

Organic Chemistry.

Composition of Petroleum from the Caucasus. By P. SCHÜTZENBERGER and N. IONINE (*Compt. rend.*, **91**, 823—825).—An examination of the crude naphtha or petroleum from the Caucasus has shown that a very large portion of the oil, both of high and low boiling points, is formed of hydrocarbons of identical percentage composition, which are isomeric with the olefines, C_nH_{2n} , but sharply distinguished from them by an absence of marked chemical affinities, neither bromine, fuming sulphuric acid, nor fuming nitric acid having any action upon them in the cold. The hydrocarbons were isolated by treating the various fractions first with fuming sulphuric acid and then with nitric acid; they were afterwards washed with an alkaline solution, dried over solid potassium hydroxide, and lastly distilled from sodium. The first fraction began to boil under ordinary pressure at 112° , and the thermometer eventually rose to 230° ; the distillation was then conducted in a partial vacuum of 20 mm., when the distillate came over between 216° and 300° . The analytical numbers obtained from every fraction were almost identical, $C = 86.02$, $H = 14.10$, representing the percentage composition of the first fraction. A closer study of these hydrocarbons has enabled the authors to identify them with the bodies obtained by Wreden in hydrogenising benzene and its

homologues with hydriodic acid. Beilstein and Kurbatow had already arrived at the same conclusion, after an examination of the more volatile portions only of a similar petroleum from the Caucasus; their opinion is therefore confirmed and extended by the present work, it having been shown that not only the light but also the heavy oils possess the same characteristics.

By the action of a bright red heat, these *paraffènes*, as the authors call them, are converted into members of the benzene series, together with naphthalene and anthracene. At a lower temperature, products may be obtained which unite energetically with bromine, and are converted into resinoid polymerides by the action of concentrated sulphuric acid.

When volatilised through a red-hot iron tube, they give an abundant deposit of carbon, which quickly blocks up the tube; the deposit is uniformly impregnated with iron, and is evidently due to the action of the metal upon the hydrocarbon, since this change does not take place when a copper tube is substituted for the iron one.

Only two products of tolerably constant boiling point could be isolated; one at 220—222°, and another between 230° and 232°: the vapour-density of the latter led very nearly to the formula $C_{14}H_{28}$.

J. W.

Action of Palladium, Rhodium, and Platinum on Coal-gas. By T. WILM (*Ber.*, **14**, 874—879).—The author has studied more closely the curious action of palladium, rhodium, and platinum on coal-gas first observed by Wöhler (*Ber.*, **9**, 1713) in the case of ethylene.

If a current of coal-gas is passed over spongy palladium (reduced from the ammonium palladiochloride), heated over a Bunsen burner in a bulb-tube or small porcelain crucible, a large quantity of carbon is deposited on the inner walls of the crucible or tube, and after a time this collects over the edges of the crucible in cauliflower-like masses. This carbon, on combustion by a stronger heat, does not leave the least trace of palladium, nor does any deposition take place on the metal, which suffers no change of volume during the experiment. This action does not depend on the formation of a compound of carbon and palladium, but is due to the (?) "catalytic" action of the metal, whereby the ethylene is decomposed with deposition of carbon. The action of rhodium on coal-gas is quite different from that of palladium, for under the same circumstances not the slightest deposition of carbon takes place on the sides of the crucible or bulb-tube, as is the case with palladium, but it appears to enter into a loose combination with the rhodium, which is largely increased in volume, and assumes an appearance like tea-leaves, or the chromic oxide obtained by the ignition of ammonium chromate. On admitting air to the tube the contents begin to glow, but do not suffer any diminution in volume; when this has ceased no further combustion of carbon could be observed on passing in a current of air or oxygen. Only after cooling in oxygen and then passing in hydrogen did the glowing recommence, but still without producing any alteration in the volume of the contents of the tube. The volume left after the above treatment was

equal to three or four times that of the original metal, and was free from carbon. The composition of the mass left after the action of the coal-gas approximates to the formula RhC .

The action of platinum on coal-gas differs from that of palladium on the one hand, and of rhodium on the other. Only after a long time can any deposition of carbon be observed, which then takes place on the margin of the platinum, whilst the middle maintains its grey metallic appearance, nor does any alteration in volume occur. When the action had gone on for an hour and a half, the weight of the metal had increased by 3.28 per cent., the formula PtC requiring 5.7 per cent. C. On exposure to the air, the contents of the vessel underwent no change, but on passing a current of air over the heated mass, the carbon was completely burnt.

Platinum, therefore, appears to produce a separation of carbon by contact action, as in the case of palladium, but, unlike the latter, the carbon is deposited in the pores of the metal without changing its volume, and not on the surrounding walls of the crucible, whilst rhodium forms a loose combination with the element.

These results have, undoubtedly, an important bearing on the manufacture of platinum vessels, and appear to account for the fact, which has been frequently observed, of vessels giving way under circumstances which would be otherwise inexplicable; the effect in these cases being probably due to the presence of rhodium.

T. C.

Action of Molecular Silver on Carbon Chlorides. By H. GOLDSCHMIDT (*Ber.*, 14, 927—930).—Carbon tetrachloride is decomposed by molecular silver at 200° , forming hexachlorethane, C_2Cl_6 . Heated at 250° with an excess of water, it is split up into hydrochloric acid and carbonic anhydride, but if only a small quantity of water is taken, carbonyl chloride is produced.

Hexachlorethane is converted into tetrachlorethylene by the action of molecular silver at 280° .

From these results, the author infers that the four affinities by which the chlorine is united to the carbon-atom in carbon tetrachloride, are not equal.

W. C. W.

Double Platinocyanides. By R. SCHOLTZ (*Wien. Akad. Ber.*, 82 [2], 1233—1240).—The author has prepared and made crystallographic measurements of several double platinocyanides.

Hydroxylamine platinocyanide, $PtCy_2.(NH_3.OH.CN)_2 + 2H_2O$, crystallises in dark orange, prismatic crystals, which deliquesce rapidly in the air. The crystals exhibit a blue fluorescence, and, on heating, are decomposed with formation of platinum cyanide.

Ethylamine platinocyanide, $PtCy_2.(NH_3Et.CN)_2$, forms large colourless deliquescent crystals belonging to the tetragonal system with axial ratio $a : a : c = 1 : 1 : 0.7738$. This substance is soluble in water and alcohol.

Diethylamine platinocyanide, $PtCy_2.(NH_2Et_2.CN)_2$, forms colourless crystals of the triclinic system with axial ratio $a : b : c = 1.75 : 1 : 1.39$.

Triethylamine platinocyanide, $PtCy_2.(NHEt_3.CN)_2$, forms colourless

glistening monoclinic crystals, with axial ratio $a : b : c = 1.8014 : 1 : 0.8959$.

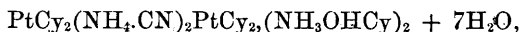
Triethylamine platinocyanide, $\text{PtCy}_2(\text{NHEt}_3\text{CN})_2$, crystallises in colourless glistening crystals (m. p. 80°) of the monoclinic system, with axial ratio $a : b : c = 1.8014 : 1 : 0.8959$.

Aniline platinocyanide, $\text{PtCy}_2(\text{NH}_3\text{Ph.CN})_2$, forms pearly leaflets, easily soluble in water. On heating it is decomposed, at first with separation of aniline, and finally leaving only a residue of platinum. The crystals are in the triclinic system, with axial ratio $a : b : c = 1.33 : 1 : 1.25$.

Paratoluidene platinocyanide, $\text{PtCy}_2(\text{NH}_3\text{C}_7\text{H}_7\text{CN})_2$, crystallises in rosy cuneiform crystals of the monoclinic system, with axial ratio $a : b : c = 0.6382 : 1 : 0.4465$.

α -*Naphthylamine platinocyanide*, $\text{PtCy}_2(\text{NH}_3\text{C}_{10}\text{H}_7\text{CN})_2$, forms greyish glassy crystals of the rhombic system, with axial ratio $a : b : c = 0.5112 : 1 : 1.2033$.

Ammonium hydroxylamine platinocyanide,



forms golden prismatic crystals, possessing a copper-like lustre.

Lithium hydroxylamine platinocyanide,



forms purple-red, prismatic hygroscopic needles with an emerald-like metallic lustre.

V. H. V.

Action of Ammonium Chloride on Glycerol. By A. ÉTARD (*Compt. rend.*, **92**, 795—797).—The crude products of the distillation of glycerol with ammonium chloride have a strongly acid reaction. When they are mixed with dilute sulphuric acid, distilled with water, and the aqueous distillate is extracted with ether, a chlorinated compound is obtained, which boils at 175° . The acids accompanying this product decompose potassium carbonate with effervescence, but the salts formed have not been isolated. On evaporation, their solution is decomposed, with formation of compounds which attack the eyes like acrolein. Complete analyses of the alkaloid previously described, which the author proposes provisionally to name *glycoline*, prove that its formula is $\text{C}_6\text{H}_{10}\text{N}_2$, and not $\text{C}_6\text{H}_9\text{NO}$, as at first supposed. The platinochloride and aurochloride have the composition $\text{C}_6\text{H}_{10}\text{N}_2 \cdot 2\text{HCl} \cdot \text{PtCl}_4$ and $\text{C}_6\text{H}_{10}\text{N}_2 \cdot \text{AuCl}_3$ respectively. The hydrochloride, $\text{C}_6\text{H}_{11}\text{N}_2\text{Cl}$, is obtained in small mammillary groups of needles, when its aqueous solution is evaporated over sulphuric acid. It is very soluble in water and alcohol, but the crystals do not deliquesce except in a very moist atmosphere. By heating glycoline with an excess of ethyl iodide at 100° for about an hour, an ethiodide, $\text{C}_6\text{H}_{10}\text{N}_2\text{EtI}$, is obtained in lemon-coloured needles, unaltered when exposed to the air, and only slightly soluble in ether, but extremely soluble in alcohol. Apparently sodium nitrite is without action on the acid sulphate of glycoline; hence the latter cannot be regarded as containing the group NH_2 . When treated with nitric acid, glycoline, as previously stated, is entirely converted into carbonic anhydride and

hydrocyanic acid, but oxidation with permanganic acid appears to proceed more regularly.
C. H. B.

Rotatory Power of Carbon Compounds. By T. THOMSEN (*Ber.*, 14, 807—808).—This is a reply to Landolt's criticism (this vol., 403) on former publications (*ibid.*, 215) by the author, in which it is shown that Landolt has entirely overlooked the chemical side of the question.
P. P. B.

Acetic Derivatives of Cellulose. By FRANCHIMONT (*Compt. rend.*, 92, 1053—1054).—On treating cellulose (Swedish filter-paper) with acetic anhydride and sulphuric acid, the author has obtained two bodies in addition to the crystalline derivatives already described by him. The first is a white powder (m. p. 232°), which dissolves readily in amyl alcohol: with hot baryta-water it gives a white precipitate, insoluble in acids and alkalis, but soluble in ammoniacal copper solution. It is found to contain—C (1) 49.12, (2) 49.21 per cent., H 5.57 per cent., acetic acid (1) 62.2, (2) 62.5 per cent. The author assigns no formula to the substance.

The second body is insoluble in amyl alcohol, but dissolves in boiling acetic acid, from which solution it is precipitated as a jelly on adding water. Its melting point is indefinite, and it blackens at a high temperature.
J. I. W.

Ethyl Peroxide. By BERTHELOT (*Compt. rend.*, 92, 895—897).—Ethyl peroxide is obtained by passing a slow current of perfectly dry and strongly ozonised oxygen over anhydrous ether. The ozone is gradually, although incompletely, absorbed, and a dense syrupy liquid is formed, which becomes viscous, but does not solidify at -40° . When heated it distils partially, but finally decomposes with a violent explosion. It is dissolved by water, and is at the same time decomposed into alcohol and hydrogen peroxide. The aqueous solution behaves with potassium permanganate and dichromate and other reagents, like a solution of hydrogen peroxide. Estimation of the amount of hydrogen peroxide formed by its decomposition showed that the composition of ethyl peroxide is Et_4O_3 . The reaction with water may be represented by the equation $\text{Et}_4\text{O}_3 + 3\text{H}_2\text{O} = 4\text{EtHO} + \text{H}_2\text{O}_2$. This production of ethyl peroxide by the direct action of ozone furnishes a method of preparing hydrogen peroxide by means of the latter.
C. H. B.

Action of Phosphorus Pentachloride on Isobutaldehyde. By S. ECONOMIDÉS (*Compt. rend.*, 92, 884—886).—The action of phosphorus pentachloride on isobutaldehyde at ordinary temperatures gives rise to monochlorisobutylene and isobutylene dichloride, the latter being formed in larger quantity. *Monochlorisobutylene*, $\text{Me}_2\text{C}:\text{CHCl}$, is a limpid colourless liquid, with an agreeable odour; sp. gr. at 12° = 0.9785; b. p. = $66-70^{\circ}$; vapour density, 89.7. The same compound is formed in small quantity when dichlorisobutylene is treated with alcoholic potash. The liquid thus obtained has an odour resembling that of fennel, and somewhat different from that of

the monochlorisobutylene. *Isobutylene dichloride*, $C_4H_6Cl_2$, is a colourless liquid, with an agreeable odour; b. p. $103-105^\circ$; sp. gr. at $12^\circ = 1.0111$; vapour density, 127. It cannot be distilled without partial decomposition. When this compound is heated at 180° with twice its weight of aqueous ammonia, there is formed, together with other chlorinated compounds, pure monochlorisobutylene boiling at $65-68^\circ$, and having an odour of fennel. When exposed to moist air, it deposits a white crystalline substance. The action of aqueous or alcoholic ammonia on the isobutylene dichloride also gives rise to certain bases not yet isolated.

C. H. B.

Condensation-products of Aldehydes and their Derivatives.

By A. LIEBEN and S. ZIESEL (*Wien. Akad. Ber.* [2], **82**, 960—981).—*Crotonaldehyde and its derivatives* (see also this Journal, **36**, 615).—The crotonaldehyde used in these experiments was prepared by heating 1 vol. of a concentrated solution of sodium acetate with about 10 vols. of aldehyde in a sealed tube for 24 hours at 100° , and separating the crotonaldehyde by fractional distillation. On warming with a concentrated solution of sodium hydrogen sulphite, crotonaldehyde dissolves, and on cooling a crystalline magma of the sulphite compound is formed, but the aldehyde cannot be separated from this by distilling with sodium carbonate. The acrolein compound behaves in a similar manner; this peculiarity is to be investigated.

Crotonaldehyde combines directly with two atoms of bromine, forming a heavy oil, which neither distils without decomposition, nor solidifies even when cooled to -35° , and on standing turns dark and evolves hydrobromic acid. It forms a bisulphite, thus showing an aldehyde character, and is perhaps dibromobutaldehyde. Of several methods tried for the reduction of crotonaldehyde, digestion with acetic acid and iron filings was found to be the best. On distillation, an oil is obtained, which consists of normal butyraldehyde, normal butyl alcohol, and crotonyl alcohol. The aldehyde may be removed by treatment with hydrogen sodium sulphite, and the two alcohols separated by means of bromine, which leaves the butyl alcohol unattacked. By distilling under 50 mm. pressure, the butyl alcohol passes over at 56° . The crotonyl alcohol is separated with greater difficulty. The brominated compound left in the residue is treated with sodium-amalgam in presence of water, then distilled, digested with potash and lime, and repeatedly distilled over sodium. The crotonyl alcohol thus obtained contains about 10 per cent. of butyl alcohol (b. p. $117.5-120^\circ$); its odour somewhat resembles that of allyl alcohol, but is not so unpleasant; it combines readily with bromine.

The alcohol mixture contains about 88.36 per cent. crotonyl alcohol. By the action of hydriodic acid or iodine and phosphorus on the mixture of alcohols (boiling at 117°) at the ordinary temperature of the air, a product boiling at $124-129^\circ$ is obtained, which is shown, by V. Meyer's reaction, to be a mixture of normal and secondary butyl iodide; the latter is the product of the action of hydriodic acid on crotonyl alcohol. By boiling the above-mentioned brominated mixture with excess of water, then distilling off about two-thirds of the whole to get rid of butyl alcohol and an aldehyde, and treating with lead

oxide to remove hydrobromic acid, a liquid is obtained, which, on evaporating, leaves butenylglycerol as a thick yellow liquid. It has a sweet taste, distils at $172\text{--}175^\circ$ (uncorr.) under 27 mm., with slight decomposition; it does not crystallise, and, in a freezing mixture of solid carbonic anhydride and ether, turns to a vitreous mass. Its triacetin, $\text{C}_4\text{H}_7(\text{AcO})_3$, made by heating the glycerol with acetic anhydride at 150° for 20 hours, distils at $153\text{--}155^\circ$ (uncorr.) under 27 mm., and boils under 740.2 mm. at 261.8° (corr.); it is a thick, colourless liquid, not miscible with water, with a feeble but pleasant odour. On treating the glycerol with fuming hydriodic acid, even in the cold, iodine separates out, and by digesting for 6 hours at 100° in a sealed tube, secondary butyl iodide is formed, whilst with phosphorus and iodine it yields crotonyl iodide, a yellow oil (b. p. $131\text{--}133^\circ$), with odour somewhat like allyl iodide. On shaking with mercury it yields a body, crystallising from absolute alcohol in white crystals, which very quickly turn yellow. This butenylglycerol, when heated to about 255° with oxalic acid containing 0.5 per cent. of both ammonium and sodium chlorides, employing Tollens' method, yields crotonyl alcohol along with carbonic oxide and formic acid.

D. A. L.

Preparation of Isobutylal. By S. ECONOMIDÉS (*Compt. rend.*, **92**, 886).—A current of hydrochloric acid gas is passed through a well-cooled mixture of equal parts of isobutaldehyde and absolute alcohol. The upper layer of liquid which separates out is washed with water, dried over potassium carbonate, and heated with sodium ethylate until no more sodium chloride is formed. The isobutylal is then separated by addition of water. It is a colourless liquid (b. p. $134\text{--}136^\circ$), with an odour recalling that of essence of fennel. Sp. gr. at $12.4 = 0.9957$; vapour density, 143.5.

C. H. B.

Production of Crotonyl Chloral. By A. LIEBEN and S. ZIESEL (*Wien. Akad. Ber.* [2], **82**, 982—985).—The method of reduction mentioned on p. 710 is employed in this case also, the quantities used being 1 part crotonyl chloral, 4 parts iron filings, and 8 parts of 50 per cent. acetic acid. With exception of a small quantity of a body boiling at $157\text{--}160^\circ$, and containing 28.02 per cent. chlorine, the products are the same, namely, normal butyl alcohol, crotonyl alcohol, and normal butaldehyde. Sarnow (*Annalen*, **164**, 93), by a partial reduction of crotonyl chloral, obtained monochlorcrotonaldehyde and crotonyl alcohol.

D. A. L.

Formation of Acetone and Thiacetone. By W. SPRING (*Ber.*, **14**, 758—760).—Propidene dichloride, CCl_2Me_2 , when heated with silver acetate and alcohol in sealed vessels at 100° , yields acetone, acetic anhydride, and silver chloride. This dichloride is decomposed by sodium thioacetate in a similar manner, yielding sodium chloride and a thiabetic ether, $\text{CMe}_2(\text{AcS})_2$. The latter yields thiacetone when heated.

P. P. B.

New Method of Brominating Organic Acids. By C. HELL (*Ber.*, **14**, 891—893).—This consists in first converting the acid into

its anhydride or bromide, which are very much more easily brominated than the acid itself, and then submitting these to the action of bromine.

T. C.

Compound of Calcium Chloride with the Fatty Acids. By A. LIMBEN (*Wien. Akad. Ber.*, **82**, [2], 1255—1283).—The author and G. Janecek (*Annalen*, **187**, 132) have already indicated the existence of crystalline compounds of calcium chloride with several of the fatty acids. In the present research, he has investigated the combinations of calcium chloride, butyric acid, and water, the nature of which depends on the condition of the experiment. Allusion is also made to the readiness with which the compounds decompose, whether by heat, or by absorption of moisture when exposed even for a short time to the air. In order to purify the crystals from the mother-liquors it was found necessary to wash them with dry butyric acid, and to dry them on a porous plate over sulphuric acid.

Compound of Butyric Acid, Calcium Chloride, and Water.—On the addition of a few drops of water to a saturated solution of calcium chloride in butyric acid, a white voluminous precipitate is thrown down which after some time assumes a crystalline form. The compound after purification has the composition $\text{CaCl}_2 + 2\text{C}_4\text{H}_8\text{O}_2 + 2\text{H}_2\text{O}$.

Compound of Butyric Acid, Calcium Chloride, and Butyrate.—On evaporating a saturated solution of calcium chloride in butyric acid in a vacuum, crystalline needles separate out having the composition—



the sides of the flask are at the same time covered with a milk-white efflorescence of the compound. The author does not consider that the formation of calcium butyrate is due to an impurity of lime in the calcium chloride, but to the decomposition of the calcium chloride. When this dissolves in the butyric acid, incipient decomposition ensues, with liberation of hydrochloric acid, which remains dissolved in the butyric acid, and prevents the action going further until it is removed by boiling the solution or evaporating it over lime.

Compound of Calcium Chloride with Butyric Acid.—The crystals of $\text{CaCl}_2 + 2\text{C}_4\text{H}_8\text{O}_2 + 2\text{H}_2\text{O}$, obtained by the process mentioned above, when kept for several months over sulphuric acid, lose all their water and part of the butyric acid. They are thus converted into a fine delicate milk-white powder of composition $\text{CaCl}_2 + \text{C}_4\text{H}_8\text{O}_2$.

The probable existence of a whole series of such compounds is pointed out by the author.

V. H. V.

β -Iodolactic Acid. By MELIKOFF (*Ber.*, **14**, 937—939).—Hydriodic acid, like hydrochloric and hydrobromic acids, combines directly with glycidic acid. In this case, β -iodolactic acid is formed. This acid crystallises in transparent prisms, freely soluble in water, alcohol, and ether. β -Iodolactic acid melts at 101° ; the chloro- and bromo-lactic acids melt at 79° and 90° respectively. Alcoholic potash converts β -iodolactic acid into glycidic acid. Zinc β -iodolactate forms a crystalline powder; the calcium salt is amorphous and the silver salt is very unstable.

Zinc glycidate, $\text{Zn}(\text{C}_3\text{H}_2\text{O}_3)_2 + \text{H}_2\text{O}$, is amorphous; ammonium glycidate can be obtained in prismatic crystals which are easily soluble in water. W. C. W.

Amido-acids derived from Iso-hydroxyvaleric Acid. By E. DUVILLIER (*Ann. Chim. Phys.* [5], **21**, 433–448).—The methyl, ethyl, and phenyl amido-derivatives of hydroxybutyric acid have been already described: in the present paper the author gives the details of his work on iso-hydroxyvaleric acid.

Methylamidovaleric acid, $\text{CHMe}_2\text{CH}(\text{NHMe}).\text{COOH}$, was obtained by adding a pure concentrated solution of methylamine to bromovaleric acid. It is a crystalline substance, soluble in water and alcohol, but insoluble in ether. It is neutral to litmus, and has a slightly sweet taste. The pure acid may be heated to 120° without alteration, but at a higher temperature it sublimes without melting or blackening; it nevertheless undergoes at the same time a partial decomposition.

The sulphate, hydrochloride, platinochloride, and aurochloride were prepared and analysed; they present no characteristics requiring special mention.

Ethylamidovaleric acid, $\text{CHMe}_2\text{CH}(\text{NHEt}).\text{COOH}$, and its salts were prepared by the use of ethylamine, in the same manner as the methyl-derivatives: they resemble the latter so closely that it is practically impossible to distinguish between them, except by ultimate analysis.

By the action of an ethereal solution of aniline on bromovaleric acid, *phenylamidovaleric acid* was obtained, $\text{CHMe}_2\text{CH}(\text{NHPh}).\text{COOH}$. The mixture requires to be heated in an oil-bath at 130° , after which it is washed with water to remove the aniline hydrobromide which is formed. The amido-acid occurs as a viscid mass, insoluble in cold water, but which by crystallisation from boiling water can be obtained in the form of brilliant colourless needles, becoming brown by exposure to light. Heated above 110° , it first melts and finally sublimes with partial decomposition.

It may be distinguished from its methyl and ethyl analogues by the fact that its aqueous solution reduces solutions of silver and mercurous nitrates. Phenylamidovaleric acid dissolves easily in dilute hydrochloric acid, and the solution when evaporated in a vacuum deposits crystals of the hydrochloride in radiated mammillary groups. The hydrochloride is anhydrous, soluble in water and alcohol, but insoluble in ether. J. W.

Iron Oxalates and some of their Double Salts. By J. M. EDER and E. VALENTA (*Wien. Akad. Ber.*, **82**, 614–627).—*Ferric oxalate* in solution was found to have the constitution $\text{Fe}_2(\text{C}_2\text{O}_4)_3$. It may be prepared by digesting freshly precipitated ferric hydrate with oxalic acid, light being excluded. It forms a greenish-yellow solution, in which alcohol does not cause a precipitate. It cannot be obtained in a crystalline form.

Basic Ferric Oxalates.—On mixing solutions of ferric salts and ammonium oxalate, a red-brown precipitate was obtained, especially on

adding alcohol, after repeated washings with which, and drying at 100° , it has the composition $\text{Fe}_2(\text{C}_2\text{O}_4)_3 + \text{Fe}_2(\text{OH})_6 + 4\text{H}_2\text{O}$. This oxalate when heated with water, gives up oxalic acid, and yields $\text{Fe}_2(\text{C}_2\text{O}_4)_3 + 9\text{Fe}_2(\text{OH})_6$.

Normal *potassium ferric oxalate*, $\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{K}_6 + 6\text{H}_2\text{O}$, agrees in properties with the salt described by Busz. A potassium ferric oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3\text{K}_2 \cdot 5\text{H}_2\text{O}$, of an olive-brown colour, seems to have the same relation to the above green salt as the red chromium potassium oxalate to the green one.

Normal *sodium ferric oxalate* has the composition $\text{Fe}_3(\text{C}_2\text{O}_4)_3\text{Na}_6 + 11\text{H}_2\text{O}$, and normal *ammonium ferric oxalate*, $\text{Fe}_2(\text{C}_2\text{O}_4)_3(\text{NH}_4)_6 + 8\text{H}_2\text{O}$, forms bright green crystals permanent in the air.

Ferrous oxalate is permanent in the air even when in a moist condition, but is very rapidly oxidised in the presence of alkalis. It is soluble in 5,000 parts of water at 15° , but is soluble in 29 parts of a 14 per cent. solution of ferric oxalate at 15°C . *Potassium ferrous oxalate*, $\text{Fe}(\text{C}_2\text{O}_4)_2\text{K}_2 + \text{H}_2\text{O}$, form small golden-yellow crystals almost permanent in the air when dry, but oxidising rapidly in a moist condition. *Ammonium ferrous oxalate*, $\text{Fe}(\text{C}_2\text{O}_4)_2(\text{NH}_4)_2 + 3\text{H}_2\text{O}$, is very similar to the potassium salt.

It is partially decomposed by water.

A corresponding sodium salt has not yet been obtained in a pure state, sodium oxalate separating on crystallising. W. R. H.

Tartronic Acid. By C. BÖTTINGER (*Ber.*, **14**, 729—730).—Tartronic acid is obtained from glyoxylic acid in the same manner as oxyethylidenesuccinic acid is from pyroracemic acid (*Ber.*, **14**, 87, and this vol., 234), viz., by treating finely powdered potassium cyanide with glyoxylic acid and boiling the product with baryta water. A mixture of barium carbonate and tartronate is thus formed, from which tartronic acid is obtained by decomposing it with sulphuric acid. The author finds the melting point to be 183° and not 175° , as is usually stated, and regards it as probable that by heat the tartronic acid is first converted into glycollide, which melts at 180° .

P. P. B.

Action of Zinc Ethyl on Ethyl Tartrate. By E. MULDER and H. G. L. v. DER MEULEN (*Ber.*, **14**, 918—919).—If ethyl tartrate is slowly added to zinc ethyl diluted with absolute ether, a gelatinous mass is produced, which when dried, forms a white amorphous powder

of the composition $\text{Zn} \begin{cases} \text{O.CH.COOEt} \\ | \\ \text{O.CH.COOEt} \end{cases}$

W. C. W.

Tanatar's Trioxymaleic Acid. By A. KÉKULÉ and R. ANSCHÜTZ (*Ber.*, **14**, 713—717).—This acid which Tanatar obtains by the oxidation of maleic acid, the authors show, from the properties of its calcium salt, to be inactive tartaric acid.

P. P. B.

Derivatives of Pyromucic Acid. By O. WALLACH (*Ber.*, **14**, 751—754).—Pyromucamide ($\text{C}_4\text{H}_3\text{O}$). CONH_2 (m. p. 140 — 142°), like benzamide, is converted by phosphorus pentachloride into the correspond-

ing nitril, viz., *furfuronitril* (C_4H_3O).CN, a colourless liquid (b. p. $146-148^\circ$), turning brown on exposure to the air. It is converted into a base by nascent hydrogen, probably furfonylamine.

Pyromucethylamide (C_4H_3O).CO.NHEt, obtained by the action of ethylamine on ethyl pyromucate is a thick, mobile, colourless oil (b. p. 258°). Phosphorus pentachloride converts it into a crystalline chloride (C_4H_3O).CCl₃.NHEt, which is volatile with but slight decomposition.

Ethylamine pyromucate when distilled with phosphorus pentachloride yields *pyromucyl chloride*, a pungent smelling liquid (b. p. $160-180^\circ$). On treating the residue with potassium hydroxide, it yields a base boiling above 200° , the platinochloride of which has the formula $[C_9H_{14}N_2(OH)Cl]_2PtCl_4$, and hence the base is an amidine having the formula (C_4H_3O).CNEt.NHEt.

Analysis of Platinum Salts.—To determine the platinum and chlorine in such a salt, the salt is evaporated in a water-bath with a concentrated solution of sodium ethylate representing 1 gram of sodium. It is further heated by a naked flame, and the alcohol ignited and allowed to burn. After the flame is extinguished, the heating is continued and a residue obtained consisting of sodium carbonate and chloride, platinum and carbon. When cold, the chlorine and platinum are determined in this by the usual methods. P. P. B.

A Compound of Thiocyanacetic Acid and Carbaminthioglycollic Acid. By P. CLAESSON (*Ber.*, **14**, 731—732).—Thiocyanacetic acid in presence of a small quantity of water is converted into a solid, which was formerly regarded as a polymeride (*Ber.*, **10**, 1346). This substance, however, proves to be a compound of thiocyanacetic acid and carbaminthioglycollic acid, and to it the author attributes the following constitution: $NH : C < \begin{matrix} S.CH_2.COOH \\ NH.COS.CH_2.COOH \end{matrix}$, and is therefore carbamido-carbaminthioglycollic acid. Its constitution is similar to Nencki and Jäger's phenylcarbodiimidothioglycollic acid (*J. pr. Chem.* [2], **16**, 17). It is soluble in hot water, and insoluble in cold. By boiling with hydrochloric acid it is resolved into thioglycollic acid, carbonic anhydride, and ammonia. It melts and decomposes at 149° . It reacts with alkaline carbonates forming carbaminthioglycollic acid, and with metallic salts yields metallic thioglycollates, carbonic anhydride and ammonia, as do both thiocyanacetic and carbaminthioglycollic acids. P. P. B.

Thiocyanuracetic Acid. By P. CLAESSON (*Ber.*, **14**, 732—734).—On distilling ethyl thiocyanacetate it is decomposed, and from the residue Heintz (*Annalen*, **136**, 223) obtained a crystalline compound, which is a polymeride of ethyl thiocyanacetate, and is styled by the author ethyl thiocyanuracetate. It crystallises from ether in beautiful needles (m. p. 81°); it is converted by alcoholic potash into the potassium salt, which is easily soluble in water, but insoluble in alcohol and concentrated potassium hydroxide.

Thiocyanuracetic acid is obtained by acidifying the solution of the potassium salt; it crystallises in needles (m. p. 199.5°), which are

soluble in alcohol and ether. The salts with the exception of those of the alkali metals are insoluble or only sparingly soluble. It is a tribasic acid. The neutral barium salt obtained by adding barium chloride to a solution of the potassium salt, crystallises in sparingly soluble prisms, containing 6 mols. H_2O . The di-acid barium salt is obtained by heating a mixture of barium chloride and potassium thiocyanurate with acetic acid; it crystallises in large prisms containing 2 mols. H_2O . When thiocyanuracetic acid is heated with hydrochloric acid, it is resolved into cyanuric and thioglycollic acids.

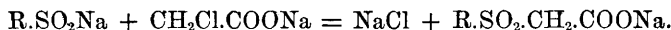
Amongst the products of the decomposition of ethyl thiocyanacetate, the following have been found: alcohol, ether, carbon bisulphide, ethyl thioglycollate, thiocyanacetyl, ethylcarbylamine, and cyanogen gas.

P. P. B.

Action of Sulphuric Acid on Acetic Anhydride. By FRANCHIMONT (*Compt. rend.*, **92**, 1054—1056).—When acetic anhydride and sulphuric acid are mixed in molecular proportions, and the mixture, after remaining at rest for some time is heated to 130° , and when cold dissolved in water, almost the whole of the sulphuric acid enters into combination with the acetic anhydride, and forms sulphacetic acid. The author states that it appears as if an acetylsulphuric acid were first formed and this, on treatment with water, decomposed, with formation of sulphacetic acid. He proposes further to investigate the matter.

J. I. W.

Sulphonacetic Acids. By S. GABRIEL (*Ber.*, **14**, 833—834).—The synthesis of these acids can be effected by acting on sodium chloracetate with the sodium salt of a sulphinic acid, thus:



The fact that the acids so obtained are identical with those formed by the oxidation of thioacetic acids, confirms Otto's views of the constitution of the sulphinic acids (this Journal, 1880, 810).

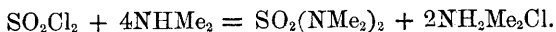
Phenylsulphonacetic acid, $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{COOH}$, is obtained by dissolving 1 mol. benzenesulphinic acid and 1 mol. of chloracetic acid in water, neutralising with potassium hydroxide and heating the resulting liquid; after the separation of sodium chloride, the syrupy mass is evaporated to dryness on a water-bath. The free acid is obtained by decomposing the sodium salt with hydrochloric acid, and extracting with ether. The acid is easily soluble in alcohol and ether, and crystallises from hot benzene in colourless needles (m. p. $110-111^\circ$). It is identical with the acid obtained by Claesson by oxidising phenylthioacetic acid.

Paratoluenesulphonacetic acid, $\text{C}_7\text{H}_7\text{SO}_2\text{CH}_2\text{COOH}$, is prepared in a similar manner from paratoluenesulphinic acid. It is sparingly soluble in hot water, and crystallises from benzene in small crystals (m. p. $117-118.5^\circ$). Its silver salt is obtained in shining, rhombic tablets by adding silver nitrate to the solution of its ammonium salt.

P. P. B.

Action of Sulphuryl Chloride on Dimethylamine. By R. BEHREND (*Ber.*, **14**, 722—723).—A cold solution of dimethylamine in

chloroform reacts with a similar solution of sulphuric dichloride, producing tetramethylsulphamide, as follows :—



Tetramethylsulphamide is sparingly soluble in water, but soluble in alcohol, ether, and benzene; it crystallises from alcohol in colourless well-formed tablets (m. p. 73°), and may be sublimed without decomposition. When it is boiled with potassium hydroxide, the tetramethylsulphamide decomposes with evolution of dimethylamine.

Sulphuric dichloride reacts on the amido-bases of the aromatic series, producing chloro-substitution products. P. P. B.

Phosphorus Betaines. By E. A. LETTS (*Proc. Roy. Soc. Edin.*, **11**, 40—46).—The researches were instituted to determine whether the compounds of thetine would show greater analogies to the phosphobetaines than to the compounds of betaine itself.

The action of chloracetic acid on triethylphosphine forms triethylphosphobetaine, $\text{PEt}_3\text{Cl} \cdot \text{CH}_2\text{COOH}$, which is not deliquescent; it has an acid reaction, and forms a well-defined platinumchloride, sulphate, and base. The anhydrous base is obtained by exposure in a vacuum for some months.

Ethyl chloracetate and triethylphosphine form a brown syrup; the platinumchloride has the composition $(\text{C}_6\text{H}_{17}\text{PO}_3\text{EtCl})_2\text{PtCl}_4$, and this ethylchloride of triethylphosphobetaine is decomposed by silver oxide, the anhydrous base before referred to being produced. The ethylbromide and ethiodide have also been prepared; the compounds of phosphobetaine like the oxy-salts of dimethylthetine, yield carbonic anhydride when heated. The experiments described prove a close analogy to exist between the compounds of phosphobetaine and of thetine; but these analogies do not exist between these two substances and the corresponding nitrogen compound betaine, for the salts of the latter when heated, either volatilise unchanged, or dissociate into trimethylamine and a derivative of acetic acid.

E. W. P.

Substituted Oxamides, Formamides, and Diethyloxamic Acid. By O. WALLACH (*Ber.*, **14**, 735—751).—Former experiments have shown that the amides of oxalic acid are easily converted into bases, by the action of phosphorus pentachloride; the following is an account of the preparation of di-substituted oxamides and the products obtained from them by the action of phosphorus pentachloride.

Isodiethyl oxamide, $\text{Et}_2\text{N} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$, obtained by the action of ammonia on ethylic diethyloxamate (b. p. 253 — 254°), crystallises in well-formed transparent crystals (m. p. 126° , b. p. 266 — 268°), and sublimes at 100° . Phosphorus pentachloride acts on this body, and the resinous product yields the base chloroxyethylene, $\text{C}_6\text{H}_5\text{ClN}$, which is also obtained from the symmetrical diethyloxamide $(\text{CO} \cdot \text{NH} \cdot \text{Et})_2$. (*This Journal*, 1877, **11**, 184.)

Diethylcarbamine cyanide, $\text{CN} \cdot \text{CO} \cdot \text{NEt}_2$, is obtained by heating isodiethyloxamide with phosphoric anhydride; it is a colourless liquid (b. p. 219 — 220°), lighter than water, volatile in steam. By the action of phosphorus pentachloride, it is also converted into chlor-

oxaethylene. Its formation is explained as follows: The first product is the chloride $\text{CN.CCl}_2.\text{NEt}_2$, which when heated loses ethyl chloride, and is converted into $\text{CN.CCl}:\text{NEt}$, with which the ethyl chloride unites to form $(\text{CCl}:\text{NEt})_2$; by the action of heat, this is converted into chloroxaethylene and hydrochloric acid. The formation of this base from iso-diethyloxamide is now easily understood, inasmuch as the first product, viz., $\text{NH}_2.\text{CCl}_2.\text{CCl}_2.\text{NEt}_2$, would, by loss of hydrochloric acid, be converted into the chloride of diethylcarbamine cyanide. It would thus appear that the unsymmetrical di-substituted oxamides are not likely to yield any clue to the formation of bases from the oxamides.

Diphenyloxamide, $(\text{CO.NHPh})_2$, is converted by phosphorus pentachloride into a chloride which forms a thio-compound with sulphuretted hydrogen (this Journal, **36**, 784; **38**, 556); when heated, it yields no base, a fact attributed to the presence of two aromatic nuclei.

Ethylphenyloxamide, EtHN.CO.CO.NHPh , is converted into a chloride by the action of phosphorus pentachloride. The chloride is converted by sulphuretted hydrogen into a thiamide, NHEt.CS.CS.NHPh , which crystallises in red tabular crystals (m. p. $36-37^\circ$), and is soluble in ether and chloroform. When heated by itself, the chloride loses hydrochloric acid and is converted into a base, $\text{C}_{10}\text{H}_9\text{ClN}$.

Monethyloxamide and *monophenyloxamide* do not yield bases when treated with phosphorus pentachloride.

Triethyloxamide, NHEt.CO.CO.NEt_2 , is obtained by the action of aqueous ethylamine on ethyl diethyloxamate; it is a liquid miscible with water, volatile in steam, and boiling at $257-259^\circ$; phosphorus pentachloride converts it into resinous products.

Attempts to prepare tetrethylloxamide by the action of diethylamine on ethylic diethyloxamate, and by the action of heat on the salt of diethylamine and diethyloxamic acid, led to negative results.

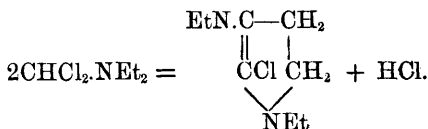
For the preparation of diethyloxamic acid, the author recommends that instead of decomposing ethyl diethyloxamate with potassium hydroxide, as recommended by Heintz (*Annalen*, **127**, 53), a solution of sodium ethylate should be employed. The author finds that diethyloxamic acid melts at $99-101^\circ$, and not at 80° , as stated by Heintz (*loc. cit.*).

Diethylamine diethyloxamate, $\text{NEt}_2.\text{CO.COONH}_2\text{Et}_2$, is obtained by dissolving diethyloxamic acid in diethylamine, or by mixing the alcoholic solutions of these compounds. It is decomposed by dry distillation into diethylamine and *diethylformamide*, HCO.NEt_2 . Since diethyloxamic acid when heated above its melting point is resolved into carbonic anhydride and diethylformamide, the formation of the latter compound in the above case is explained by the dissociation of the salt into diethylamine and diethyloxamic acid, which latter is converted into diethylformamide, thus: $\text{NEt}_2.\text{CO.COOH} = \text{HCO.NEt}_2 + \text{CO}_2$.

The author confirms Linnemann's observations (*Chem. Centr.*, 1880, 139), regarding the properties of diethylformamide; further, it is observed that this compound has basic properties; a platinumchloride, $[\text{HCO.NEt}_2\text{HCl}]_2.\text{PtCl}_4$, was obtained, by adding platinum chloride to the solution obtained by passing hydrochloric acid gas into the ethereal solution of the formamide.

Chloride of diethyloxamic acid, $\text{NEt}_2\text{CO}\cdot\text{COCl}$, is formed when phosphorus pentachloride reacts with diethyloxamic acid at low temperatures. Its existence is shown by the fact that when the product of the reaction is dissolved in ether and treated with ammonia, isodiethyloxamide is obtained. Attempts to prepare tetraethyloxamide by substituting diethylamine for ammonia in the above reaction, led to negative results. This chloride when heated is resolved into diethylcarbamic chloride, $\text{NEt}_2\cdot\text{COCl}$, and carbonic oxide. Hence the former is the product of the action of phosphorus pentachloride on diethyloxamic acid when heat is employed to remove the phosphorus oxychloride. *Diethylcarbamic chloride* is a liquid boiling at $190-195^\circ$, it belongs to the "urea-chlorides" described by Michler (*Ber.*, **8**, 1866; **9**, 396 and 710); when exposed to the air it combines with water to form carbonic anhydride and diethylamine hydrochloride, thus: $\text{NEt}_2\cdot\text{COCl} + \text{H}_2\text{O} = \text{CO}_2 + \text{NEt}_2\text{H}\cdot\text{Cl}$. Further, diethylamine converts it into tetrethylurea $\text{CO}(\text{NEt}_2)_2$ (Michler, *Ber.*, **8**, 1665).

Phosphorus pentachloride acts on *diethylformamide*, and after removal of phosphorus oxychloride by distillation under reduced pressure, the residue consists of the hydrochloride of a base having the composition $\text{C}_{10}\text{H}_{19}\text{ClN}_2$, as deduced from that of its platinumchloride $(\text{C}_{10}\text{H}_{19}\text{ClN}_2\cdot\text{HCl})_2\text{PtCl}_4$. The free base is a transparent liquid, which is decomposed by heat, with the formation of a derivative of pyrroline, shown by the production from it of pyrrol red. The formation of this base and its relation to pyrroline is expressed by the following equation:—



P. P. B.

Action of Ozone, Nascent Oxygen, and Hydrogen Peroxide on Benzene. By A. R. LEEDS (*Ber.*, **14**, 975—977).—Benzene is oxidised by ozone with formation of carbonic, oxalic, formic, and acetic acids: the explosive ozobenzene described by Houzeau and Renard (*Compt. rend.*, **76**, 572) was not obtained. When benzene is exposed to air which is in contact with moist phosphorus, phenyl and oxalic acid are produced, if the reaction takes place in direct sunlight; but in diffused light only oxalic acid is obtained. Hoppe-Seyler (*Ber.*, **12**, 1551, this Journal, 1880, Abstr., 3), has shown that phenol is produced when the alloy of hydrogen and palladium is shaken with air, water, and benzene. Benzene is also converted into phenol by boiling with a dilute solution of hydrogen peroxide. W. C. W.

Researches on Isomerism: Benzene and Dipropargyl. By BERTHELOT and OGIER (*Compt. rend.*, **91**, 781—787).—L. Henry, of Louvain, the discoverer of dipropargyl, having placed a quantity of this substance at the disposal of the authors, they have determined its heat of combustion and formation, and compared them with those of its isomeride, benzene. Dipropargyl, C_6H_6 , boils at 85° ; benzene at 81° . Its density is distinctly less than that of benzene, 0.82 instead

of 0.89; it is also much less stable, is very easily polymerised, and forms an addition-product with 8 atoms of bromine.

The heat of combustion was measured (*Ann. Chim. Phys.* [5], 13, 15), by placing a known quantity of the substance on cotton, vaporising it in a current of air, and exploding the mixture in a suitable vessel. The combustion was not complete, although no carbon was deposited, but this was allowed for in the calculation. In this way 776 units (kil.-deg.) were obtained for 78 grams (1 mol.) of liquid benzene. Another determination in the calorimetric bomb gave + 783.2 units.

C_6 (diamond) + H_6 = C_6H_6 gas, absorbs - 12.2 units.

C_6 (charcoal) + H_6 = „ „ evolves - 5.8 „

Thus the sum of the work done in the formation of benzene from its elements is small, the heat disengaged being positive or negative, according to the nature of the carbon from which it may be supposed to be derived.

The combustion of the dipropargyl was effected in the calorimetric bomb. As in the case of benzene, the combustion was never complete, no matter how carefully it was executed, and there was always a deposit of carbon. However, a comparison between the initial weight of the hydrocarbon and of the carbonic anhydride produced, enables a valuation to be made of the portion which has been incompletely burnt; this in the best experiments amounted to 1.9 per cent., and in less favourable ones to 6.0 per cent. of the total weight. It was further necessary to reckon the unburnt carbon as corresponding with a portion of the hydrocarbon, of which the hydrogen alone was burnt, whilst the carbon was precipitated.

Ten combustions of dipropargyl gave as a mean + 853.6 units, on supposition that the portion incompletely burned furnished elementary carbon and water, or + 842.8 units if it be reckoned as carbonic oxide and water. The former figure is considered to be nearer the truth. This heat of combustion exceeds by nearly one-tenth the heat of combustion of benzene, and gives for the heat of formation of dipropargyl—

C_6 (diamond) + H_6 = C_6H_6 gas. - 82.8 units.

C_6 (charcoal) + H_6 = „ „ - 64.8 „

Dipropargyl is therefore formed with a considerable absorption of heat, in a manner similar to acetylene (- 61.1), allylene (- 46.5), and ethylene (- 15.4). Its formation from acetylene would disengage 100.5 units, whilst benzene from the same source would evolve nearly double, namely, 171.1 units; the transformation of dipropargyl into benzene would therefore evolve + 70.6 units.

All experiments with a view of effecting this direct change were without result. Heated in a sealed tube to 225°, dipropargyl first polymerised and then decomposed, with carbonisation. At 300°, it was destroyed, with production of a large quantity of gas, but without formation of benzene. Nitric acid attacked it violently, with formation of resinous looking nitro-bodies, but no nitrobenzene; iodine and sulphuric acid polymerised it in a similar manner.

As a rule, it may be taken as proved that there is a disengagement of heat, that is to say, a loss of energy—

(1.) When several distinct elements combine to form a new substance.

(2.) When several identical molecules unite to form a more condensed substance.

(3.) When a body endowed with a certain capacity of saturation is transformed into an isomeride of the same condensation, whose power of forming addition-products is less, as in the conversion of terpene into cymene; in this case there appears to be effected in the substance a sort of internal saturation, which may be supposed to correspond with or be the representative of the "exchange of atomicities" in the case of elements.

J. W.

Electrolysis of Toluene. By A. RENARD (*Compt. rend.*, **92**, 965—966).—The products obtained by electrolysing toluene are mixed with 2 to 3 times their volume of water, the oil which rises to the surface being separated, washed with soda, and dried. After the excess of toluene has been distilled off, the remaining portion boils at 190° , and yields a crystalline mass with hydrogen sodium sulphite, which, on distilling with a concentrated solution of sodium carbonate, gives benzaldehyde. The author obtains phenose from the aqueous solution which remains after separating the oil.

J. I. W.

Preparation of Metatoluidine. By VIENNE and STEINER (*Bull. Soc. Chim.* [2], **35**, 428—429).—The authors state that they have been unable to obtain metatoluidine by following the directions given by Widman. They have employed the following method: Benzaldehyde is nitrated by treating it with a mixture of nitric and sulphuric acids, the product is poured into water, and allowed to stand. The yellow needles which separate out are freed from the oil with which they are mixed by pressure, and then recrystallised from alcohol. They have the composition $C_6H_4(NO_2).COH$. On treating with phosphorus pentachloride, $C_6H_4(NO_2).CCl_2H$ is obtained; but on reduction with either sodium-amalgam or zinc and hydrochloric acid, only a resinous mass of the composition $C_{14}H_{13}N_2ClO_2$ is obtained.

J. I. W.

Dry Distillation of the Mucates of Aniline and Paratoluidine. By L. LICHTENSTEIN (*Ber.*, **14**, 933—937).—On dry distillation, aniline mucate yields phenylpyrroline, $C_{10}H_9N$, and a compound insoluble in benzene, having the composition $C_{16}H_{14}N_2$. Benzylpyrroline, $C_{11}H_{11}N$, and a substance, $C_{18}H_{18}N_2$, insoluble in benzene, are formed by the distillation of paratoluidine mucate. Identical products were obtained by Altmann from aniline and paratoluidine saccharates. Strong nitric acid acts energetically on each of these bodies, converting them into oxalates.

Benzylpyrroline unites with mercuric chloride, forming a crystalline compound, $2(C_4H_4N.C_7H_7)HgCl_2$, and when heated at 50° with acetic chloride in sealed tubes, it yields a crystalline *tetracetic* derivative, $C_4Ac_4N.C_7H_7$.

When bromine is added to a solution of $C_{18}H_{18}N_2$ in benzene, a black

precipitate is produced: the filtrate is evaporated, and the residue extracted with weak alcohol, which leaves triclinic prisms of the compound $C_{18}H_8Br_{10}N_2$ undissolved. This substance is not attacked by ammonia, but by the action of sodium and ethyl or ethylene bromide 2 bromine-atoms can be replaced by ethyl or ethylene, forming $C_{18}H_8Br_8Et_2N_2$ and $C_{18}H_8Br_8(C_2H_4)_2N_2$ respectively. A crystalline powder, having the composition $C_{15}H_{24}N_2(HBr)_2$, is obtained from the black precipitate previously mentioned, by extracting it with alcohol, evaporating the solution to dryness, and digesting the residue in water.

The author represents the constitution of the compound $C_{18}H_{18}N_2$, by the formula $C_7H_7.N \begin{array}{c} \diagup CH.CH \diagdown \\ | \quad | \\ CH.CH \end{array} N.C_7H_7$, and regards it as a derivative of $HN \begin{array}{c} \diagup CH.CH \diagdown \\ | \quad | \\ CH.CH \end{array} NH$.

W. C. W.

New Synthesis of Organic Bases containing Oxygen. By W. STAEDL and O. SIEPERMANN (*Ber.*, **14**, 983—985).—When bromoacetylbenzene is dissolved in dimethylaniline at 70° , trimethylphenylammonium bromide and a base containing oxygen are produced, $2NPhMe_2 + PhCO.CH_2Br = NMePh.CH_2.COPh + NPhMe_3Br$. A similar reaction occurs when bromoacetylbenzene acts on dimethylmetatoluidine. The properties of this base have been already described (*Ber.*, **13**, 841; this Journal, Abstr., 1880, 639).

On heating the base with methyl or ethyl iodide, the reverse of the preceding reaction takes place, iodacetylbenzene and the iodide of an ammonium base being formed.

W. C. W.

Action of Haloid Compounds of Hydrocarbon Radicals on Phosphide of Sodium, and on the Salts of Tetrabenzylphosphonium. By E. A. LETTS and N. COLLIE (*Proc. Roy. Soc. Edin.*, **11**, 46—50).—The exact method for preparing the chloride of tetrabenzylphosphonium from sodium phosphide and benzyl chloride is not detailed in the present paper, but the chloride, $(C_7H_7)_4PCl$, is dissolved out by boiling water, from which it crystallises in large needles (m. p. 224 — 225°). The platinochloride and acid sulphate have likewise been prepared. The hydroxide, $(C_7H_7)_4P.OH$, which is soluble in water, is formed when a dilute solution of the acid sulphate and baryta are brought together; when, however, the solutions are not sufficiently dilute, the oxide of tribenzylphosphine, $(C_2H_7)_3PO$, which is insoluble in water, is produced.

E. W. P.

Arsenobenzene. By A. MICHAELIS and C. SCHULTE (*Ber.*, **14**, 912—914).—*Arsenobenzene*, $PhAs:AsPh$, is deposited as a crystalline mass on gently warming a moderately concentrated alcoholic solution of phenylarsene oxide, $PhAsO$, to which an excess of phosphorous acid has been added. The crystals are collected on a filter, and washed with absolute alcohol. Arsenobenzene is soluble in benzene, chloroform, carbon bisulphide, and in boiling xylene. It combines directly

with chlorine to form phenylarsene dichloride, PhAsCl_2 . Arsenobenzene melts at 196° , and at a higher temperature splits up, forming metallic arsenic and triphenylarsine.

Phenylarsene iodide, PhAsI_2 , is a red oily liquid, obtained by the action of strong hydriodic acid on phenylarsene oxide. On the addition of phosphorus acid to the hot alcoholic solution of the iodide, yellow needle-shaped crystals of iodarsenobenzene, $(\text{PhAsI})_2$, are deposited. This compound is very unstable; it rapidly deliquesces, even when placed over sulphuric acid in a vacuum.

Arseno-naphthalene, $\text{C}_{10}\text{H}_7\text{As} \cdot \text{AsC}_{10}\text{H}_7$, can be prepared by the action of reducing agents on an alcoholic solution of naphthylarsene oxide.
W. C. W.

Preparation of Pure Phenol. By W. ALEXEJEFF (*Bull. Soc. Chim.* [2], 35, 379).—In order to prepare pure phenol, the author adds 5 per cent. of water to the commercial substance, and, after having melted the mixture, allows it to stand. The crystals which gradually form are drained, and after repeating the operation from two to three times, the product is distilled.

Calvert stated that when 4 parts of phenol were agitated with 1 part of water at a temperature below 4° , a hydrate with the composition $2\text{PhHO} + \text{H}_2\text{O}$ (m. p. 16°) was formed. The author has been unable to confirm his observations. He finds, however, that when phenol is allowed to stand for several months with an excess of water, crystals are formed which melt at 37° .
J. I. W.

Action of Nitric Acid on some Phenol Ethers. By W. STAEDEL and others (*Ber.*, 14, 898—906).—The ethers employed in this investigation were obtained by the action of methyl iodide, ethyl bromide, and benzyl chloride respectively on the potassium salts of the phenols. For the nitrations, nitric acid of sp. gr. 1.5 was employed, and the action allowed to proceed at 0° .

Orthocresyl ethyl ether, $\text{C}_6\text{H}_4\text{Me} \cdot \text{OEt}$, is a colourless liquid (b. p. 180 — 181° uncorr.; sp. gr. = 0.97123 at 5°), with a pleasant odour; gives on nitration mononitrocresyl ethoxide, $[\text{Me} : \text{OEt} : \text{NO}_2 = 1 : 2 : 3 \text{ or } 1 : 2 : 5]$ (m. p. 71°), dinitrocresyl ethoxide

$$[\text{Me} : \text{OEt} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 3 : 5]$$

(m. p. 51°), and a little dinitro-orthocresol (m. p. 82°).

Paracresyl ethyl ether on nitration gives dinitroparacresol

$$[\text{Me} : \text{NO}_2 : \text{OH} : \text{NO}_2 = 1 : 3 : 4 : 5]$$

(m. p. 84°), ethyl nitrate, and dinitrocresyl ethoxide

$$[\text{Me} : \text{NO}_2 : \text{OEt} : \text{NO}_2 = 1 : 3 : 4 : 5]$$

(m. p. 75°).

Orthocresyl ethylene ether, $(\text{C}_6\text{H}_4\text{Me})_2\text{C}_2\text{H}_4\text{O}_2$, crystallises in white silky leaflets (m. p. 79°), which are only sparingly soluble in cold, but more easily in hot alcohol.

Benzyl phenyl ether on nitration gives trinitrobenzylphenyl oxide $[\text{C}_6\text{H}_3\text{NO}_2 \cdot \text{NO}_2 \cdot \text{OCH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 = 1 : 3 : 4; 1 : 4]$ (m. p. 198°), which by the action of alcoholic ammonia at a low temperature

gives paranitrobenzyl alcohol (m. p. 91°), and α -dinitraniline (m. p. 174°).

Benzyl orthocresyl ether, $C_6H_4Me.OCH_2Ph$, is a thick colourless oil (b. p. $285-290^{\circ}$), which gradually becomes yellow, and does not solidify in a freezing mixture. On nitration it gives trinitrobenzyl-cresyl ether [$C_6H_2Me.NO_2.NO_2.OCH_2.C_6H_4.NO_2 = 1 : 3 : 5 : 6 ; 1 : 4$] (m. p. 145°), which by the action of alcoholic ammonia at low temperatures is converted into paranitrobenzyl alcohol and a new dinitro-toluidine (m. p. 208°).

Benzyl paracresyl ether consists of white silky leaflets or transparent six-sided prisms (m. p. 41°), which are insoluble in water, but very easily soluble in alcohol, ether, and benzene. On nitration it gives dinitroparacresol (m. p. 84°), and a compound (m. p. 71°) having the composition and properties of Beilstein and Kuhlberg's (*Annalen*, **147**, 351) dinitrobenzyl alcohol, but which really appears to be paranitrobenzyl nitrate, $C_6H_4(NO_2).CH_2.O.NO_2$, since it gives paranitrobenzoic acid on oxidation.

Benzyl β -naphthyl ether, $C_{10}H_7.OCH_2Ph$, crystallises from alcohol in white brilliant leaflets (m. p. 99°).

Methyl α -naphthyl ether, $C_{10}H_7.OMe$, is a colourless liquid (b. p. 258° , sp. gr. = 1.0974 at 15° ; compare Marchetti, *Gazzetta*, **9**, 544, and Hantzsch, *Ber.*, **13**, 1347), which on nitration gives the trinitro-product $C_{10}H_4(NO_2)_3.OMe$ (m. p. 128°).

Methyl β -naphthyl ether, $C_{10}H_7.OEt$, crystallises from alcohol in large silky plates (m. p. 72°), and on nitration gives a trinitro-product (m. p. 213°). *Ethyl α -naphthyl ether* and *ethyl β -naphthyl ether* on nitration each give a trinitro-product melting at 148° and 186° respectively.

The *dinitroparacresol* (m. p. 84°) referred to above is identical with the compound already known. It forms a methyl ether (m. p. 122°) and an ethyl ether (m. p. 75°), and by the action of alcoholic ammonia at the ordinary temperature gives Beilstein and Kuhlberg's dinitro-toluidine (m. p. 166°), which on oxidation with chromic acid is converted into chrysanic acid (m. p. 258°).

The new *dinitro-orthotoluidine* (m. p. 208°) obtained as above described crystallises in yellow prisms or plates, which have a beautiful blue reflection. It is insoluble in alcohol, and only sparingly soluble in toluene.

Trinitro-naphthylamines.—The two trinitro- α -naphthyl ethers referred to above give trinitro- α -naphthylamine by the action of alcoholic ammonia at a gentle heat. This compound is but sparingly soluble in all solvents, and crystallises from toluene in small yellow leaflets, which darken at 240° , and appear to melt at 264° with decomposition. The two trinitro- β -naphthyl ethers also give a trinitro- β -naphthylamine, which is almost insoluble in all solvents, and crystallises from toluene in yellow needles, which are decomposed at 266° . Both trinitronaphthylamines give a trinitronaphthalene melting at 210° .

Dinitrotoluene, $C_6H_3Me(NO_2)_2$ [$Me : NO_2 : NO_2 = 1 : 3 : 5$], may be obtained either from the dinitroparatoluidine (m. p. 166°), or from the above-described dinitro-orthotoluidine (m. p. 208°), by the diazo-

reaction. It crystallises in needles or prisms (m. p. 91—92°), and from benzene in prisms containing crystallisation benzene, of the composition $C_7H_6(NO_2)_2 + C_6H_6$. On oxidation with chromic acid it gives dinitrobenzoic acid (m. p. 203—204°), the ethyl salt of which crystallises in needles (m. p. 90°). T. C.

Nitro-cresols. By E. NÖLTING and E. SALIS (*Ber.*, **14**, 986—987).—*Dinitroparacresol ethyl ether*, $C_6H_2Me(NO_2)_2.OEt$ [4 : 2 : 6 : 1], formed by the action of ethyl iodide on the silver, lead, or potassium salt of dinitroparacresol, on reduction with tin and hydrochloric acid yields the hydrochloride $EtO.C_6H_2Me(NH_3HCl)_2$. The addition of diazobenzene chloride to a neutral solution of this hydrochloride precipitates chrysoidine.

Dinitro-orthocresol, $[OH : Me : NO_2 : NO_2 = 1 : 2 : 4 : 6]$, prepared by the action of dilute nitric acid on the diazo-compound of orthotoluidine, or by heating the sulphonic acid from orthocresol with dilute nitric acid, melts at 86°.

Trinitrocresol from metacresol melts at 106°, and resembles picric acid in many respects.

Commercial cresol on nitration yields a mixture of dinitro-ortho- and dinitro-para-cresol, which can be separated by the difference in the solubility of their barium salts. No trinitro-derivative is formed.

W. C. W.

Crystallisable Constituents of Corallin. By K. ZULKOWSKY (*Wien. Akad. Ber.*, **82**, 598—605).—The author has continued his work on this subject (*Abstr.*, 1879, 58).

Action of Ammonia on Aurin and Methylaurin.—Aurin heated with alcoholic ammonia at 180° C. gives an orange solution, which becomes deep magenta on concentration. The dry residue dissolves in hydrochloric acid to a brown solution, giving a brassy solid on evaporation. Its aqueous solution is of the same colour as rosaniline salts, of which it gives all the reactions. It dyes with a yellowish magenta tint.

Methylaurin also requires a temperature of 180° for the ammonia reaction, but is more easily converted than aurin. The hydrochloric acid solution of the base is soluble in water and alcohol, giving all the reactions of rosaniline salts. It dyes with a blue or violet magenta tint.

In his previous communication, the author described the formation of oxidised aurin, by direct oxidation of alcoholic solution of aurin. On boiling this oxidised aurin with water, a very complete reduction takes place, aurin being produced in a very pure form; indeed, if filtered boiling, the filtrate will come through after a little time almost colourless.

Aurin, repeatedly and slowly recrystallised, appears to be mixed with the oxidation product, which alters its appearance, and accounts for the supposed existence by the author of an aurin of the formula $C_{18}H_{12}O_3$.

Methylaurin, obtained from rosaniline by the azo-reaction, forms a colourless crystalline hydrocyanide, $C_{20}H_{17}NO_3$, as also does the aurin hydrocyanide. Methylaurin from corallin, however, when treated with potassium cyanide until colourless, and then acidified with

hydrochloric acid, gives a white precipitate, which could not be obtained crystallised.

The methylaurin from corallin behaves towards hydrocyanic acid quite differently from aurin itself or its isomeride from rosaniline.

Both aqueous and alcoholic solutions of aurin rapidly absorb atmospheric oxygen when a large surface of liquid is exposed. The oxidation does not cease at the formation of the compound $C_{19}H_{16}O_6$, its alkaline solution absorbing oxygen more rapidly than aurin itself.

Alkaline solutions of methylaurin also absorb oxygen, but not quite so rapidly as those of aurin. Only one product seems to be formed in both cases.

The author is of opinion that the large amount of tarry products obtained during the recrystallisation of aurin, although previously purified by acid sodium sulphite, is produced by oxidation, only about 60 per cent. of crystallisable substance being obtained from corallin.

W. R. H.

Resorcinol Colouring-matters. By P. WESELSKY and R. BENEDIKT (*Wien. Akad. Ber.* [2], **82**, 1219–1232).—The authors allude at the outset to the incompleteness of former experiments, and the present uncertainty of the constitution of colouring-matters obtained from resorcinol and other phenols.

Diazoresorcinol (of Weselsky).—By the action of nitric acid containing nitrous acid, two mononitroresorcinols are obtained—one new, and the other already known, besides diazoresorcinol. From new analyses it would appear that the formula of diazoresorcinol is $C_{18}H_{20}N_2O_6$, and not $C_{18}H_{12}N_2O_6$, as formerly given by Weselsky. The reaction is as follows:— $3C_6H_5O_2 + N_2O_4 = C_{18}H_{10}N_2O_6 + 4H_2O$.

The nitrate of diazoresorcinol forms golden-green crystals soluble in boiling water.

Ethyl Ether of Diazoresorcinol.—Diazoresorcinol is mixed with alcohol, hydrochloric acid passed in to saturation, and the mixture heated in a sealed tube. The ether, $C_{18}H_{18}Et_2N_2O_6$, forms delicate red-brown interlaced needles (m. p. 202°), which can be sublimed unchanged. It is insoluble in water, soluble in alcohol and ether, and taken up by sulphuric acid, with formation of a blue colour. As this ether is insoluble in potassium hydroxide, it follows that the hydroxylic hydrogen atoms are replaced by ethyl, and also that it is probable that diazo-resorcinol contains two unattacked hydroxyl groups.

Action of Nitrous Acid on the Methyl and Ethyl Ethers of Resorcinol.—The resorcinol ether is saturated with nitric acid containing nitrous acid in a flask cooled with ice, and the crude product of the reaction treated with ether, which throws down “insoluble colouring-matters,” whilst “soluble colouring-matters” remain in the ethereal solution. Among the subsidiary products of the reaction are mononitro-derivatives of the ethers.

Colouring-matters from the Monethyl Ether of Resorcinol Insoluble in Ether.—This body, $C_{21}H_{20}N_2O_6$, forms delicate microscopic claret-red needles (m. p. 230°), insoluble in water and ether, soluble in alcohol; with sulphuric acid it forms an intensely deep purple colour. The colouring-matter soluble in ether forms orange-red needles (m. p. 228°),

of composition $C_{14}H_{11}NO_3$; it gives a blue colour with sulphuric acid.

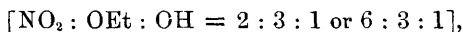
The *monomethyl ether of resorcinol* forms two colouring-matters which resemble the corresponding ethyl derivatives in their external appearance and their reactions.

Nitro-derivatives of resorcinol, one volatile and the other non-volatile, are obtained by the above process; the former crystallises in orange-red prisms (m. p. 88°), which volatilise slowly in the air. With bromine, it is converted in a dibromonitro-resorcinol (m. p. 117°).

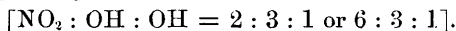
Nitro-derivatives of the Monethyl Ether of Resorcinol.—Two nitro-derivatives are obtained from the monethyl ether of resorcinol; these can be separated by distillation in a current of steam, one being volatile and the other non-volatile. The latter crystallises in compact needles or leaflets (m. p. 131°). It can also be obtained by the oxidation of Aronheim's monethyl ether of nitrosoresorcinol (Abstr., 1879, 465). With bromine, the non-volatile mononitro-derivative forms a dibromo-compound crystallising in needles (m. p. 69°). The volatile ethyl ether of mononitroresorcinol forms sulphur-gold needles (m. p. 79°) having a pungent odour; it is sparingly soluble in water, easily soluble in alcohol and ether. The same compound may also be obtained by the action of potassium ethylsulphovinate on the non-volatile mononitroresorcinol. With bromine, it forms a monobromo-compound crystallising in golden needles (m. p. 114°).

The *methyl ether of resorcinol* also gives a non-volatile (m. p. 144°) and a volatile (m. p. 95°) nitro-derivative.

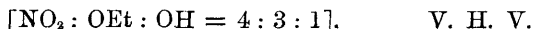
If the volatility of the nitrophenol depends on the close proximity of the hydroxyl and nitro-groups, some insight may be obtained into the corresponding resorcinol derivatives. It is thus probable that the volatile mononitroresorcinol derivative has the constitution



and the corresponding mononitroresorcinol the constitution



But inasmuch as the ordinary non-volatile nitroresorcinol corresponds with the volatile ethyl ether of nitroresorcinol, it follows that the former has the constitution $[NO_2 : OH : OH = 6 : 3 : 1]$, and the volatile ethyl ether of mononitroresorcinol must then have the groupings in the position $[NO_2 : OH : OH_2 = 3 : 2 : 1]$. As the non-volatile ethyl ether of mononitroresorcinol is obtained by the oxidation of the mononitroso-compound, which has the nitroso-group in the paraposition to the hydroxyl group, then it must have the composition



Derivatives of Piperonal. By C. LORENZ (*Ber.*, **14**, 785—795).—*Methylenedioxyphenylangelic acid*, $C_{12}H_{12}O_4$, is prepared in a similar manner to methylenecaffeic acid (this Journal, 1881, 48), viz., by heating piperonal sodium acetate and butyric anhydride together for six hours in a vessel with an inverted condenser. The product is treated with water, then extracted with ether, and the ethereal extract treated with sodium carbonate. The free acid is obtained as a white

crystalline precipitate by decomposing the solution of the sodium salt with hydrochloric acid. It is sparingly soluble in water, but largely in alcohol and ether, and crystallises from alcohol in long needles (m. p. 120—160°). Sodium-amalgam acts on an alkaline solution of this acid, forming an oily acid liquid, probably methylenedioxyphenylvaleric acid. The constitution of methylenedioxyphenylangelic acid is represented by the formula $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_3.\text{CH} : \text{C}\text{Et}.\text{COOH}$; it is isomeric with the hydropiperic acid obtained by treating the aqueous solution of piperic acid with sodium-amalgam. The fact that piperic acid, when so treated, combines with only two atoms of hydrogen, and further, that on oxidation the chief product is piperonal, shows that its constitution is different from that attributed to it by Fittig (*Annalen*, **152**, 25; **172**, 134; **159**, 129).

The following table contains some of the more important reactions of solutions of the ammonium salts of these acids:—

Reagents.	Piperic acid, $\text{C}_{12}\text{H}_{10}\text{O}_4$; m. p. 216—217°.	Hydropiperic acid, $\text{C}_{12}\text{H}_{12}\text{O}_4$; m. p. 75—76°.	Methylenedioxy- phenylamylic acid, $\text{C}_{12}\text{H}_{12}\text{O}_4$.	Methylenedioxy- phenylvaleric acid; an oil.
Calcium chloride	White floccu- lent precipitate; insoluble in hot water.	No precipitation.	White crystal- line precipitate; soluble in hot water.	White precipi- tate; sparingly soluble in hot water.
Barium chlor- ide	A white, crystalline precipitate, soluble in hot water.			
Zinc sul- phate	Yellow, sparing- ly soluble salt.	Yellow, sparing- ly soluble salt.	White crystal- line salt; sparing- ly soluble in hot water.	White crystal- line precipitate, sparingly soluble in hot water.
Copper sul- phate	Greenish blue precipitate; slightly soluble in water, solu- ble in NH_3 to a blue solution.	Green, crystal- line precipitate; soluble in NH_3 to a green solu- tion.	Green, curdy precipitate; so- luble in NH_3 to a blue solution.	Bluish-green crystalline pre- cipitate; soluble in NH_3 to a deep blue solution.
Silver ni- trate	—	White precipi- tate, blackening on exposure to light; decom- posed by NH_3 .	White, curdy precipitate; un- stable salt.	White, curdy precipitate; sta- ble salt, soluble in NH_3 .
Lead acetate	—	Yellow crystal- line precipitate; soluble in acetic acid.	White precipi- tate; insoluble in acetic acid.	White precipi- tate; sparingly soluble in acetic acid.
Concentra- ted sulphur- ic acid and free acid	Brownish-red solution, black- ening when heated.	Cherry-red solu- tion.	Becomes cherry- red on heating.	Cherry-red solu- tion.

Piperonal forms a sparingly soluble compound with sodium hydrogen sulphite, and also exhibits the reaction with rosaniline sulphite, supposed to be characteristic for aldehydes (Schiff, *Annalen*, **150**, 131), viz., the formation of a yellow colour gradually changing to a deep red. This reaction, Tiemann states in a foot-note, is also exhibited by ketones.

When digested with alcoholic ammonia in presence of hydrocyanic acid, piperonal yields a compound having the formula $C_{24}H_{18}N_2O_6$, which crystallises in prisms (m. p. 213°), and is insoluble in alcohol, ether, and glacial acetic acid. It has neither basic nor acid properties. A compound, having the same composition, is obtained by digesting piperonal with alcoholic ammonia at $60-70^\circ$; it is insoluble in water and ether, but soluble in hot alcohol, from which it crystallises in needles (m. p. 172°).

A compound, $C_{14}H_{11}NO_2$, is obtained by heating piperonal and aniline; by crystallisation from light petroleum, it is obtained in colourless needles (m. p. 65°).

Methylenedioxyphenylglycollic acid, $CH_2 : O_2 : C_6H_3.CH(OH).COOH$, is obtained by heating piperonal with hydrocyanic acid at $60-70^\circ$, and saponifying the resulting nitril with hydrochloric acid. It crystallises in granular slightly red crystals (m. p. $152-153^\circ$); it is very unstable, and is decomposed by boiling its aqueous solutions: concentrated sulphuric acid dissolves it, forming a violet solution, which blackens on adding water. Zinc sulphate and silver nitrate produce white precipitates in solutions of the ammonium salt.

Methylenedioxyphenylamidacetic acid,



is obtained by heating the cyanhydrin of piperonal with alcoholic ammonia, and saponifying the resulting amidonitrile. It crystallises in white needles (m. p. 210°), sparingly soluble in water, and insoluble in alcohol and ether; it dissolves in acids and alkalis. In solution of the ammonium salt of this acid, barium and calcium chlorides produce white precipitates, soluble in hot water. The lead salt is obtained as a white amorphous precipitate, soluble in hot water; the zinc salt is a white flocculent precipitate. The copper salt is obtained as a blue precipitate, soluble in ammonia; the ammonium salt gives a green precipitate with ferrous salts, and an orange-coloured precipitate with ferric salts.

P. P. B.

Action of Bromine on Paranitrobenzoic Acid. By W. HALBERSTADT (*Ber.*, **14**, 907—912).—Paranitrobenzoic acid is not readily attacked by bromine, but when it is heated with this reagent in sealed tubes at $270-290^\circ$, the nitro-group is completely eliminated. The chief products of the reaction are parabromobenzoic acid and tetrabromobenzene: parametadibromobenzoic acid and paradibromobenzene are also formed in small quantities.

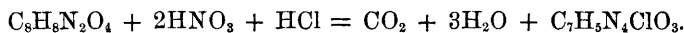
W. C. W.

Dinitrophenylacetic Acid. By S. GABRIEL and R. MEYER (*Ber.*, **14**, 823—833).—Dinitrophenylacetic acid is prepared by dissolving 1 part of phenylacetic acid in 6 parts of fuming nitric acid and adding

to the solution 6 parts of concentrated sulphuric acid; the whole is then poured into water; when crystallised from water, the precipitated dinitro-acid forms fine yellow concentrically grouped needles (m. p. 160°). As shown by Radziszewski (*Ber.*, **2**, 210; **3**, 648), when this acid is heated above its melting point, it is resolved into carbonic anhydride and dinitrotoluene, $[\text{Me} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4]$ (m. p. 71°). Hence dinitrophenylacetic acid is $[\text{CH}_2.\text{COOH} : \text{NO}_2 : \text{NO}_2 = 1 : 2 : 4]$.

Paramido-orthonitrophenylacetic acid, $\text{C}_6\text{H}_3(\text{NO}_2)(\text{NH}_2).\text{CH}_2.\text{COOH}$, is obtained by reducing the dinitro-acid with ammonium sulphide. It crystallises in long, broad, reddish-brown needles (m. p. $184\text{--}186^{\circ}$); easily soluble in boiling water and alcohol, sparingly in ether, and insoluble in benzene and carbon bisulphide. Its *ethyl* salt forms long yellow slender needles (m. p. 100°). The *methyl* salt melts at 94° .

The diazo-compounds cannot be prepared from the amidonitro-acid, as decomposition takes place with liberation of carbonic anhydride and the formation of diazo-derivatives of nitroso-methylnitrobenzene. Thus when the amidonitro-acid, dissolved in hydrochloric acid, is treated with amyl nitrite, the *chloride of nitrosomethyl nitro-diazobenzene*, $\text{CH}_2(\text{NO}).\text{C}_6\text{H}_3(\text{NO}_2).\text{N}_2\text{Cl}$, is formed, thus:

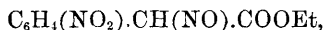


This diazo-compound, when boiled with alcohol, yields a compound having the formula $\text{C}_7\text{H}_5\text{N}_2\text{O}_3$, crystallising from water in slender branching needles (m. p. $96\text{--}97^{\circ}$). It is soluble in fixed alkalis, in benzene, alcohol, and ether, and, to some extent, in carbon bisulphide and light petroleum. That this compound is nitroso-methyl-orthonitrobenzene, $\text{CH}_2(\text{NO}).\text{C}_6\text{H}_4.\text{NO}_2$, is shown (1) by its conversion into orthonitrobenzoic acid when heated with hydrochloric acid at $150\text{--}160^{\circ}$, and (2) by its conversion into orthonitrobenzaldehyde, $\text{C}_7\text{H}_5\text{NO}_3$, by oxidation with potassium dichromate and sulphuric acid. The constitution of the oxidation-product was shown by its melting point ($43.5\text{--}44.5^{\circ}$) and by its conversion into orthonitro-cinnamic acid by the action of acetic anhydride and sodium acetate.

Nitrosomethyl-orthonitroparabrombenzene, $\text{CH}_2(\text{NO}).\text{C}_6\text{H}_4.\text{Br}.\text{NO}_2$, is obtained by treating the diazo-compound, $\text{C}_7\text{H}_5\text{N}_4\text{ClO}_3$, already described, with hydrobromic acid; it crystallises from hot water in groups of slender needles (m. p. $151\text{--}153^{\circ}$) soluble in the ordinary solvents.

Ethyl nitrophenyl-nitrosoacetate, $\text{C}_7\text{H}_5\text{N}_2\text{O}_3.\text{COOEt}$, is obtained by acting on a solution of ethyl amidonitrophenylacetate in hydrochloric acid with an alcoholic solution of ethyl nitrite. After expelling the alcohol, a resin is left from which the ethyl salt may be obtained by extracting with boiling water; it crystallises in long slightly yellow needles (m. p. 163°). It is sparingly soluble in carbon bisulphide and water, but more soluble in alcohol, ether, and benzene. Ammonia does not dissolve it, but it is dissolved by the fixed alkalis to form a yellow solution which gives a yellow precipitate with silver nitrate.

That the constitutional formula for this compound is



is shown by its resolution when heated with hydrochloric acid, into

orthonitrobenzoic acid, carbonic anhydride, ammonia, and ethyl chloride. Like many other nitroso-compounds, *e.g.*, nitroso-oxindol, nitrosomalonyl urea, &c., it combines with alkalis.

Paramido-oxindol, $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{CH}_2\\ \text{NH}\end{smallmatrix}\rangle\text{CO}$, is obtained by reducing dinitrophenylacetic acid with tin and hydrochloric acid. It crystallises from hot water in long needles, having a vitreous lustre (m. p. about 200°). It is easily oxidised, yielding resinous products; it is a strong base, and is soluble in water, alcohol, and ether, but only sparingly in benzene and carbon bisulphide.

Paradiazio-nitroso-oxindol chloride, $\text{C}_6\text{H}_3(\text{N}_2\text{Cl})\langle\begin{smallmatrix}\text{CH}(\text{NO})\\ \text{NH}\end{smallmatrix}\rangle\text{CO}$, is obtained by treating the hydrochloric acid solution of paramido-oxindol with amyl nitrite. It crystallises in yellowish-brown needles, and is decomposed but slowly by hot alcohol. P. P. B.

Synthesis of Ketonic Acids. By L. ROSER (*Ber.*, **14**, 940—941).—By the action of amyl chloroxalate on benzene in presence of aluminium chloride, a small quantity of an acid was obtained which dissolved in strong sulphuric acid with a violet coloration. According to the author it is identical with Claisen's benzoylcarboxylic acid. Acids were also obtained by the action of amyl chloroxalate on toluene, naphthalene, and orthonitrotoluene. W. C. W.

Compounds of Phthalic Anhydride with Hydrocarbons of the Benzene Series. By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, **92**, 833—837).—Phthalic anhydride reacts readily with the hydrocarbons of the benzene series when equal weights of the anhydride, the hydrocarbon, and aluminium chloride are mixed together and heated for two or three hours on a sand-bath. When the hydrocarbon can be obtained in a state of purity, it is advantageous to employ an excess, about 5 parts to 1 part phthalic anhydride and 1 part aluminium chloride. With benzene and toluene, almost the theoretical yield of the products is obtained, and the excess of the hydrocarbon can be recovered in a state of purity. The product of the reaction is poured gradually into water, and boiled with excess of the latter in order to remove the unaltered aluminium chloride and the greater part of the phthalic anhydride left unattacked. The acid obtained is dissolved in ammonia, precipitated from a boiling solution by means of hydrochloric acid, and purified by crystallisation. Phthalic anhydride and benzene give ortho-benzoyl-benzoic acid, no isomeride of which can exist. The existence of an isomeride of the corresponding toluene compound is theoretically possible, but, as a matter of fact, only one toluyyl-benzoic acid has been obtained by this method. It would indeed appear that in all cases of the reaction of phthalic anhydride with a benzene hydrocarbon, only one of the possible isomerides is produced. The authors have not been able to obtain an acid formed by the action of two molecules of phthalic anhydride on the same molecule of benzene. By fusion with potassium hydroxide, benzoyl- and toluyyl-benzoic acids are converted into benzoic and paratoluic acids, the latter being free from isomerides. With the deriva-

tives of the higher hydrocarbons the decomposition is more complicated, duroyl-benzoic acid, for example, being converted into durene, benzoic acid, and carbonic anhydride. When an acid homologous with benzoic acid is produced simultaneously with the latter, the reaction affords an excellent means of determining the position of the hydrogen atom replaced by the phthalic group. Investigations have been made in this way with respect to the influence exerted by the position of the methyl groups on the physical properties, especially crystalline form, of compounds of the aromatic series.

Paratoluyyl-orthobenzoic acid, $C_6H_4Me.CO.C_6H_4.COOH$, is obtained by adding 150 grams of aluminium chloride, in small portions at a time, to a mixture of 200 grams toluene and 100 grams phthalic anhydride, and heating the mixture. The following reaction takes place: $-Al_2Cl_6 + C_6H_4(CO)_2O + C_7H_8 = C_7H_7.CO.C_6H_4.COOAl_2Cl_5 + HCl$. This product is decomposed when poured into water, and the new acid may be purified by crystallisation from boiling toluene. It forms hard yellowish crystals which, when dried at 110° melt at 146° , and cannot be distilled without decomposition. The acid and a number of its insoluble salts melt under boiling water. It is only very slightly soluble in hot water, but dissolves readily in alcohol, acetone, and ether. It also dissolves easily in benzene, but the best solvent is boiling toluene, which deposits the greater part of the acid on cooling. The acid is deposited from its solution in a mixture of alcohol and toluene, in the form of small brilliant, transparent triclinic prisms, with curved faces. These crystals contain 1 mol. of water of crystallisation, melt a little above 100° , and gradually give off their water at this temperature, the melting point at the same time rising. The anhydrous acid is obtained in short thick needles by deposition from solution in boiling toluene. Most of its salts form microscopic crystals. The potassium, sodium, and calcium salts are very soluble in water; the barium compound which contains 4 mols. H_2O is only slightly soluble. The cadmium salt forms acicular prisms containing $\frac{1}{2}H_2O$; the copper salt crystallises in long plates containing $4H_2O$, and the silver salt forms slender needles which do not fuse in boiling water. The methyl salt forms short prisms which melt at 53° ; the ethyl salt melts at $68-69^\circ$. Both are soluble in alcohol, and may be distilled with partial decomposition. When the sodium salt is fused with 5 or 6 parts of potassium hydroxide at a little above 300° , it is entirely converted into benzoic and paratoluic acids, indeed this reaction affords the best method of obtaining the latter free from isomerides.

Duroyl-benzoic acid, $C_6HMe_4.CO.C_6H_4.COOH$, is obtained by the preceding method, substituting durene (tetramethylbenzene) for toluene. It melts at above 260° , but the majority of its salts melt when heated with a quantity of water insufficient to dissolve them. It is insoluble in water, but dissolves easily in alcohol, ether, acetone, benzene and toluene, and may be obtained in crystals by deposition from its solution in glacial acetic acid. The ammonium, sodium, and potassium salts are soluble in water; the barium and calcium salts are only slightly soluble and crystallise in needles containing 1 mol. H_2O . The salts of silver, lead, and copper are insoluble, and do not fuse under water.

C. H. B.

Phthalic Anhydride Condensation Products. By S. GABRIEL (*Ber.*, **14**, 919—927).—By the action of acetic anhydride and sodium acetate on acetophenonecarboxylic acid, a derivative, $C_8H_7\ddot{A}cO_3$, is obtained, which crystallises in long colourless needles (m. p. 71°) soluble in alcohol, ether, chloroform, light petroleum, and carbon bisulphide, but is insoluble in alkalis. This body is not an acetic derivative of a hydroxy-acid, but a mixed anhydride of acetic and acetophenonecarboxylic acids, viz., $MeCO.C_6H_4.COO\ddot{A}c$.

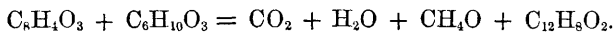
Since acetophenonecarboxylic acid is a derivative of phthalylacetic acid, the formation of the preceding compound is evidence in favour of phthalylacetic acid having the constitution $C_6H_4(CO)_2:CH.COOH$, and not $CO<\overset{O}{\underset{C_6H_4}{\curvearrowright}}>C:CH.COOH$.

On boiling a mixture of phthalic anhydride, phenoxacetic acid and anhydrous sodium acetate, carbonic anhydride is evolved and *phenoxy-methylenephthalyl*, $C_6H_4(CO)_2:CH.OPh$, and a substance melting at 91° are formed. Phenoxy-methylenephthalyl is deposited from an alcoholic solution in needles (m. p. 143°). When boiled with sodium hydroxide it takes up a molecule of water, and on the addition of hydrochloric acid to the alkaline solution, *phenoxyacetophenonecarboxylic acid*, $COOH.C_6H_4.CO.CH_2.OPh$, is deposited in needle-shaped crystals (m. p. 110°).

Cresoxymethylenephthalyl, $C_6H_4(CO)_2:CH.OC_7H_7$, prepared by boiling paracresoxacetic acid with phthalic anhydride and sodium acetate, crystallises in flat needles and plates (m. p. 173°), which are sparingly soluble in hot alcohol.

By the action of phthalic anhydride on ethyl malonate at 130° to 150° (in presence of anhydrous sodium acetate), a mixture of orthotribenzoylbenzene, $C_6(C_6H_4.CO)_3$, and methylenephthalyl is produced. These substances are separated by the solubility of the latter compound in hot glacial acetic acid. Methylenephthalyl forms yellow needles (m. p. 218°).

If ethyl acetoacetate is substituted for the ethyl malonate in the preceding experiment, orthotribenzoylbenzene and a crystalline compound (m. p. 210°) having the composition $C_{12}H_8O_2$, are obtained.



W. C. W.

Mesitylenedisulphonic Acid. By L. BARTH and J. HERZIG (*Wien. Akad. Ber.*, **82** [2], 815—824).—The acid is prepared by warming a solution of 1 part of mesitylene in 10 parts of fuming sulphuric acid, for two or three days, at 30 — 40° , and adding to the solution, at intervals of about 10 hours, 3 to 4 parts of phosphoric anhydride. The product is then poured into water, the sulphurous acid boiled off, and the solution saturated with lead carbonate; the filtrate, after evaporation to dryness, is treated with alcohol to remove any monosulphonate, and the insoluble residue is decomposed with sulphuretted hydrogen. The acid may be further purified by converting it into the potassium salt, crystallising this from 90 per cent. alcohol, and decomposing the lead salt prepared from this with sulphuretted hydrogen. The pure acid crystallises in needles,

which redden slightly in the air, and deliquesce very easily. The potassium salt, $C_6HMe_3(KSO_3)_2 \cdot 2H_2O$, crystallises from alcohol in very beautiful needles, and loses its water of crystallisation at 125° ; the sodium salt forms dull white needles with $1\frac{1}{2}H_2O$, which go off at 100° ; the copper salt, $C_6HMe_3(SO_3)_2Cu$, is deposited from a very concentrated solution, when it is left over sulphuric acid, in whitish-green deliquescent needles, which blacken at 120 – 130° ; the barium salt forms small pointed needles with $3H_2O$, which it loses at 105° ; it decomposes and turns brown at 115° . On fusing the potassium salt with potassium hydroxide, not above 250° , it gives hydroxymesitylenic acid, identical with Fittig's (*Annalen*, **150**, 334) from the monosulphonic acid, the barium salts differ slightly, in the latter case (*loc. cit.*) forming hard crystals with $5H_2O$, in the former soft leaflets with $6H_2O$.

Sodium hydroxide acts at first like potassium hydroxide, but on raising the temperature it completely carbonises the acid. Distillation with potassium cyanide yields chiefly mesitylene, there is also a very small quantity of a nitrogenous body formed crystallising in needles. By fusion with sodium formate, it yields chiefly tarry products with very little acid; on distilling potassium mesitylenedisulphonate alone, it gives a quantitative yield of mesitylene. Bromine acts on the potassium salt, producing dibromomesitylene. From the last two reactions, it would seem that both sulphonic groups are in the benzene-nucleus. As the authors could not prepare a trisulphonic acid, and as Senhofer under similar conditions made benzene and phenoltrisulphonic acids, but with toluene got only a disulphonic acid, it seems almost as if the presence of hydrocarbon side-chains in the benzene nucleus generally renders the introduction of sulphonic groups more difficult.

D. A. L.

Methylketole. By O. R. JACKSON (*Ber.*, **14**, 879–888).—This compound, which appears to be a secondary base, and probably a homologue of indole, was prepared by the process previously described by Baeyer and the author (*Ber.*, **13**, 187).

It is sparingly soluble in hot water, and on cooling crystallises therefrom in needles (m. p. 59°). It is easily soluble in ether and in alcohol, has the odour of indole, although less intense, and imparts a red stain to a piece of pine wood which has been exposed to the action of hydrochloric acid gas. It differs from indole in its action towards nitrous acid, being coloured yellow thereby, and after a time deposits an amorphous yellow powder. It forms a somewhat unstable *platinochloride* $(C_9H_9N.HCl)_2.PtCl_4 + 3H_2O$, which is decomposed into its constituents by cold water. The vapour-density of the free base corresponds with the formula C_9H_9N , and the compound has probably the

following constitution: $NH \begin{array}{c} \diagup C_6H_4 \\ \diagdown CMe \end{array} = CH$.

Acetylmethylketole, $C_9H_9N\bar{A}c$, crystallises in colourless needles (m. p. 195 – 196°), sparingly soluble in water, but easily soluble in alcohol and in benzene. It is soluble in concentrated hydrochloric acid, and forms a platinochloride. It is not decomposed by

boiling sodium hydroxide, but on heating it with concentrated hydrochloric acid, methylketole is re-formed.

Hydromethylketole, $C_9H_{11}N$, obtained by the action of tin and hydrochloric acid on methylketole, is a colourless oil, heavier than water, and having a characteristic pungent odour, similar to that of piperidine. It is a strong base, and forms a crystalline hydrochloride and platinochloride. *Acetylhydromethylketole*, $C_9H_{10}N\dot{A}c$, is formed by the action of acetic anhydride on hydromethylketole, and crystallises in snow-white needles (m. p. $55-56^\circ$), which are easily soluble in all the ordinary solvents, except water. It is a feeble base, dissolving only in concentrated hydrochloric acid, and forming a solution from which the platinochloride may be obtained. *Nitrosohydromethylketole*, $C_9H_{10}N.NO$, is obtained by the action of sodium nitrite on the hydrochloric acid solution of the base, as an oil which subsequently becomes crystalline. It forms compact yellow crystals (m. p. $54-55^\circ$), which are easily soluble in alcohol, in ether, and in hot light petroleum. It dissolves in strong sulphuric acid with a violet colour, and gives Liebermann's reaction with phenol and sulphuric acid.

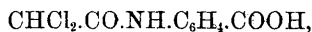
It dissolves in concentrated hydrochloric acid with a red colour; and the solution on reduction with tin gives hydromethylketole. These reactions show that the latter is a secondary base, and that the

nitroso-compound must have the constitution $NO.N \begin{matrix} \diagup C_6H_4 \\ \diagdown CHMe \end{matrix} CH_2$.

Methylketole on oxidation with potassium permanganate gives *acetylorthoamidobenzoic acid*, crystallising in plates or needles (m. p. $179-180$), which are moderately soluble in hot, only sparingly in cold water, but easily in alcohol, ether, and glacial acetic acid. It is only slightly basic, and does not give a platinochloride. It is decomposed into anthranilic acid (m. p. $143-144^\circ$), and acetic acid on boiling with concentrated hydrochloric acid. It is therefore identical with the acid obtained by Bedson and King (this Journal, Trans., 1880, 752) by the oxidation of orthoacetoluide.

Monobromacetylorthoamidobenzoic acid, $C_9H_5BrNO_3$, obtained by the action of bromine on the preceding compound, crystallises in white needles (m. p. $214-215^\circ$).

By the action of phosphorus pentachloride acetylorthoamidobenzoic acid gives an acid having the constitution—



crystallising in yellow needles (m. p. 173°). It is devoid of basic properties, and on boiling with hydrochloric acid, gives anthranilic acid, but no acetic acid.

By slightly varying the mode of treatment after the action of the phosphorus pentachloride on the acetylorthoamidoacetic acid, the compound $C_9H_5ClNO_3$ is obtained, as a yellow crystalline body, which on heating cakes together at $135-140^\circ$, and is decomposed at 200° without melting completely. It is possibly a mixture of the original acid with the dichlorinated product.

T. C.

β -Derivatives of Naphthalene. By P. JACOBSEN (*Ber.*, **14**, 803—807).— β -Naphthylamine nitrate, $C_{10}H_7.NH_2.HNO_3$, crystallises in colourless leaflets, soluble in cold water.

β -Iodonaphthalene, $C_{10}H_7I$, is obtained by decomposing β -diazonaphthalene sulphate with hydriodic acid; it is volatile in steam, and crystallises in colourless leaflets, soluble in ether, alcohol, and glacial acetic acid (m. p. 545°). Its ethereal solution is unacted on by sodium and iodides of alcohol-radicles, and also by zinc ethide. Sodium and ethyl iodide, when heated with the benzene or toluene solution, yield naphthalene, and with the solution in higher boiling liquids, small quantities of ethylnaphthalene are formed.

Nitro- β -acetonaphthalide, $C_{10}H_6(NO_2).NHAc$, is obtained by adding nitric acid (sp. gr. 1.5°) to a solution of acetonaphthalide in glacial acetic acid. It crystallises from alcohol in beautiful yellow needles (m. p. 123.5°); it is soluble in hot water, in alcohol, and glacial acetic acid.

Nitro- β -naphthol, $C_{10}H_6(NO_2).OH$, is obtained, like the corresponding α -derivative (Andreoni and Biedermann, *Ber.*, **6**, 342), by boiling the nitro-acetonaphthalide with potassium hydroxide. It crystallises from alcohol in short needles, soluble in hot water (m. p. 103°).

Amido- β -naphthol, $C_{10}H_6(NH_2).OH$, is obtained by reducing the nitro-derivative with tin and hydrochloric acid. The hydrochloride of amido- β -naphthol, $C_{10}H_6(OH).NH_2.HCl$, crystallises in white needles. The picrate forms yellow needles, and ferric chloride and bleaching powder give brown precipitates, with solutions of the hydrochloride. This amido- β -naphthol was oxidised in order to convert it into β -naphthoquinone, which, according to Stenhouse and Groves (*Annalen*, **189**, 153), melts at 96° , whereas the author obtained a product which did not melt at 140° . This difference is perhaps to be explained by the fact that the nitro- β -naphthol of these authors melts at 96° , whereas that of the author melts at 103° .
P. P. B.

Synthesis of Homologues of Anthracene. By C. LIEBERMANN and G. TOBIAS (*Ber.*, **14**, 795—803).—In the preparation of amylanthranol by the method already described (this vol., 608), the formation of an oil is observed. In some cases, its alcoholic solution, when treated with hydrochloric acid, yields amylanthracene, $C_{14}H_9.C_5H_{11}$. This is easily soluble in light petroleum, ether, benzene, and hot alcohol, and crystallises from the latter in long needles (m. p. 59°), having a pale sea-green colour. Its solutions exhibit a blue fluorescence. It dissolves in concentrated sulphuric acid, forming a green solution, which becomes red when heated. Its picric acid compound crystallises in brownish-red crystals (m. p. 115°). The hydrocarbon is oxidised by chromic acid to amyloxanthrol

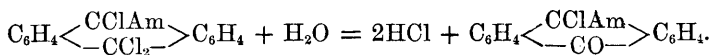
(*loc. cit.*): hence its constitution is $C_6H_4 \begin{array}{c} \diagup \text{C} \text{Am} \diagdown \\ | \\ \text{CH} \end{array} C_6H_4$.

Amylmonobromanthracene, $C_6H_4 \begin{array}{c} \diagup \text{C} \text{Am} \diagdown \\ | \\ \text{CBr} \end{array} C_6H_4$, is obtained by adding

bromine to a solution of amylanthracene in carbon bisulphide; it crystallises from alcohol in yellow needles (m. p. 76°); its solutions

exhibit fluorescence. The picric acid compound crystallises in orange-yellow needles (m. p. 110°).

Amylmonochloranthracene, $C_{14}H_9Cl.C_5H_{11}$, is obtained by the action of chlorine on a solution of the hydrocarbon in chloroform; it crystallises from alcohol in yellow needles (m. p. 70—71°), and forms a compound with picric acid. If the hydrocarbon is dissolved in carbon bisulphide, some sulphur dichloride is formed, together with amyl-oxanthrol chloride (*ibid.*, **14**, 459). The formation of this latter is explained by the action of the moisture of the air upon amylchloranthracene dichloride, thus:—



The production of amylanthracene is explained by the formation of *amylhydroanthranol*, when anthraquinone is treated with zinc-dust (free from oxide), sodium hydroxide, and amyl bromide. Amylhydroanthranol is precipitated from its alcoholic solution by water as an oil, which solidifies on cooling, and may then be crystallised from alcohol. Its constitutional formula is $C_6H_4 \left\langle \begin{array}{c} \text{CAm(OH)} \\ -\text{CH}_2- \end{array} \right\rangle C_6H_4$; it is resolved into water and amylanthracene, when its solution is treated with hydrochloric acid or sulphuric acid, or by boiling with solution of picric acid. It loses water when dried over sulphuric acid or in a vacuum.

Isobutylhydroanthranol is prepared like the above by substituting isobutyl bromide for amyl bromide. It yields *isobutylanthracene*, $C_{14}H_9.C_4H_9$, crystallising in fluorescent needles (m. p. 57°), and forming a brownish-red compound with picric acid.

The above substituted hydroanthranols may also be obtained in a similar manner to hydroanthranol (Perger, *J. pr. Chem.*, **23**, 137), viz., by heating the substituted oxanthranol with zinc-dust and ammonia. In this manner, ethylhydroanthranol was prepared, and by boiling its alcoholic solution with picric acid, the picric acid compound of ethylanthracene was obtained, which, when decomposed with ammonia, yields the hydrocarbon *ethylanthracene*, $C_{14}H_9Et$. This is more easily soluble in alcohol than the butyl compound, and crystallises in large leaflets united to globular masses (m. p. 60—61°). It is isomeric with Fittig's atranol and Goldschmidt and Hepp's dimethyltolane.

P. P. B.

Anthraquinone Derivatives. By A. CLAUS and A. HERTEL (*Ber.*, **12**, 977—982).—Dibromanthracene dissolves in cold nitric acid (sp. gr. 1.49), forming *mononitro-anthraquinone* (m. p. 230°), which is precipitated on the addition of water. This process gives a better yield of mononitro-anthraquinone than the method described by Böttger and Petersen (*Annalen*, **166**, 148). If the solution of dibromanthracene in nitric acid is heated, the α -dinitroanthraquinone of Böttger and Petersen (*Annalen*, **160**, 147) is produced. When an alcoholic solution of mononitro-anthraquinone is treated with sodium amalgam, the nitroquinone is first formed, but by using an excess of the amalgam, *amidoanthraquinone* is obtained. After removing a portion of the

alcohol by evaporation, water is added to throw down the amido-anthraquinone. This substance crystallises in needles of a beautiful red colour (m. p. 254°). It is identical with the amido-anthraquinone of Böttger and Petersen, but differs from that described by Perger (*Ber.*, **12**, 1566, this Journal, 1880, Abstr., 49).

Strong nitric acid (sp. gr. 1.49) acts energetically on tribromanthracene, forming monobromanthraquinone and other products, which have not yet been isolated.

Mononitromonobromanthraquinone is prepared by boiling tetrabromanthracene in fuming nitric acid and pouring the solution into water. By recrystallising the precipitate from hot acetic acid, white needles (m. p. 261°) are obtained, which are sparingly soluble in ether, alcohol, and chloroform. On reduction with sodium amalgam, the alcoholic solution of nitrobromanthraquinone yields the same amido-anthraquinone as that obtained from nitroanthraquinone.

Dibromanthracene tetrabromide dissolves slowly in hot fuming nitric acid. The addition of water to the acid solution precipitates *dinitrotetrabromanthraquinone* and a small quantity of a white powder, sparingly soluble in water.

Dinitrotetrabromanthraquinone (m. p. 105°) is soluble in alcohol, ether, benzene, and glacial acetic acid. On reduction with sodium amalgam, α -diamidoanthraquinone, described by Böttger and Petersen (*Annalen*, **160**, 149), is formed. W. C. W.

Essence of Linaloes. By H. MORIN (*Compt. rend.*, **92**, 998—1000).—Essence of linaloes, or *Licari kanali*, the white cedar of Cayenne, is a slightly coloured limpid liquid, of agreeable aromatic odour, like rose and lemon. It burns with a smoky flame. In order to obtain it pure, it is dried over calcium chloride and then distilled. It boils at 198° at 755 mm. Its sp. gr. at 15° is 0.868. Its lævoro-rotatory power at 15° is -19° . It is soluble in alcohol, ether, and glycerol. It is violently acted on by bromine, iodine, and nitric acid. It absorbs hydrochloric acid gas in the cold, forming a thick liquid, with a camphor-like odour. The composition of the essence is identical with that of Borneo-camphor, $C_{20}H_{18}O_2$. When treated with fused zinc chloride, it loses water and yields, like the essences of eucypt and *Osmitopsis astericoides*, a hydrocarbon, $C_{20}H_{16}$, with an odour resembling turpentine. J. I. W.

Products of the Distillation of Colophony. By A. RENARD (*Compt. rend.*, **92**, 887—890).—In addition to the hydrocarbon *heptene*, described in a previous paper (this Journal, 1880, Abstr., 893), the author has obtained two new products, one of which boils at about 154° , and apparently consists of a mixture of terebenthene, with a hydrocarbon, $C_{10}H_{18}$; the other boils at 170 — 173° . This latter product consists mainly of a hydrocarbon, $C_{10}H_{16}$, which is lævorotatory, and absorbs oxygen more rapidly than terebenthene. When left in presence of water or a mixture of alcohol and nitric acid for several months, it forms no crystalline hydrate. It is attacked violently by fuming nitric acid, but the ordinary acid only reacts at about 80° , forming nitro-toluic and oxalic acids, and a soluble syrupy acid which has not been

studied. When hydrochloric acid is passed into an ethereal solution of the hydrocarbon, the hydrochloride, $C_{10}H_{16}.2HCl$, is formed. It crystallises from alcohol in large nacreous plates, which melt at 49° . The prolonged action of bromine with exposure to light yields a tetrabromo-derivative, $C_{10}H_{12}Br_4$, a very thick, orange-coloured liquid. If the action be allowed to go on for one day only in the dark, crystals are obtained of the composition $C_{10}H_{12}Br_4$, apparently isomeric with the preceding compound. When an ethereal solution of the hydrocarbon is added to an ethereal solution of bromine until the latter is decolorised, the compound $C_{10}H_{16}Br_4$ is obtained in colourless crystals, which melt at 120° . Both bromine and hydrochloric acid combine only with a portion of the hydrocarbon. Treated with its own volume of sulphuric acid, the hydrocarbon is converted into a cymene-sulphonic acid, the barium salt of which has the composition $(C_{10}H_{13}SO_3)_2Ba + H_2O$. By long contact with one-twentieth its volume of sulphuric acid, the hydrocarbon is converted into a polymeride, $C_{20}H_{32}$, which boils at $305-310^\circ$, and is but little altered by exposure to air, cymene, and a hydrocarbon, $C_{10}H_{16}$ (b. p. $171-173^\circ$), which absorbs oxygen much less rapidly than terebenthene. Its sp. gr. at $11^\circ = 0.8611$. With nitric acid, bromine, and sulphuric acid, it forms the same compounds as the original hydrocarbon, but the action in each case takes place much less readily. C. H. B.

Hesperidin and its Derivatives. By F. TIEMANN and W. WILL (*Ber.*, **14**, 946—974).—Hesperidin is contained in the fruit, leaves and stalks of several members of the *Aurantaceæ*. It is best obtained from dried unripe oranges by Hilger's process (*Ber.*, **9**, 26—31; this Journal, 1876 [i], 709). Instead of purifying the crude product by recrystallisation from acetic acid, it is better to dissolve it in a cold dilute solution of potassium hydroxide, to which a small quantity of alcohol has been added, and then precipitate slowly with carbonic anhydride. The pure glucoside, $C_{22}H_{36}O_{12}$, is a white crystalline hygroscopic mass, devoid of taste and smell. It is insoluble in ether, and only sparingly soluble in alcohol and in water. It melts at 251° with decomposition. On adding hydrochloric acid to the orange-coloured solution produced by treating hesperidin with sodium amalgam, a precipitate is thrown down which dissolves in alcohol, forming a reddish-violet liquid. It has been previously pointed out by E. Hoffmann (*Ber.*, **9**, 685—690; this Journal, 1876 [ii], 420) that hesperidin is resolved into glucose and *hesperetin*, $C_{16}H_{14}O_6$, by dilute acids. This reaction is best accomplished by heating the glucoside at 115° with six parts of a mixture of equal volumes of alcohol and water, containing 2 per cent. of sulphuric acid. The hesperetin, precipitated from the mixture by the addition of water, is dissolved in alcohol, and the colouring matter removed by precipitation with lead acetate. The filtrate is acidified with acetic acid and mixed with warm water, which causes the pure hesperetin to be deposited in white glistening plates. The crystals dissolve freely in alcohol, and sparingly in ether, chloroform, and benzene. Hesperetin melts at 226° with decomposition. On treatment with sodium amalgam, the same product is obtained as in the case of hesperidin. Hoffmann (*loc. cit.*) observed that hesperetin

is decomposed by potassium hydroxide at 100° , forming *hesperitic acid* and phloroglucin. This acid melts at 228° , and is identical with *isoferrulic acid*, $C_6H_3(CH:CH.COOH)(OH)(OMe)$ [1 : 3 : 4], which Tiemann and Nagai (*Ber.*, **11**, 654; this Journal, 1878, Abstr., 580) obtained from caffeic acid. On fusion with potassium hydroxide, protocathechuic acid is formed, and when heated at 160° with dilute hydrochloric acid, an alcoholic chloride and caffeic acid are produced. When a solution of hesperitic acid in methyl alcohol is boiled with methyl iodide and potassium hydroxide, the methyl salt of methylhesperitic acid is obtained, crystallising in prisms (m. p. 64°). Methylhesperitic acid, $C_{11}H_{12}O_4$, prepared by the saponification of the methyl salt, crystallises in needles (m. p. 180°), which are soluble in alcohol and ether. By oxidising a dilute alkaline solution of methylhesperitic acid with potassium permanganate, *veratric acid*, $C_6H_3(COOH)(OMe)(OMe)$ [1 : 3 : 4], is obtained.

Acetylhesperitic acid, $C_6H_3(C_3H_3O)(O\bar{A}c)(OMe)$ [1 : 3 : 4], a crystalline compound formed by boiling hesperitic acid with acetic anhydride, is converted into *isovanillic acid* by oxidation with potassium permanganate; at the same time a small quantity of isovanillin is produced.

Methyl hesperitate, $C_6H_3(C_2H_2.COOMe)(OH).OMe$, crystallises in colourless needles (m. p. 79°), soluble in alcohol and ether.

Hesperetol, $C_6H_3(CH:CH_2)(OH)(OMe)$ [1 : 3 : 4], is best prepared by the dry distillation of calcium hesperitate. It melts at 57° , and is soluble in alcohol, ether, and in strong sulphuric acid, forming in the latter case a carmine-coloured solution. It is dissolved by alkalis and reprecipitated by acids.

The authors represent the constitution of hesperetin by the formula $(MeO)(OH)C_6H_3-CH^1:CH^2.CO.O-(C_6H_3)(OH)(OH)$.

The *Aurantiacae* contain, in addition to hesperidin, a more soluble glucoside, which appears to have almost the same percentage composition as hesperidin.

W. C. W.

Constituents of the Seeds of *Cocculus Indicus*. By E. SCHMIDT and E. LÖWENHARDT (*Ber.*, **14**, 817—822).—The authors agree with Paternò and Ogialoro (this vol., 440) in regarding picrotoxin as a compound of picrotoxinin and picrotin. In support of their statement, the following facts are cited:—(1.) Picrotoxin melts constantly at $199-200^\circ$. (2.) It does not lose weight when heated at 100° , whereas picrotoxinin crystallises with 1 mol. H_2O , which it loses at 100° . (3.) Picrotoxin, when heated with a large quantity of benzene in the cold, expands considerably, a phenomenon not exhibited by either picrotoxinin or picrotin. Moreover picrotoxin so treated undergoes no change in composition, which would scarcely be the case if it were a mixture of two compounds so differently soluble in benzene as picrotoxinin and picrotin (100 parts of benzene dissolve 0.346—0.359 of picrotoxinin, and 0.0199—0.0216 of picrotin at $21-22^\circ$).

Picrotoxinin crystallises from water in rhombic tables having the composition $C_{15}H_{16}O_6 + H_2O$ (m. p. $200-201^\circ$). Its monobrom-

derivative, $C_{15}H_{15}BrO_6$ (m. p. 245°), is obtained by the action of bromine on its ethereal solution or on the ethereal solution of picrotoxin, which is first decomposed into picrotoxinin and picrotin. The authors regard $C_{21}H_{24}O_{10}$ as the formula for picrotin (m. p. $240-245^\circ$), and picrotoxin is said to have the formula $C_{36}H_{40}O_{16}$: hence its decomposition into picrotin and picrotoxinin is expressed as follows:—



Picrotoxinin dissolves in concentrated sulphuric acid with an orange-red coloration; picrotin gives a pale yellow, becoming orange when heated. Picrotoxin exhibits Langley's reaction with nitric acid, whereas picrotin gives a yellow coloration only.

Acetic chloride acts on picrotoxin, forming an acetyl derivative; picrotoxinin and picrotin are also produced, and the former is converted into a polymeride (m. p. 225°). Hydrochloric acid gas in some cases acts on picrotoxin suspended in ether, and it is then resolved into picrotin and picrotoxinin, the latter being converted into the polymeride, "picrotoxide" (Abstracts, 1879, 729).

By fusing picrotoxin with potassium hydroxide, or heating it with an alcoholic potash solution, resinous bodies are obtained, and some oxalic, formic, and acetic acids. The distillation of picrotoxin with soda-lime and zinc-dust yielded no definite results.

Beside picrotoxin, the authors have obtained from the seeds of *C. indicus* a compound crystallising in white needles, sparingly soluble in hot water, insoluble in cold water, alcohol, and ether. Analysis indicates the formula $C_{19}H_{26}O_{10}$, and the authors designate the compound as *cocculin*. Its taste is not bitter, neither does it exhibit Langley's nitric acid reaction; it dissolves in concentrated sulphuric acid, with a slightly yellow colour. The authors regard it as possibly identical with Barth and Kretschy's *anamirtin* (this vol., 286). P. P. B.

Bromine-derivatives of Quinoline. By W. LA COSTE (*Ber.*, 14, 915—918).—A solution of quinoline hydrochloride combines with bromine to form unstable addition compounds. When a concentrated solution of quinoline hydrochloride is heated with bromine at 180° in sealed tubes, a mixture of mono-, di-, and tri-bromoquinoline is produced. The contents of the tubes are treated with warm dilute hydrochloric acid, which leaves the greater portion of the tribromoquinoline undissolved; the remainder is precipitated by the addition of water. After extracting the dibromoquinoline from the filtrate by ether, sodium hydroxide is added to the aqueous solution, and a mixture of quinoline and monobromoquinoline is precipitated. The quinoline is removed by means of a hot solution of tartaric acid, and the residue is dissolved in dilute hydrochloric acid. The solution, after treatment with animal charcoal and evaporation, deposits monoclinic prisms of monobrombquinoline hydrochloride, $C_9H_6BrN.HCl$. This salt is decomposed by sodium hydroxide, yielding monobromoquinoline in the form of an oily liquid (b. p. 270°). The free base combines with methyl iodide to form a compound crystallising in golden needles or plates. The *platinochloride*, $(C_9H_6BrN.HCl)_2.PtCl_4$, crystallises in needles of an orange colour.

Dibromoquinoline, $C_9H_5Br_2N$, is deposited from alcoholic or acid solutions in needles (m. p. 125°). On the addition of the alcoholic solution to platinum chloride dissolved in alcohol, the compound $(C_9H_5Br_2N.HCl)_2.PtCl_4$ is precipitated. W. C. W.

Tetrahydromethyl-quinoline. By O. R. JACKSON (*Ber.*, **14**, 889—891).—This compound, which is a homologue of methyl-ketole (p. 734),

and has the constitution $HN \begin{array}{c} \diagup C_6H_4 \cdot CH_2 \\ \diagdown CHMe \cdot CH_2 \end{array}$, was obtained, as previously

described by Bayer and the author (*Ber.*, **13**, 115), by the nitration and subsequent reduction of methylphenethyl ketone. It is an oil (b. p. $243-246^\circ$) with a somewhat sweet taste. The hydrochloride is but sparingly soluble in water, and crystallises therefrom in needles. It is easily soluble in alcohol, but insoluble in ether, and forms a platino-chloride.

The methylphenethyl ketone employed in the above reaction was obtained more easily than by Ehrlich's process (*Annalen*, **187**, 11), by heating together a mixture of the calcium salts of hydrocinnamic and acetic acids. It boils at $233-234^\circ$ (bar. 725 mm.). T. C.

Cinchonic Acid and Quinoline-derivatives. By H. WIEDEL and A. COBENZL (*Wien. Akad. Ber.*, **82** [ii], 986—1010).— α -Cinchoninesulphonic acid, $C_{10}H_6NO_2.HSO_3 + H_2O$, is made by heating for six hours at $170-180^\circ$ a mixture of 1 part cinchonine, 2 parts phosphoric anhydride, and 2 parts sulphuric acid. The product when cold is poured into water, and the acid separates out. When pure it forms colourless transparent glistening crystals* (triclinc), only soluble in water when boiled with it for some time, insoluble in all ordinary solvents. At 100° it loses its 1 mol. of water; at a tolerably high temperature it remains undecomposed, and neither sublimes nor melts; at a very high temperature it burns, and leaves a dense coke. It is strongly acid, with a lasting and intensely bitter taste. The *potassium salt* forms slender silky needles, only slightly soluble in water; the *ammonium salt*, $C_{10}H_5NSO_5(NH_4)_2 + 2H_2O$, large colourless shining plates* (monoclinic), very soluble in water, slightly in alcohol, losing their water of crystallisation at 100° . The *calcium salt*, $C_{10}H_5NSO_5Ca + 2\frac{1}{2}H_2O$, precipitated from the ammonium salt, small, feebly brilliant needles in drusy aggregations, very slightly soluble in water; they lose their water at 240° . The *barium salt*, sparingly soluble, hard, white, glistening crystalline grains* (triclinc), with $3H_2O$, of which 2 mols. H_2O are driven off at 150° , and the remaining H_2O at $260-280^\circ$. The *neutral copper salt*, $C_{10}H_5NSO_5Cu + H_2O$, from the ammonium salt by copper acetate, separates on standing as a hard crust of sea-green microscopic crystals, almost insoluble in water, losing the 1 mol. H_2O at $150-160^\circ$: from the acid, a light green heavy crystalline precipitate is formed, apparently a double compound of the above normal salt with copper acetate. The *lead salt*, obtained by adding basic lead acetate to a dilute solution of the acid, and leaving the liquid at rest for some

* There are measurements by Brezina of the crystals marked thus *.

days, crystallises out in globular masses of long fine silky needles, with 1 mol. H_2O , which it loses at 200° , sparingly soluble in water.

By carefully fusing the acid with potassium hydroxide, α -hydroxy-cinchonic acid, $\text{C}_{10}\text{H}_6\text{NO}_2\cdot\text{OH} + \text{H}_2\text{O}$, is formed, which, after purification by means of its barium salt, crystallises in pale yellow microscopic glittering needles, very sparingly soluble in water, &c., more soluble in alcohol, fusel oil, and glacial acetic acid. On heating, it partly sublimates and partly fuses (m. p. $254\text{--}256^\circ$, uncorr.).

In the aqueous solution, silver nitrate gives a yellow crystalline precipitate; lead acetate, a precipitate soluble in excess of the reagent; basic lead acetate, no precipitate; ferric chloride produces a green coloration, which turns blackish-green on adding sodium carbonate; and copper acetate precipitates yellowish-green flocks.

The acid combines with both acids and bases; the former compounds are very easily decomposable. It loses its water of crystallisation at 105° . The neutral salts decompose easily, turn dark in the air, crystallise badly, and are coloured greenish even by the smallest trace of iron. The neutral barium salt, $(\text{C}_{10}\text{H}_6\text{NO}_3)_2\text{Ba}$, forms irregular aggregations of very small pale yellow crystals, soluble in water. On adding barium hydrate to this solution, the basic barium salt, $\text{C}_{10}\text{H}_5\text{NO}_3\text{Ba} + \text{H}_2\text{O}$, is precipitated in very pale yellow pointed needles, losing the water of crystallisation at 130° . The silver salt, $\text{C}_{10}\text{H}_6\text{NO}_3\text{Ag}\cdot\text{C}_{10}\text{H}_7\text{NO}_3 + \text{H}_2\text{O}$, is precipitated from the acid in lemon-yellow flocks, which quickly change to microscopic needles. They are almost insoluble, and are not affected by light. The water of crystallisation goes off at 105° . On adding silver nitrate to the barium salt, the salt, $\text{C}_{10}\text{H}_6\text{NO}_3\text{Ag}$, is obtained in small yellowish-white needles, which turn brown on standing. The hydrochloride, $\text{C}_{10}\text{H}_7\text{NO}_3\cdot\text{HCl} + \text{H}_2\text{O}$, orange-yellow glittering needles* (monoclinic), on heating loses part of its hydrochloric acid. The platinochloride, $(\text{C}_{10}\text{H}_7\text{NO}_3\cdot\text{HCl})_2\cdot\text{PtCl}_4$, forms pale yellow needles, somewhat like asbestos, easily decomposed both by water and hydrochloric acid. Its water of crystallisation goes off very easily.

By dry distillation, α -hydroxycinchonic acid yields hydroxyquinoline, called by the authors α -quinophenol, which, after repeated distillations crystallises in beautiful long glassy needles, only slightly soluble in water, easily in alcohol, &c. When cold, it smells like saffron, at higher temperatures like phenol; its taste is bitter, and afterwards burning (m. p. $69\text{--}70^\circ$, uncorr.). Vapour-density by V. Meyer's method, 5.05. It sublimes in colourless glistening needles, boils under 748 mm. at $257\text{--}260^\circ$, and can be partially distilled with steam. Its aqueous solution reacts neutral, causes a turbidity in basic and neutral lead acetates; with silver nitrate it gives a white flocculent precipitate, redissolved on warming: by adding ammonia to this and boiling, silver is deposited. Copper acetate forms a green flocculent precipitate, also redissolved on warming. The ferric chloride and ferrous sulphate reactions are especially delicate; the first gives a deep green coloration, which turns brownish-yellow on adding sodium carbonate; the second produces a reddish colour, and afterwards a black precipitate. It combines with both acids and metals. These latter compounds are very uninviting. The hydrochloride,

C_9H_7NO, HCl , forms yellowish glistening fibrous pointed needles, soluble in alcohol and water; the *platinochloride*, $(C_9H_7NO, HCl)_2, PtCl_4 + 2H_2O$, crystallises in clear yellow silky pointed needles, which lose their water of crystallisation at 100° , and are scarcely soluble in cold, but easily in hot water.

By oxidation with permanganate, α -hydroxycinchonic acid yields hydroxycinchomeronic acid, C_8H_5NO (this Journal, **38**, 406—409). The authors suggest the name *carbocinchomeronic acid*. From this result it follows that the sulphonic group in the α -cinchoninesulphonic acid, and the hydroxyl groups in the α -hydroxycinchonic acid and the α -quinophenol, are contained in the benzene nucleus.

According to Koenigs, there are 42 possible hydroxyquinoline-carboxylic acids; of these there are only two known, and they are the hydroxycinchonic acid made by Koenigs (this Journal, **36**, 471), and the α -hydroxycinchonic acid described in this paper. Kynuric acid probably is a third (Kretschy, this Journal, **38**, 44). The α -quinophenol is the first representative of the seven possible hydroxy-quinolines.

If sulphuric anhydride is allowed to act on the cinchoninesulphonic acid at 240° , a disulphonic acid is produced. This cannot be obtained if the tubes of cinchonic acid, phosphoric anhydride, and sulphuric acid are subjected to this temperature, for in this case besides the α -cinchoninesulphonic acid an isomeric acid easily soluble in water is formed.

D. A. L.

Pyridinecarboxylic Acids. By S. HOOGWERFF and W. A. VAN DORP (*Ber.*, **14**, 974).—The polybasic pyridinecarboxylic acids, which are decomposed by the action of heat, forming carbonic anhydride and a lower acid, undergo a similar change when boiled with glacial acetic acid. For example, tricarboxypyridic acid yields cinchomeronic acid; quinolinic acid forms nicotinic; and methylquinolinic gives methylpyridinecarboxylic acid.

W. C. W.

Isomerism in the Pyridine and Quinoline Series. By Z. H. SKRAUP (*Wien. Akad. Ber.*, **82**, 748—754).—The close connection between benzene and pyridine derivatives renders it very likely that the laws and regularities of the one series will apply very closely to the other also, as may be seen in the case of the three amidobenzoic acids compared with the three pyridinecarboxylic acids.

Amidobenzoic Acids.

1 : 2	1 : 3	1 : 4
145°	174°	186°

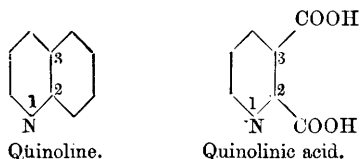
Pyridinecarboxylic Acids.

Picolinic	$134.5-136^\circ$
Nicotinic	$229.5-230$
γ -Pyridinecarboxylic	302.5

The analogy is further shown in the pyrrolcarboxylic acids, the synthetic acid being doubtless the *ortho*, as it splits up most easily into pyrrol and carbonic anhydride.

The two picolines again are probably ortho and meta, the former giving picolinic acid (b. p. 133·9°), the latter nicotinic acid (b. p. 140°).

It seems improbable that the cinchomeronic or pyridinedicarboxylic acid from the oxidation of quinolic acid has the constitution $[N : COOH : COOH = 1 : 2 : 3]$ assigned to it by Weidel and others, since the pyridinedicarboxylic acid obtained by Hoogewerff and by the author from the oxidation of *quinoline*, either synthetical, from coal oil or from cinchonine, appears to be identical with it, and from the direct formation of quinolic acid there is little doubt that the dicarboxylic acid has the constitution—



Such a dicarboxylic acid gives a possibility of three arrangements of the three mono-acids, corresponding to—

Nicotinic and picolinic acids.

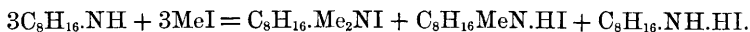
Nicotinic „ γ -pyridinecarboxylic acids.

Picolinic „ γ -pyridinecarboxylic „

As quinolic acid is undoubtedly $[1 : 2 : 3]$, cinchomeronic acid must be $[1 : 2 : 5]$, as it yields γ -pyridinecarboxylic and nicotinic acids on heating. Wischnegradsky's ethylpyridine is probably a *meta*-derivative, as it yields *nicotinic* acid, which is also the case with the *iso*-cinchomeronic acid of Weidel and Herzig, and which may therefore be either $[1 : 3 : 5]$ or $[1 : 3 : 6]$. W. R. H.

Action of Heat on Ammonium Bases. By A. W. HOFMANN (*Ber.*, **14**, 705—713).—From the analyses of conine hydrochloride and hydrobromide, and the action of methyl iodide on conine, the author concludes that the formula of this base is $C_8H_{17}N$, as found by Blyth (*Annalen*, **70**, 73). *Conine hydrochloride*, $C_8H_{17}N.HCl$, is obtained as a white crystalline mass by passing hydrochloric acid gas into a solution of conine in anhydrous ether. *Conine hydrobromide*, $C_8H_{17}N.HBr$, is obtained by adding bromine to an ethereal solution of conine; a soluble substitution product is formed, and the hydrobromide separates out.

Methyl iodide reacts with conine in a manner similar to piperidine (*Ber.*, **14**, 659), thus—



Dimethylconylammonium iodide, $C_8H_{16}Me_2NI$, crystallises from alcohol in crystals melting at 100°. By silver oxide it is converted into the hydrate, which on distillation yields *dimethylconine*, $(C_8H_{15}Me)MeN$, a liquid boiling at 182°. Its *platinochloride*,



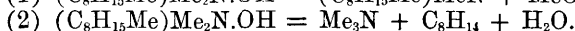
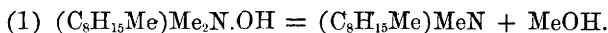
is sparingly soluble, and crystallises in slender needles, and melts below 100° to a deep red liquid.

Trimethylconylammonium iodide ($C_8H_{15}Me$) Me_2NI , is obtained by the action of methyl iodide on dimethylconine. It is easily soluble in water and alcohol, from which solutions ether precipitates it as an oil, solidifying after some time. The *platinochloride*,



is sparingly soluble in water, more soluble in alcohol, and crystallises in shining leaflets.

Trimethylconylammonium hydrate is decomposed by heat in a similar manner to the corresponding piperidine derivatives (*loc. cit.*), yielding dimethylconine and methyl alcohol, also trimethylamine, conylene, and water, thus:—

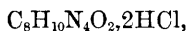


Conylene is a transparent, strongly refractive liquid (b. p. 125°). From experiment, its vapour density is 55.6 (C_8H_{14} requires 55). This hydrocarbon is identical with that discovered by Wertheim (*Annalen*, 123, 157; 130, 269).

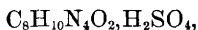
By the aid of the new formula for conine, the formation of azoconydrine is easily explained, namely, it is a nitrosoconine (C_8H_{16})'NON. It would also appear that conine is a homologue of piperidine. Kronecker finds that both these bases act on the nervous system, conine acting upon the motor, whilst piperidine acts on the sensitive nerves.
P. P. B.

Caffeine. By E. SCHMIDT (*Ber.*, 14, 813—817).—Caffeine saturated with hydrochloric acid gas and heated in sealed tubes at 240 — 250° for several hours, yields carbonic anhydride, and a residue containing ammonium chloride and methylamine hydrochloride. Heated with hydrochloric acid at 260° , caffeine undergoes partial carbonisation. Theobromine behaves very similarly to caffeine.

Salts of caffeine are formed only when concentrated acids react with the base; they are all decomposed by water, alcohol, and ether, and those salts with volatile acids are decomposed by exposure to the air. *Caffeine hydrochloride*, $C_8H_{10}N_4O_2.HCl + 2H_2O$, crystallises in colourless prismatic crystals. A hydrochloride having the formula



appears to be formed by the action of hydrochloric acid gas on the base; it loses a molecule of hydrochloric acid when kept over sulphuric acid. *Caffeine hydrobromide*, $C_8H_{10}N_4O_2.HBr + 2H_2O$, is obtained in colourless crystals. Caffeine appears to form two *iodides*, viz., $C_8H_{10}N_4O_2.HI$ and $C_8H_{10}N_4O_2.2HI$. *Caffeine nitrate*, $C_8H_{10}N_4O_2.HNO_3 + H_2O$, forms yellow thick needle-shaped crystals; like the above salts it is decomposed at 100° , yielding caffeine. *Caffeine sulphate*—



crystallises from a hot alcoholic solution in colourless, shining, needle-

shaped crystals. *Caffeine acetate*, $C_8H_{10}N_4O_2(C_2H_3O_2)_2$, forms colourless needles, decomposed by exposure to the air. *Caffeine normal butyrate*, $C_8H_{10}N_4O_2.C_4H_9O_2$, forms short white needles. The *isovalerate* has been obtained in colourless lustrous needles. The composition of the above salts, save the acetate and sulphate, appear to show that caffeine is a monacid base, a view which is supported by the composition of the auro- and platino-chlorides (Nicholson, *Annalen*, **62**, 71).

Caffeidine was prepared from caffeine by decomposing it with baryta; the aqueous solutions of its salts are decomposed by continued heating, forming ammonium and methylamine salts. *Caffeidine hydrochloride*, $C_7H_{12}N_4O.HCl$, crystallises in colourless needles, which are easily soluble in water.

The *platinochloride*, $(C_7H_{12}N_4O.HCl)_2.PtCl_6$, is formed by the spontaneous evaporation of its aqueous solutions in orange-yellow needle-shaped crystals. In some cases, it is obtained with 2 or 4 mols. H_2O . The *aurochloride* is very easily decomposed. Moist silver oxide decomposes caffeidine sulphate, forming amongst other products, ammonium and methylamine sulphates.

Caffeidine combines with ethyl iodide, forming *caffeidine ethiodide*, $C_7H_{12}N_4O.EtI$, and the base ethylcaffeidine also unites with ethyl iodide to form the iodide of a further ethylated base, hence it would appear that caffeidine is not a tertiary base like caffeine.

P. P. B.

Caffeine and Theobromine. By R. MALY and F. HINTEREGGER (*Ber.*, **14**, 723—728 and 893—897).—By the oxidation of caffeine with chromic mixture, cholestrophane is obtained, in quantities varying from 35.4—41.8 per cent.

Cholestrophane or *dimethylparabanic acid* is easily soluble in hot water, and at 20° 1 part is soluble in 53.4 parts of water. It crystallises from its aqueous solutions in thin rhombic tablets, or in leaflets (m. p. 145°). When heated with caustic alkalis, it is decomposed into oxalic acid and symmetrical dimethyl-urea, thus: $C_6H_8N_2O_3 + 2KHO = CO(NMeH)_2 + K_2C_2O_4$. That this urea is the symmetrical dimethyl-urea is shown by its melting point, viz., 97—100° (according to Wurtz, 99.5°), and further by its yielding methylamine when heated with baryta-water.

Theobromine when oxidised in a similar manner yields *monomethylparabanic acid*, which is easily soluble in hot water, from which it crystallises in transparent prisms, m. p. 148°. Caustic alkalis resolve it into methyl-urea and oxalic acid, thus: $C_4H_4N_2O_3 + 2NaHO = NH_2.CO.NMeH + Na_2C_2O_4$.

In their second communication, the authors state that the complete products of the oxidation of caffeine are dimethylparabanic acid, ammonia, methylamine, and carbonic anhydride, $C_8H_{10}N_4O_2 + 3O = 2H_2O + C_5H_8N_2O_3 + 2CO_2 + NH_2Me + NH_3$; whilst theobromine yields monomethylparabanic acids, $C_7H_8N_4O_2 + 3O + 2H_2O = C_4H_4N_2O_3 + 2CO_2 + NH_2Me + NH_3$.

P. P. B.

Strychnine. By A. CLAUS and R. GLASSNER (*Ber.*, **14**, 773—778).—The authors find that different preparations of strychnine differ in

composition, and it may either have the formula $C_{21}H_{22}N_2O_2$ or $C_{22}H_{22}N_2O_2$; the free base melts at 284° , without decomposition.

Schützenberger (*J. pr. Chem.*, **75**, 122) found that by acting on strychnine salts with potassium nitrite, two bases are formed which he regarded as oxy-strychnines; these compounds have been obtained by the authors, who regard them as nitro-derivatives.

Dinitrostrychnine nitrate, $C_{22}H_{20}(NO_2)_2N_2O_2.HNO_3$, is obtained by passing nitric trioxide into an alcoholic solution of strychnine, or by boiling strychnine nitrate with concentrated nitric acid. It is soluble in alcohol and hot acetone, from which it crystallises in warty masses, is sparingly soluble in water, and insoluble in ether and chloroform.

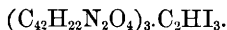
Dinitrostrychnine, $C_{22}H_{20}(NO_2)_2N_2O_2$, is obtained by adding ammonia to the nitrate, it crystallises from alcohol in orange-yellow leaflets, which darken on exposure to the air, m. p. 226° . It is insoluble in all ordinary solvents save alcohol. Its platinochloride is obtained as a yellow precipitate, which is easily decomposed. It is easily reduced, forming unstable compounds.

Cacostrychnine, $C_{21}H_{14}(NO_2)_3N_2O_4$, is obtained by treating an aqueous solution of strychnine nitrate with nitric acid; its formation is attended with evolution of carbonic anhydride. It is sparingly soluble in the ordinary solvents, more soluble in hot acids, and from boiling nitric acid it crystallises in golden-yellow needles, united concentrically in groups, and from concentrated solutions in yellow hexagonal tablets. It dissolves in alcoholic potash, forming violet solutions, and in aqueous potassium hydroxide to red solutions.

By reducing agents, it is converted into colourless compounds, which oxidise rapidly in the air. The existence of three nitro-groups is shown by the modification of Limpricht's method, used in the analysis of dinitrobrucine (p. 749).

P. P. B.

A Compound of Strychnine with Iodoform. By LEXTRAIT (*Compt. rend.*, **92**, 1057—1059).—The author has obtained a compound of strychnine with iodoform of the composition—

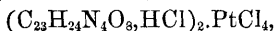


It is best obtained by dissolving 5 grams of crystallised iodoform, and 12 grams of strychnine in 500 c.c. of alcohol at 85° , and allowing the mixture to cool in a closed vessel. After about 24 hours, the crystals are filtered off, and washed with a small quantity of alcohol; then rapidly pressed between filter-paper, and finally dried, protected from light and air. The compound is very unstable. It is decomposed by light, iodoform being eliminated. It is not soluble in either hot or cold water, but readily dissolves in ether and chloroform. A litre of 98 per cent. alcohol dissolves 3.40 grams at 15° . It is decomposed by dilute acids, iodoform being set free, and salts of strychnine formed. On heating to 90° , it begins to decompose, and at 130° it blackens. When it is boiled with water, iodoform distils off. Alcohol partially decomposes it, and hence cannot be employed as a crystallising medium.

Quinine appears to form a similar compound with iodoform.

J. I. W.

Brucine. By A. CLAUS and R. RÖHRE (*Ber.*, **14**, 765—773).—*Dinitrobrucine*, $C_{23}H_{24}(NO_2)_2N_2O_4$.—This compound is obtained by passing nitric trioxide into an alcoholic solution of brucine; brucine nitrate separates out at first and again dissolves, forming a red solution, from which the dinitrobrucine separates as a heavy, granular, blood-red precipitate. By washing with alcohol and ether, it is obtained as an amorphous, vermilion, velvety-lustrous powder. It is easily soluble in water, sparingly in alcohol, and insoluble in ether. By treatment with ammonia and other bases, it is decomposed, forming coloured unstable compounds. The *platinoclride*—



is obtained as a yellow precipitate, on adding platinic chloride to the aqueous solution of dinitrobrucine. By reduction, it is converted into colourless compounds, which are very unstable. In estimating the NO_2 -groups in dinitrobrucine by Limpricht's method (this Journal, **34**, 335), the titration with iodine solution is continued until a drop of the solution no longer gives a brown precipitate with sulphuretted hydrogen. In this manner the presence of two nitro-groups has been demonstrated.

Cacoteline, $C_{20}H_{22}(NO_2)_2N_2O_6$, also yields unstable compounds when reduced; but by the above modification of Limpricht's method, the presence in it of two nitro-groups has been shown.

The authors have been unable to confirm Sonnenschein's statement (*Ber.*, **8**, 212) that strychnine is formed by the action of dilute nitric acid on brucine; chromic acid has no action on brucine; and further, the compound of brucine and methyl iodide, when heated with potassium hydroxide, yields a resinous product.

Brucine dried at 150° melts at 178° , forming a colourless liquid.

P. P. B.

Test to Distinguish Ptomaines from Vegetable Alkaloids.

By P. BROUARDEL and E. BOUTMY (*Compt. rend.*, **92**, 1056).—The authors find that potassium ferricyanide forms a convenient reagent for distinguishing ptomaines (alkaloids extracted from a dead body) from vegetable alkaloids, inasmuch as the former reduces it, whilst the latter exerts no action on it. In order to test a base extracted from a body in cases of suspected poisoning, the authors convert it into sulphate, and add a few drops of the solution to a small quantity of ferricyanide in a test-tube; on adding neutral ferric chloride, if a ptomaine be present, Prussian blue will be formed; but if the base is a vegetable alkaloid, no reaction occurs.

Morphine and veratrine, however, form exceptions to the rule.

J. I. W.

Oxidation of Cholic Acid. By P. T. CLÈVE (*Bull. Soc. Chim.* [2], **35**, 373—379 and 429—433).—On oxidising cholic acid with permanganate, the author finds that two acids are produced. One is precipitated from the aqueous solution on adding dilute sulphuric acid; the other, oxalic acid, remains in solution. The author finds that the latter is not formed in sufficient quantity to warrant the conclusion that it is produced by the direct oxidation of the cholic acid. He finds that the other acid is only obtained in a crystalline state, when the

action of the permanganate is prolonged. He allows it to extend over several weeks. The acid which is then obtained crystallises from water in scales or brilliant rhombic prisms.

By acting on cholic acid with chromic mixture, the same acid is obtained. The author believes, however, that a second new acid is formed in the reaction, but in such small quantity that he has been unable to obtain it pure. He was unable, by oxidising cholic acid by Tappeiner's method, to obtain the cholesteric acid described by that chemist, but he obtains the above new acid. He also did not find acetic or any fatty acids among the products of oxidation, although when cholic acid is crystallised from alcohol, the crystals appear to occlude small quantities of the liquid, and this on oxidation yields acetic acid and aldehyde. The main product consisted of a resinous substance, which on treating, according to Tappeiner's method, yielded cholanic acid and the above new acid, which the author calls *bilanic acid*. The latter has not the same bitter taste as cholic acid, and does not give the Pettenkofer reaction. It is easily soluble in alcohol and in acetic acid; it separates from a solution of the latter on cooling in a soapy mass, which after a short time becomes transformed into rhombic crystals 5—6 mm. long. The rotatory power of the acid crystals containing $4\text{H}_2\text{O}$ is $[\alpha] = 47.4^\circ$. The calcium salt, $\text{C}_{50}\text{H}_{66}\text{Ca}_3\text{O}_{18} + 5\text{H}_2\text{O}$, is obtained by treating the acid with milk of lime. It is soluble in cold water, but on warming, the solution deposits small needles, which disappear as the liquid cools. The barium salt, $\text{C}_{50}\text{H}_{66}\text{Ba}_3\text{O}_{18} + \text{H}_2\text{O}$, crystallises from very concentrated solutions in spheroidal masses of transparent prisms. The normal lead salt, obtained by precipitating with acetate of lead, crystallises in microscopic scales or tables. The acid lead salt is obtained by adding lead nitrate to a warm saturated solution of the acid in dilute ammonia. It forms brilliant hexagonal plates. The neutral silver salt is precipitated when silver nitrate is added to a solution of the calcium salt. It forms white microscopic scales. The acid silver salt is obtained in a similar manner to the lead salt. It forms colourless needles.

Cholanic Acid.—Tappeiner gave to this acid the formula $\text{C}_{20}\text{H}_{28}\text{O}_6$. The author has prepared the free acid and some of its salts, and finds that his analyses, as well as those of Tappeiner, accord very well with the formula $\text{C}_{24}\text{H}_{36}\text{O}_7$. The acid is tribasic. The author was unable to prepare the acid barium salt mentioned by Tappeiner.

J. I. W.

Papaine; a New Contribution to the History of Soluble Ferments. By A. WURTZ (*Compt. rend.*, 91, 787—791).—It has been already shown that papaine, the soluble ferment of the *Carica papaya*, is closely connected with the albuminoids, both in its composition and chemical properties; further researches having been made, the author is now able to give some details regarding its digestive power, and to express an idea as to its mode of action.

0.1 gram of papaine was digested with 100 grams of moist fibrin, diffused in 500 c.c. of distilled water to which a few drops of hydrochloric acid were added. At the end of 36 hours, there was obtained from the mixture 2.5 grams of insoluble dyspeptone; 8.9 grams of parapeptone precipitable by alcohol; and a brown residue after eva-

poration weighing 10·3 grams. This residue when taken up again by water, no longer gave a precipitate on addition of nitric acid; but on careful evaporation and standing, it eventually deposited crystals, which, after purification, presented the appearance of leucine.

From this experiment, it is evident that the papaine had dissolved 1000 times its weight of moist fibrin, of which the largest portion had been transformed into peptone not precipitable by nitric acid, and that, in consequence of the complete hydration of the fibrin, it had even formed a small quantity of an amido-body, the same being known to occur in the process of good peptic digestion.

In another experiment, 0·05 gram of the same papaine liquefied 100 grams of moist fibrin, or 2000 times its weight, with the exception of a small residue of dyspeptone weighing 4·2 grams. In order to ascertain if the ferment was capable of assimilating water itself, a solution of 3 grams of papaine in 20 c.c. of water was heated for 15 days to 50°; after filtration and evaporation in a vacuum, it was precipitated by alcohol, and the modified papaine thus obtained was submitted to analysis. As was anticipated, the ferment had undergone partial hydration, in such a manner that its carbon was lowered by about 2 per cent. Several similar experiments were made at various temperatures with like results, the extent of the hydration appearing within certain limits to proceed *pari passu* with the temperatures.

The following experiment may, perhaps, throw some light upon the mode of action of the papaine. 0·3 gram was dissolved in 50 c.c. of water, and 10 grams of fibrin digested with the solution, and at the end of 20 minutes the liquid was expressed, and the fibrin subjected to prolonged washing with cold water. In the liquid obtained by the expression of the fibrin a new portion of 15 grams was digested, and at the expiration of half an hour this second portion of fibrin was expressed, and washed as the first. Both portions (the first reduced to 7 grams by the beginning of digestion, the second to 14 grams) were digested at 40° with pure water, when both became dissolved, the second leaving a residue of 4 grams of moist dyspeptone.

In these two experiments, the washings had certainly removed the *dissolved* ferment, and the washed fibrin would not have been able to dissolve, except by the action of a portion of the ferment fixed upon, or perhaps combined with it; the ferment fixed upon the fibrin in an insoluble state had then redissolved it, in consequence of the hydration of the fibrin.

By the above and similar experiments it was sought to establish that the papaine begins by combining with the fibrin, and that the insoluble product then gives by the action of water the soluble substances resulting from the hydration of the fibrin; at the same time, the ferment, being again set free, is necessarily at liberty to exercise its action on a new portion of fibrin.

J. W.

Blood-crystals. By H. STRUVE (*Ber.*, 14, 930—932).—Freshly prepared blood-crystals which have been rendered insoluble by treatment with alcohol, are decolorised by ammonia or by chlorine-water without undergoing any change in their crystalline form. Hence the

author concludes that the blood-crystals consist essentially of globulin mixed with a minute quantity of the red colouring-matter of the blood.

W. C. W.
