are the same, and are formed almost in the same proportion; they consist of a small quantity of acetic acid, carbon dioxide, and the cholesteric acid,  $C_8H_{10}O_6$ , obtained by Redtenbacher as a product of the oxidation of bile. The author is of opinion that the formula for cholesteric acid ought to be  $C_9H_{12}O_6$ , or  $C_9H_{10}O_8$ , instead of  $C_8H_{10}O_8$ .

L. T. O'S.

**The Colouring Matter of Birds' Egg-shells.** By C. LIEBERMANN (*Deut. Chem. Ges. Ber.*, xi, 606—610).—The blue or green colour of birds' eggs is due to a bile pigment, which resembles biliverdin in certain respects. The shells frequently contain a second colouring matter, not a bile pigment, which exhibits a characteristic absorption spectrum.

W. C. W.

**Invertin.** By M. BARTH (*Deut. Chem. Ges. Ber.*, xi, 474—482).



—Yeast dried at a temperature not exceeding  $40^{\circ}$ , is finely powdered and heated at  $105^{\circ}$  for 6 hours. It is then well mixed with water, and left at rest for 12 hours at  $40^{\circ}$ . The aqueous extract is rapidly filtered into five times its volume of alcohol of 95 per cent., and the precipitated invertin is collected on a filter, and washed with alcohol. This crude product, after being pressed between bibulous paper, to remove the alcohol, is digested with water. The invertin dissolves, leaving an insoluble residue of albuminous matter. The addition of alcohol to the solution precipitates pure invertin, which is washed with absolute alcohol and dried *in vacuo*. 500 grams of yeast yield about 2 grams of invertin in the form of a white powder, soluble in water.

If the precipitated invertin is washed with alcohol of 95 per cent., instead of absolute alcohol, it retains water, and when dried forms a brown, horny mass, not completely soluble in water. This modification is inactive, and is identical in its properties with the invertin described by Donath (*Ber.*, viii, 795), Gunning (*ibid.*, v, 821), and Berthelot.

A solution of invertin is neutral to litmus; it precipitates lead, copper, and mercurous salts, but has no action on ferric chloride or potassium ferrocyanide, and is not rendered turbid by boiling with acetic acid. Invertin does not yield leucine on treatment with sulphuric acid.

Both the brown and the white substances contain 22 per cent. of ash, which consists chiefly of phosphates of calcium, magnesium, and potassium.

The composition of these two bodies (after deducting the ash) is—

	C.	H.	N.	S.	O.
Brown . . . . .	42.6	9.1	6.5	0.56	41.24
White . . . . .	43.9	8.4	6.0	0.63	41.17

Invertin is slower and more feeble in its action than other ferments. 5 milligrams of invertin can convert 3.8 grams of cane sugar into invert sugar in 48 hours.  
W. C. W.

**On the Nuclein of Milk.** By N. LUBAVIN (*Bull. Soc. Chim.* [2], xxxix, 213).—The nuclein of milk, according to the author, is not a phosphate of casein, but some other compound of phosphoric acid. It has the properties of a weak acid, and its lead salt, in which the relation of lead to phosphorus is as  $Pb_3$  to  $P_2$ , is obtained as a granular precipitate when lead oxalate is added to a solution of nuclein in sodium acetate.

The casein precipitated from an alkaline solution by hydrochloric acid may be obtained in fractions containing different quantities of phosphorus.  
L. T. O'S.

**Putrefaction of Elastin and Mucin.** By G. WÄLCHLI (*J. pr. Chem.* [2], xvii, 71—78).—Elastin was prepared from the neck-band of oxen by a method analogous to that adopted for preparing cellulose, viz., by successive treatment with a mixture of alcohol and ether, acetic acid, potash solution, and, finally, washing the product with water. 100 grams were mixed with 4 litres of water and 5 grams ox pancreas,

and maintained at 35° to 40° during 15 days. Deducting the amount of undecomposed elastin, it was found that 93 grams of this body yielded 1.74 grams ammonia, 8.15 grams valeric acid, 9.4 grams glyocol and leucin, besides carbon dioxide, and, as chief product, a syrupy peptone-like liquid. Elastin is thus shown to be analogous with gluten, and to belong to the protein compounds of the connective tissue.

Mucin was prepared by treating finely divided snails with hot water, precipitating the filtrate with acetic acid, and removing the fat by means of ether. The mucin was subjected to the action of pancreas at 35—40° until it was entirely dissolved: the main liquid product was a fetid oil: indol and phenol were produced, as also ammonia, butyric acid, and a substance which exerted a powerful reducing action on Fehling's solution. Unfortunately the whole of this sugar-like body was lost.

M. M. P. M.

**On the Composition of Wool.** By P. SCHUTZENBERGER (*Compt. rend.*, lxxxvi, 767—769).—The author finds that the decomposition of 100 grams of purified wool by an aqueous solution of barium hydrate (300—400 grams) at 170°, yields the following products:—

<i>Nitrogen</i> (evolved as ammonia).....	5.25
<i>Carbonic acid</i> (separated as BaCO <sub>3</sub> ).....	4.27
<i>Oxalic</i> „ (separated as BaC <sub>2</sub> O <sub>4</sub> ).....	5.72
<i>Acetic</i> „ (by distillation and titration)...	3.2
<i>Pyrrol and volatile products</i> .....	1 to 1.5
Elementary composition of fixed residue, containing leucine, tyrosine, and other nitrogenous products .....	{ C .... 47.85
	{ H .... 7.69
	{ N .... 12.63
	{ O .... 31.83
	<hr/>
	100.00

The author represents the decompositions by empirical formulæ.

C. F. C.