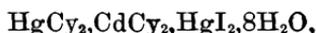


Organic Chemistry.

Mechanical Determination of the Arrangement of the Carbon Atoms in Organic Compounds. By G. HINRICHS (*Compt. rend.*, **113**, 313—315).—In the structural formulæ for the normal paraffins, the carbon atoms are shown as forming a straight line. All those properties which depend solely on structure should be continuous functions of the number of carbon atoms in the molecule, whether the number of carbon atoms is even or uneven. The melting points of the paraffinoid hydrocarbons containing an uneven number of carbon atoms are less, however, than they should be according to the above rule. If the melting point is a function of the moment of inertia of the molecule for its natural axis of rotation, the author shows that the above fact would lead to the arrangement of the carbon atoms in a zig-zag line. H. C.

Action of Boron Fluoride on Nitriles. By G. PATEIN (*Compt. rend.*, **113**, 85—87).—Boron fluoride combines in molecular proportions with aliphatic and aromatic nitriles. When a rapid current of the fluoride is passed into acetonitrile, it is absorbed with evolution of heat, and, on cooling, colourless, deliquescent, fuming crystals, having the composition MeCN, BF_3 , separate. The substance melts at 120° , sublimes, and may be preserved in sealed tubes containing boron fluoride. It is soluble in alcohol and ether, and with decomposition in water and alkalis. Similar compounds are formed with benzonitrile and toluonitrile. Hydrogen cyanide forms a similar very unstable compound with absorption of heat. JN. W.

Action of Ammonia on some Compounds of the Haloïd Salts of Mercury. By R. VARET (*Compt. rend.*, **112**, 1312—1314).—When a solution of mercury cadmium iodocyanide,



is allowed to drop into aqueous ammonia until a permanent precipitate is formed, and the precipitate is allowed to remain in contact with the mother liquor for some time with occasional agitation, a yellowish, amorphous powder is obtained, which must be dried rapidly on filter paper. It is mixture of ammonio-cadmium iodide with the compound $\text{HgCy}_2, \text{CdCy}_2, \text{HgI}_2, 4\text{NH}_3$ or its isomeride $2\text{HgCy}_2, \text{CdI}_2, 4\text{NH}_3$, the ammonia having produced a reaction the inverse of that which gave rise to the original salt, and again formed cadmium iodide. Similar results are obtained by dissolving mercury cadmium iodocyanide in ammonia.

Mercury potassium iodocyanide dissolves abundantly in aqueous ammonia at 40° , and separates unchanged on cooling.

Ammonia acts slowly on mercuric cyanide, but if the moist salt is heated in a current of the gas at 100° until quite dry and the passage of the gas is afterwards continued for some time at the ordinary temperature, the compound $\text{HgCy}_2, 2\text{NH}_3$ is obtained as a white,

amorphous powder, which alters readily when exposed to air, losing ammonia rapidly and absorbing water.

Mercury barium chlorocyanide, under similar conditions, yields the compound $2\text{HgCy}_2, \text{BaCl}_2, 4\text{NH}_3$, which alters rapidly on exposure to air, is only slightly soluble in ammonia, and is decomposed by water. The chlorocyanide absorbs ammonia much more rapidly than either of its constituent salts separately, and the compound seems to be more stable than the compound formed by either of the simple salts.

C. H. B.

The Cyanogen Compounds of Magnesium. By R. VARET (*Compt. rend.*, 112, 1449—1451).—A triple salt of the composition $\text{MgCy}_2, \text{HgCy}_2, \text{HgI}_2 + 8\text{H}_2\text{O}$ is formed when small quantities of magnesium iodide are thrown into a concentrated solution of mercuric cyanide maintained at $60\text{--}70^\circ$, using 15 grams of magnesium iodide to 25 grams of mercuric cyanide. The filtered liquid carefully evaporated on the water-bath deposits, on cooling, large, light-yellow, transparent lamellæ, which may be dried in paper. When the salt is carefully heated, it first yields hydrocyanic acid, water, and mercuric iodide, and subsequently, on fusion, an abundant sublimate of mercuric iodide and mercury, together with cyanogen. From the character of this decomposition, it is evident that the compound is more complex than would be formed by a simple union of mercuric cyanide and magnesium iodide. When a solution of the iodocyanide is boiled with ammonium picrate, the fine-red coloration of ammonium isopurpurate is produced; such a reaction does not occur with mercuric cyanide. Similarly, copper sulphate yields a precipitate of mercuric iodide and cupric cyanide, the latter further decomposing into cuprous cyanide and cyanogen. Mercuric cyanide does not react with the oxygen salts of copper.

If a concentrated solution of magnesium bromide be dropped slowly into a saturated solution of mercuric cyanide at 50° , and the mixture evaporated, white, nacreous, silky lamellæ of the formula $\text{MgCy}_2, \text{HgCy}_2, \text{HgBr}_2 + 8\text{H}_2\text{O}$ are deposited. This substance is very hygroscopic and soluble in water, and is unstable in air. Its constitution is not clearly established.

W. T.

Fulminates. By H. N. WARREN (*Chem. News*, 64, 28).—Copper fulminate, obtained by digesting a solution of silver fulminate with copper filings, when reduced by electrolysis, yielded copper, hydrocyanic acid, and ammonia in abundance, also ammonium fulminate and fulminic acid. Cuprammonium fulminate, obtained by treating copper fulminate with excess of ammonia, dried over sulphuric acid, and decomposed by hydrogen sulphide, yielded copper sulphide, carbamide, and ammonium thiocyanate. Silver fulminate, by the action of dry silicon fluoride, yielded silver fluoride and an explosive gas. By the action of chlorine, bromine, or iodine, the haloid silver salt and chloro-, bromo-, or iodo-picrin were obtained.

D. A. L.

Allyl Alcohol and its Formation from Dichlorhydrin and Sodium. By H. TORNÖE (*Ber.*, 24, 2670—2678).—Aqueous allyl

alcohol, which has been kept over freshly ignited potassium carbonate, still contains a considerable quantity of water; on repeated fractional distillation, such a mixture can be separated into two portions, boiling constantly at about 87.5° and 97° respectively. The fraction of lower boiling point seems to be a mixture of 72.3 per cent. of allyl alcohol and 27.7 per cent. of water; the fraction of higher boiling point is almost anhydrous allyl alcohol, but contains a small quantity of acraldehyde. On treating the almost anhydrous allyl alcohol with dry chlorine, a large quantity of acraldehyde is formed, and the yield of pure dichlorhydrin (b. p. $181-186^{\circ}$, with slight decomposition) is only about 20 per cent. of the theoretical.

Both the dichlorhydrins are very stable towards acid reducing agents, and are not acted on by nascent hydrogen or by stannous chloride; when heated with hydriodic acid and amorphous phosphorus, they both yield isopropyl iodide, and a small quantity of a liquid boiling at about $34-36^{\circ}$, which is most probably isopropyl chloride.

It has been previously shown by Hübner and Müller (*Annalen*, **159**, 168) that allyl alcohol is produced by the action of sodium on an anhydrous ethereal solution of dichlorhydrin (b. p. 144°); the author succeeded in isolating impure epichlorhydrin from the products of this reaction and proved its presence by converting it into dichlorhydrin.

When an anhydrous ethereal solution of epichlorhydrin is treated with sodium, only a trace of a liquid, which seems to be impure allyl alcohol, is obtained, so that it is impossible to assume that the production of allyl alcohol from dichlorhydrin, in the reaction just referred to, is due to the intermediate formation of epichlorhydrin.

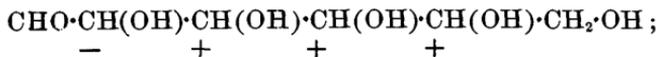
The two acetylchlorhydrins are converted into one and the same allyl acetate on treatment with sodium in anhydrous ethereal solution.

F. S. K.

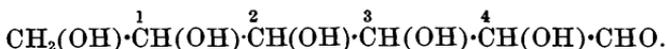
Rotatory Power of Compounds of Mannitol with Acid Molybdates. By D. GERNEZ (*Compt. rend.*, **112**, 1360—1363).—The author has previously shown (*Abstr.*, 1890, 744) that compounds such as active malic acid having both acid and alcoholic functions in aqueous solution form compounds with optically inert substances such as the molybdates, which compounds have a greater rotatory power than the original acid. The present paper describes similar compounds formed by the alcohol mannitol. Solutions were employed containing 0.7583 gram and 1.5866 grams of mannitol, to which were added varying quantities of the acid sodium or ammonium molybdates respectively, differing by $1/12$ equivalent, and sufficient water to make the total volume 24 c.c. The initial negative rotation of the mannitol is changed to a positive rotation on the addition of the first $1/12$ equivalent of acid molybdate; this rotation increases regularly on the addition of further quantities of the acid salt until maxima of $2^{\circ} 45'$ and $5^{\circ} 16'$ respectively are attained with $6.75/12$ equivalent of the acid molybdate. This proportion of the acid salt corresponds with 3.9375 equivalents of molybdic acid to 1 equivalent of mannitol. The rotation observed is slightly less if the ratio be 4 to 1 . As normal sodium molybdate has no action on mannitol, there is, considering only the molybdic acid not saturated by the soda, 2.25 equivalents of

molybdic acid to 1 equivalent of mannitol, or 9 to 4 respectively as the proportions in the compound formed. Further additions of the salt give gradually decreasing rotations, indicating the decomposition of the compound corresponding with the maximum and a tendency towards some other state of equilibrium. W. T.

Configuration of Grape Sugar and its Isomerides. By E. FISCHER (*Ber.*, **24**, 2683—2687).—In the last paper on this subject (this vol., p. 1173), the configuration of grape sugar was expressed by the formula



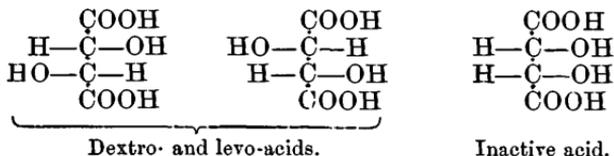
as, however, in the case of such complicated molecules, the employment of the signs + and - for denoting the arrangement in space may easily give rise to mistaken views, it becomes necessary to give a more complete explanation of the formulæ. For this purpose, the four asymmetric carbon atoms in the molecule of grape sugar may be numbered as shown below:—



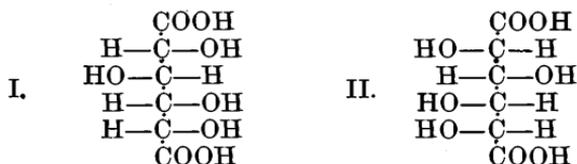
Van't Hoff, in his general considerations, on which the author's special deductions are based, only compares the carbon atom 1 with the carbon atom 4, and 2 with 3; consequently, in the case of grape sugar, the arrangement of the hydrogen atom and the hydroxyl group around 1 is the reverse of that around 4, whilst the arrangement around 2 and 3 is the same. The arrangement of the asymmetric group around the carbon atom 1 can, however, be also compared with that of the two central asymmetric groups, as was done by the author in fixing the relationship of grape sugar to xylose and arabinose; it was then shown that the arrangement of the hydrogen atom and hydroxyl group around the carbon atom 1 is identical with that around 3. From a superficial examination, it might be concluded that this is also so in the case of the carbon atoms 1 and 2, but as a matter of fact the reverse is true.

With the aid of models, it is easily seen that, in the case of the carbon atom 2, the sign varies according as it is compared with 1 or 3. As, therefore, the above method of expressing the configuration of grape sugar is ambiguous, it is advisable to do so in another way.

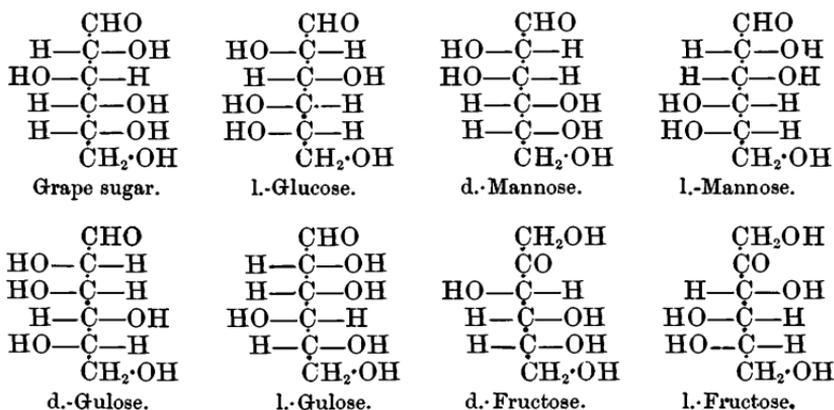
In the first place, the molecules of dextro-, levo-, and inactive tartaric acids can be constructed (with the aid of Friedländer's india-rubber models), and laid on paper in such a way that the four carbon atoms are arranged in a straight line, the hydrogen atoms and hydroxyl groups standing above the plane of the paper; the projections of these models would then be the following:—



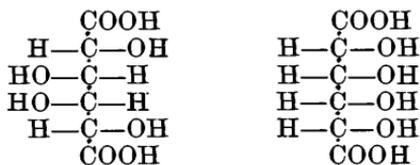
On proceeding in a similar manner with the models of d.- and l.-saccharic acids, the two following projections are obtained :—



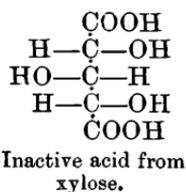
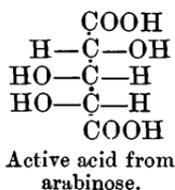
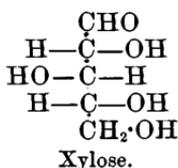
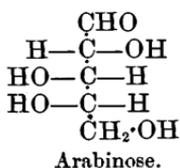
As it is immaterial which of these two configurations is assigned to d.-saccharic acid, it may be assumed to have that represented by the formula I; the configurations of grape sugar and its isomerides would then be expressed as follows :—



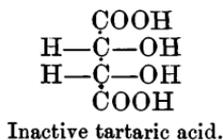
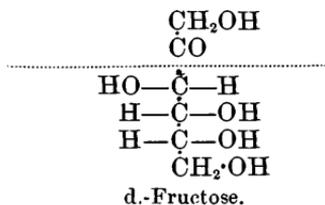
The configurations of the two inactive dicarboxylic acids of the dulcitol series, which are probably represented by mucic acid and allomucic acid, may be denoted by the following formulæ :—



This manner of expressing configuration can also be adopted in the case of the pentoses; its use is even more advantageous in the case of the more complex molecules of the heptoses, octoses, &c., where the ambiguity of the signs + and - constantly becomes greater. The configurations of the two pentoses, for example, and of the trihydroxyglutaric acids obtained therefrom, may be represented by the following projections :—



The advantage of the new formulæ is more particularly noticeable in considering those reactions in which an increase or decrease in the number of asymmetric carbon atoms takes place; as, for example, in the oxidation of levulose to inactive tartaric acid; this change is very simply expressed in the following way:—



F. S. K.

Stachyose. By A. v. PLANTA and E. SCHULZE (*Ber.*, **24**, 2705—2709).—Stachyose (Abstr., 1890, 1088), like raffinose, is a triose, and on inversion it yields galactose, grape sugar, and levulose; mannose and pentoses could not be detected in the solution of the inverted sugar. Since stachyose yields 37—38 per cent. of mucic acid on oxidation with nitric acid, it may be assumed that the molecule of this sugar is formed by the combination of 3 mols. of galactose either with 2 mols. of grape sugar and 1 mol. of levulose, or with 1 mol. of grape sugar and 2 mols. of levulose; it is probable, therefore, that stachyose has the molecular formula $\text{C}_{36}\text{H}_{64}\text{O}_{32}$.

F. S. K.

Lupeol. By A. LIKIERNIK (*Ber.*, **24**, 2709—2710).—Lupeol (this vol., p. 551) may be considered as a homologue of α - and β -amyrin (compare Vesterberg, this vol., p. 165). The relationship of lupeol to the amyryns is shown by the fact that they all give substitution, and not additive, products with bromine; a chloroform solution of each of the three compounds turns reddish-violet on the addition of acetic anhydride and a little concentrated sulphuric acid.

F. S. K.

Conversion of Starch into Dextrin by the Butyric Ferment. By A. VILLIERS (*Compt. rend.*, **113**, 144—145).—When starch paste is inoculated with the butyric ferment and kept at 40°, the rotatory power at first increases, reaches a maximum after 2½ days, and then slowly decreases, the starch almost entirely disappearing. When filtered through biscuit porcelain, and kept at 40° for several days, the rotatory power of the solutions undergoes no further change. They give no starch reaction with iodine. If a small quantity of starch is added to the sterilised solutions, and they are then kept at

40°, the starch disappears after some days, but the rotatory power of the liquid remains practically unchanged.

In the conversion of starch into dextrin by the action of the butyric ferment, the latter secretes a soluble product capable of producing the conversion in the absence of any organisms. This product is formed continually in very small quantities, and its activity seems to be exhausted almost as fast as it is formed.

C. H. B.

Bleaching of Cotton by Hydrogen Peroxide. By PRUD'HOMME (*Compt. rend.*, 112, 1374—1376).—The superiority of the results obtained in bleaching cotton when calcined magnesia is added to the hydrogen peroxide used is due to the formation of magnesium peroxide, which is more stable than hydrogen peroxide at 100°. 6 per cent. hydrogen peroxide, diluted with 10 parts water and boiled for half an hour, has its titration value reduced to one-tenth of that shown before boiling. If calcined magnesia, to the amount of 5 per cent. of the weight of hydrogen peroxide, be added, the titration value is only reduced to nine-tenths. Magnesia is subjected to the action of 3 per cent. hydrogen peroxide for some time at the ordinary temperature, filtered, washed, and dried at 100—105°; the active oxygen, titrated with permanganate, corresponds with the formula $3\text{Mg}(\text{OH})_2 + \text{MgO}(\text{OH})_2$ for the dry product. This substance has an alkaline reaction, and loses all its active oxygen at about 300°. Magnesium peroxide is also formed when the metal is dissolved in hydrogen peroxide.

Zinc and cadmium also form peroxides; that of zinc has probably the formula $2\text{ZnO} + \text{ZnO}(\text{OH})_2$.

Hydrogen peroxide has a direct action not only on the various colouring matters present, but even on such substances as cellulose. Fatty substances give off much carbonic anhydride on boiling with hydrogen peroxide, due to the oxidation of the glycerol set free by the saponification brought about by the magnesia employed in the process. Slightly acid hydrogen peroxide attacks neutral fats on boiling, liberating fatty acids and disengaging carbonic anhydride. Under the joint action of magnesia and hydrogen peroxide, the fatty acids are oxidised with production of carbonic anhydride. Oleic acid is, under these conditions, partially transformed into palmitic acid, just as when treated with caustic potash.

In bleaching by hydrogen peroxide, cellulose is converted into oxycellulose, recognised by dyeing with basic colouring matters which fix on oxycellulose without a mordant. The alteration of cellulose is greater if impregnated with concentrated caustic soda before treating it with hydrogen peroxide.

This action of hydrogen peroxide is greatly augmented by the presence of metallic oxides, which appear to serve as vehicles for the active oxygen; the bleaching, therefore, should be preceded by treatment with a very dilute acid. A piece of cloth mordanted with iron, chromium, and aluminium, and boiled for one or two hours with magnesia and hydrogen peroxide, is strongly attacked in the mordanted portions. The action of hydrogen peroxide on cellulose

presents great analogies with that of cuprammonium solutions, which also act as oxidising agents, forming oxycellulose.

Cotton cloth treated with caustic soda at 36° and thoroughly washed is acted on more strongly by cuprammonium solutions of moderate concentration than cloth not so treated. It is concluded that, contrary to the received opinion, cellulose is attacked and suffers transformation under the action of Schweitzer's reagent.

W. T.

Ureides from Normal Acids. By C. MATIGNON (*Compt. rend.*, **112**, 1367—1369).—The heats of combustion of formylcarbamide and acetylcarbamide are respectively +207·3 Cal. and +360·9 Cal.; the corresponding heats of formation are +119·3 Cal. and +129 Cal.

In accordance with the difference, 153·6 Cal., between the heats of combustion of these two successive homologues, there is great similarity in their reactions with the same reagents. Formic and acetic acids differ considerably in properties, and the difference between the heats of combustion of these acids taken in the solid state is only 140 Cal.

Formic acid and urea in solution combine with liberation of +13·4 Cal., whereas acetylcarbamide is not formed from acetic acid and urea in solution, as the reaction would require an absorption of 0·2 Cal. The synthesis of acetylcarbamide from acetamide and urea has not been accomplished; it would require an absorption of 12·5 Cal. Acetylcarbamide and formylcarbamide yield flocculent precipitates with mercuric chloride and potash. The formula of the compound with formylcarbamide is probably $\text{COH}\cdot\text{N} < \begin{matrix} \text{CO} \\ \text{Hg} \end{matrix} > \text{NH}$.

Urea acetate, $\text{CON}_2\text{H}_4, \text{C}_2\text{H}_4\text{O}_2 + 2\text{H}_2\text{O}$, forms large, deliquescent crystals; the heat of solution at 16° is -8·8 Cal. at a concentration of $\frac{1}{8}$ mol. per litre. Its heat of formation is +3·1 Cal.; the smallness of this number accounts for the easy dissociation of the salt by water.

W. T.

Products of Oxidation of Uric Acid. By C. MATIGNON (*Compt. rend.*, **112**, 1263—1266).—*Allantoin*.—Heat of combustion at constant pressure, +413·8 Cal.; heat of formation, +170·4 Cal.; heat of dissolution at 15°, -7·5 Cal.

Alloxan.—Heat of combustion, +278·5 Cal.; heat of formation, +236·7 Cal.; heat of dissolution, +4·1 Cal., -4·2 Cal., and -9·0 Cal. in the three states of hydration respectively.

Alloxantin.—Heat of combustion, +586·3 Cal.; heat of formation, +513·1 Cal.; heat of dissolution at 15°, -9 Cal.

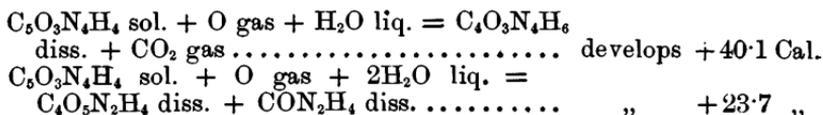
$\text{C}_4\text{O}_4\text{N}_2\text{H}_2 \text{ sol.} + \text{H}_2\text{O sol.} = \text{C}_4\text{O}_5\text{N}_2\text{H}_4$ develops +9·0 Cal.

$\text{C}_4\text{O}_5\text{N}_2\text{H}_4 \text{ sol.} + 3\text{H}_2\text{O sol.} =$

$\text{C}_4\text{O}_5\text{N}_2\text{H}_4, 3\text{H}_2\text{O sol.} \dots \dots \dots \text{ ,, } +6\cdot9 \text{ Cal. } (3 \times 2\cdot3)$.

It follows that the entrance of the first molecule of water into the molecule of alloxan causes a development of heat almost as great as the heat of hydration of phosphoric anhydride, and this result confirms

Baeyer's view, that the compound $C_4O_4N_2H_2$ is the anhydride of alloxan.



It would seem, therefore, that the oxidation of uric acid should always produce allantoin, and this is true so long as no secondary reaction takes place with the same velocity as the principal reaction; for example, when potassium permanganate is the oxidising agent. If, on the other hand, nitric acid is the oxidising agent, nitrous acid is formed, and this at once attacks the urea, and the heat developed by this simultaneous secondary reaction is sufficient to turn the balance in favour of alloxan. The thermochemical results explain the well-known fact that the action of oxidising agents on uric acid yields either allantoin or alloxan, but never both at the same time.

C. H. B.

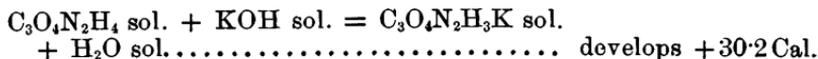
Parabanic and Oxaluric Acids. By C. MATIGNON (*Compt. rend.*, 113, 198—200).—*Parabanic Acid*.—Heat of combustion, +212.7 Cal.; heat of formation, +139.2 Cal.; heat of dissolution at 20°, -5.1 Cal.

Oxaluric Acid.—Heat of combustion, +211 Cal.; heat of formation, +209.9 Cal.

The formation of parabanic acid from oxalic acid and urea would develop +2.2 Cal., and the formation of oxaluric acid would develop +2.5 Cal. These numbers are very low, and explain the difficulty of passing directly from urea to the ureides. The conversion of parabanic acid into oxaluric acid by elimination of water would develop only +0.3 Cal.

A cold solution of potassium hydroxide, containing 1 gram-molecule in 20 litres, rapidly converts both parabanic acid and oxaluric acid into normal potassium oxalate, the change in the case of parabanic acid being accompanied by the development of +24.4 Cal., the acid being solid and the potash and the products dissolved. The heat of formation deduced from this result is 138.7 Cal., whilst the direct determination gives 139.2 Cal.

Potassium oxalurate, prepared by dissolving oxaluric acid in an equivalent quantity of potash solution and evaporating the liquid, is different from the oxalurates described by Menschutkin and Strecker respectively. It crystallises in stellate groups of slender, anhydrous, prismatic needles.



The action of the first equivalent of potash on oxalic acid develops +34.2 Cal.

C. H. B.

Action of Diazobenzene Chloride on Acetone. By E. BAMBERGER and P. WULZ (*Ber.*, 24, 2793—2797).—A study of the properties of a hydronaphthol obtained from tetrahydronaphthylene oxide

(this vol., p. 1073) led Bamberger to the conclusion that compounds containing the radicle $\text{CH}_2\cdot\text{CO}$ (or $\text{CH}\cdot\text{CH}\cdot\text{OH}$), whether belonging to the fatty or the aromatic series, must be capable of forming colouring matters on treatment with diazotised bases in the presence of alkalis. This opinion has been verified with acetone, acetaldehyde, propaldehyde, cenanthaldehyde, acetophenone, camphor, &c., all of which give intense, dark claret coloured solutions. Formaldehyde, which does not contain the radicle, does not give the reaction, but, on the other hand, substances like lactic acid and dextrose, and, in particular, ethylenic compounds, such as allyl alcohol, dihydronaphthalene, dihydrobenzaldehyde, &c., form colouring matters under the conditions named.

When a mixture of acetone (12 grams) with a solution of diazobenzene chloride (prepared from 18.6 grams aniline) is slowly stirred into carefully cooled 20 per cent. aqueous soda (200 grams), a red coloration is produced, and the mixture becomes turbid, finally depositing a brownish-black resin. The product can be obtained in a crystalline form by dissolving it in well-cooled sulphuric acid, and, after 12 hours, pouring the deep blue solution on to ice, drying the reddish-brown, flocculent precipitate, and then carefully extracting with ether. On evaporating the deep red ethereal solution, a crystalline residue is obtained which can be purified by repeated crystallisation from alcohol. The compound has the composition $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$, and is more probably a bis-hydrazone of mesoxaldehyde than a disazo-derivative of acetone. It crystallises either in lustrous, garnet-red prisms, showing an intense, steel-blue, metallic shimmer, or by rapid crystallisation in tufts of flat needles, melts at $134\text{--}135^\circ$, and dissolves easily in the ordinary organic solvents, but only very sparingly in water. It has feebly basic properties, and dissolves in concentrated mineral acids, forming deep violet-blue solutions, from which the colouring matter is precipitated unchanged on the addition of water. The compound is destitute of tinctorial power, but its sulphonic acid, contained in the aqueous solution after extraction with ether, dyes wool and silk a bright chestnut-brown in an acid bath.

In the concluding portion of the paper, the authors draw attention to the difference between this reaction and that employed by Penzoldt and Fischer for the detection of aldehydes (Abstr., 1883, 829).

W. P. W.

Ethereal Nitrosocyanacetates. By P. T. MULLER (*Compt. rend.*, 112, 1372—1373).—These salts are prepared by the action of amyl nitrite on the sodium derivatives of ethereal cyanacetates, with subsequent treatment of the sodium salts produced with sulphuric acid.

Ethyl Nitrosocyanacetate.—An equivalent quantity of sodium dissolved in absolute alcohol is added, little by little, to ethyl cyanacetate (1 mol.), and amyl nitrite (1 mol.) is added, in small portions at a time, to the resulting mass, which is then heated to $50\text{--}60^\circ$. It is cooled, washed with ether, and precipitated with dilute sulphuric acid. The oil is dissolved in ether, dried, and crystallised by evaporation. Ethyl nitrosocyanacetate, $\text{NO}\cdot\text{CH}(\text{CN})\cdot\text{COOEt}$, forms small, white

crystals, melts at 127—128°, and is very soluble in water, alcohol, and ether, less so in benzene. The sodium salt crystallises in small, yellow, fibrous prisms containing 5 mols. H₂O. It is formed directly by the action of amyl nitrite on ethyl sodiocyanacetate; the product is evaporated to dryness and dissolved in alcohol; the salt is precipitated by the addition of benzene.

Methyl nitrosocyanacetate is obtained, by the same method as its homologue, in the form of small, tabular crystals melting at 119°. The sodium salt occurs in yellow, flat prisms containing 1½ mols. H₂O.
W. T.

Cyanostearic Acid, Hexadecylmalonic Acid, and Hexadecylmalonic Acid. By C. HELL and J. SADOMSKY (*Ber.*, 24, 2778—2785).—*α-Cyanostearic acid*, CN·C₁₇H₃₄·COOH, is prepared by dissolving ethyl *α*-bromostearate (this vol., p. 1336) (50 grams) in alcohol, adding potassium cyanide (14 grams) dissolved in the smallest quantity of hot water, and heating the mixture in a reflux apparatus for 5—6 days, then collecting the dark precipitate, washing with alcohol, dissolving in water, adding sulphuric acid, filtering from the humus substance which separates, extracting with ether, and finally purifying the acid by crystallisation from glacial acetic acid, and subsequently from a mixture of alcohol and light petroleum; it forms small, iridescent, transparent plates or prisms, melts at 83·5°, and is readily soluble in alcohol, ether, and glacial acetic acid, but almost insoluble in light petroleum. When the acid is heated at 200—250°, carbonic anhydride is evolved and stearonitrile (Krafft and Stauffer, *Abstr.*, 1882, 1274) is formed.

Hexadecylmalonic acid, CONH₂·C₁₇H₃₄·COOH, is obtained by boiling *α*-cyanostearic acid with alcoholic potash for 2—3 days, distilling off the alcohol, dissolving the residue in water, precipitating with hydrochloric acid, redissolving in ether, and crystallising the plates which first separate from the ethereal solution from a mixture of light petroleum and a little alcohol. The acid forms delicate, silky scales, and is readily soluble in hot alcohol, ether, and hot benzene, but only sparingly in light petroleum; it begins to decompose below its melting point into stearamide (m. p. 108°), and when heated at 130—150°, it is completely converted into the latter.

Hexadecylmalonic acid, C₁₇H₃₄(COOH)₂, is formed by boiling hexadecylmalonic acid with alcoholic potash for 3—4 days, or *α*-cyanostearic acid with an excess of the latter for 6—7 days, isolating in the same manner as hexadecylmalonic acid, and finally crystallising from glacial acetic acid; it crystallises in lustrous, pointed, rhombic tablets, melts at 121·5—122°, and is readily soluble in alcoholic ether, hot benzene, or glacial acetic acid, but almost insoluble in light petroleum, and quite so in water. The acid is identical with the cetylmalonic acid described by Guthzeit (*Abstr.*, 1881, 408). When heated at 160—180°, hexadecylmalonic acid is converted into stearic acid with the evolution of carbonic anhydride. The salts likewise decompose on heating, as follows: the *barium salt* at 270—290°, the *cadmium salt* at 250°, the *zinc salt* at 230°, the *copper salt* at 210°, and the *silver salt* at 190°.
A. R. L.

Acids from Baku Petroleum. By O. ASCHAN (*Ber.*, 24, 2710—2724; compare *Abstr.*, 1890, 737).—Heptanaphthenecarboxylic acid, $C_8H_{14}O_2$, has been previously isolated by Markovnikoff; it boils at 237—239°, and is with difficulty rendered anhydrous. The coefficient of refraction for sodium light is $N = 1.4486$, and the molecular refractive power = 38.7, which agrees with the theory. The acid is unaffected by bromine or potassium permanganate. The *methyl salt* boils at 190—192°; the specific gravity = 0.9357, 18°/18°. The *potassium* and *sodium salts* are crystalline and readily soluble in water or alcohol. The *calcium salt*, $(C_7H_{13}CO \cdot O)_2Ca$, crystallises from water in long needles, and is deposited in an amorphous condition on heating a cold, saturated solution. The *barium salt* is obtained in anhydrous, lustrous plates; the *silver salt* is amorphous. All these compounds resemble the corresponding hexanaphthenecarboxylates in general properties. The *chloride*, $C_7H_{13} \cdot COCl$, is a strongly refractive, dense liquid, which boils at 193—195° and gradually undergoes decomposition. The *amide*, $C_7H_{13} \cdot CONH_2$, is most readily prepared by heating the acid (5 parts) with ammonium thiocyanate (4 parts) until a portion becomes crystalline on cooling; it is deposited from a mixture of ether and light petroleum in silvery, lustrous plates; it melts at 133°, but sublimes below 100°, and boils at about 250° with slight decomposition. The compound is somewhat volatile with steam, and combines with hydrochloric acid and calcium chloride. The *nitrile*, $C_7H_{13}CN$, is formed by the distillation of the preceding compound; it boils at 199—201° (corr.) and has a characteristic smell; the coefficient of refraction is $[n]_D = 1.4452$.

Heptanaphthenamine, $C_7H_{13} \cdot NH_2$, is readily prepared from the amide by Hofmann's method; the yield is 66 per cent. of theory. It boils at 151—153° (corr.), and is a colourless liquid, absorbing carbonic anhydride from the atmosphere, and giving the ordinary reactions for primary amines. The *hydrochloride* forms large, lustrous plates, which are excessively soluble in water or alcohol, and are very hygroscopic; the *platinochloride* crystallises in large, lustrous, golden, hexagonal plates. Attempts to prepare heptanaphthene alcohol by means of the diazo-reaction were not very successful; a liquid was obtained which boiled at 161—163°: it was, however, coloured, and contained nitrogen.

Heptanaphthenecarboxylic acid is oxidised on boiling with 10 parts of nitric acid (sp. gr. 1.3); acetic acid, carbonic anhydride, and oxalic acid are formed, together with a viscid, uncrystallisable liquid, which is readily soluble in water and which appears to be a polybasic hydroxy-acid; the *silver salt* contains, as the mean of several analyses, 61.12 per cent. of silver. By the prolonged action of phosphorus and hydriodic acid on heptanaphthenecarboxylic acid at 200—240°, a hydrocarbon is obtained which boils at 117—118°, and is identical with the octonaphthene, C_8H_{16} , isolated by Markovnikoff from Caucasian petroleum. The yield is 29 per cent. It thus appears that the naphthene acids are simply monocarboxylic acids of the naphthenes. This portion of the paper concludes with some polemical remarks on a recent communication of R. Zaloziecki, respecting the constitution of petroleum acids (compare this vol., p. 999).

Octonaphthenecarboxylic acid, $C_9H_{16}O_2$, has been previously described by Markovnikoff; it boils at $251-253^\circ$ (corr.), and has a sp. gr. = 0.9893 , $0^\circ/0^\circ$; its coefficient of refraction is $[n] = 1.453$, and the molecular refractive power = 43.0 . The *methyl salt* boils at $211-213^\circ$ and is very hygroscopic. The *barium* and *calcium salts* are not decomposed by carbonic anhydride; the former is crystalline and sparingly soluble in cold water, but readily dissolves in alcohol. The *chloride* is a dense, oily liquid, which boils at $206-208^\circ$ and slowly decomposes in presence of water. The amide crystallises from a mixture of benzene and light petroleum in large, thin, lustrous plates, and melts at $128-129^\circ$.
J. B. T.

Propylideneacetic Acid. By P. OTT (*Ber.*, **24**, 2600—2604).—Propylideneacetic acid is obtained by warming equal weights of malonic acid and propaldehyde with half the weight of acetic acid on the water-bath as long as carbonic anhydride is evolved. The reaction usually takes from 3 to 4 days. The mixture is then fractionally distilled; the fractions boiling at $180-200^\circ$ and $200-220^\circ$ contain the greater part of the product. From former experiments, the product is known to be a mixture (this vol., p. 821); it was worked up as follows:—The fraction boiling at $180-200^\circ$ is neutralised with barium carbonate, evaporated to dryness, and extracted with absolute alcohol until quite white. It is then dissolved in water, the solution evaporated until a crust separates, which dissolves on cooling, and to the clear cold solution alcohol is added until a considerable portion of the salt is precipitated. The precipitate is then dissolved by heating the mixture, and, on cooling, the barium salt separates in large, nacreous leaves. *Barium propylideneacetate* crystallises without water, is very characteristic, is insoluble in absolute alcohol, easily soluble in water, and more so in cold than in hot water. Pure propylideneacetic acid is obtained by decomposing the above salt with hydrochloric acid, and extracting with ether. It has an odour somewhat like that of crotonic acid, is quite colourless, boils at 193.5° , and is sparingly soluble in cold water. The *calcium salt* crystallises with 1 mol. H_2O , is more soluble in cold water than in hot, and crystallises in beautiful needles on heating the cold saturated solution in a sealed tube. It is easily soluble in cold water, less readily in absolute alcohol, and separates from the latter in aggregates of small needles.

On examining the mother liquors of the crude barium propylideneacetate, the authors separated a salt which they identified as barium ethylidenepropionate; and they point out that this explains the formation of a small quantity of lactone, observed by Zincke and Küster on boiling the bromovaleric acid obtained from their propylideneacetic acid with water.

The authors have also prepared the dibromides from the three isomeric acids, allylacetic acid, ethylidenepropionic acid, and propylideneacetic acid.

Dibromallylacetic acid is easily obtained solid, melts at 58° , is easily soluble in carbon bisulphide, more sparingly in petroleum, and crystallises from the latter in small, lustrous leaflets.

The dibromides from the other two isomerides were at first oils; but after some time the dibromide from ethylidenepropionic acid solidified, and on adding a crystal of this to the dibromide from propylideneacetic acid it also solidified. Both dibromides crystallise in large, broad needles from carbon bisulphide, and in large, measurable prisms from petroleum. They both melt at 64—65°, and are identical in crystalline form and in all other properties. E. C. R.

Polymerides of Ricinoleic Acid. By SCHEURER-KESTNER (*Compt. rend.*, **113**, 201—203).—Castor oil, when heated with water at 150°, splits up into glycerol and a mixture of ricinoleic and diricinoleic acids in about equal molecular proportions. The degree of polymerisation increases with the temperature, the molecular weight of the acid being 709 after heating at 200°. As the molecular weight increases, the energy of the acid function decreases, diricinoleic acid showing a feeble neutralising power. The polyricinoleic acids are depolymerised when heated with sodium hydroxide solution at a temperature above 100°, but very little change takes place below 100°.

When ricinoleic acid is heated alone, it gradually polymerises, and finally yields pentaricinoleic acid with a molecular weight of 1418.

C. H. B.

Solid Product of the Oxidation of Drying Oils. By A. LIVACHE (*Compt. rend.*, **113**, 136—139).—When the product of the oxidation of drying oils is placed in various solvents there is no apparent action, but after prolonged contact the product becomes more transparent and swells up, whilst at the same time the liquid becomes coloured. These phenomena are best seen when benzene is used. If the oxidised oil is triturated with one of the solvents, it rapidly swells up and becomes so finely divided that it forms a paste. If an excess of solvent is added, the particles composing the paste quickly become suspended in it. By trituration with successive quantities of the solvent until the latter no longer becomes coloured, the substance is separated into two parts, one soluble and coloured, the other insoluble, transparent, and gelatinous. If the gelatinous matter is allowed to dry, it forms an elastic and readily friable solid. When the solvent is allowed to evaporate, it leaves a sticky residue which welds at low temperatures. It is evident that the product of the oxidation of drying oils is very similar to caoutchouc. Solvents separate both of them into an insoluble and a soluble portion, and if the liquid is allowed to evaporate, the dissolved matter acts as a cement and forms a residue that is seemingly homogeneous. Oxidised oil can be prepared in large quantities by allowing oil to drop on sheets of cloth hung vertically, so that a very thin layer is exposed to the action of the air, oxidation taking place more rapidly if the room containing the cloths is heated. When the oxidised oil is triturated with a solvent and the solvent is allowed to evaporate, a residue is obtained that may be used in place of indiarubber for many purposes. C. H. B.

Preparation of Lactic Acid. By G. JACQUEMIN (*Bull. Soc. Chim.*, [3], **5**, 294—298).—A wort is made by mashing malt at 50° and completing the exhaustion at successive temperatures of 60°, 63°,

and 65°; finally the wort is boiled, cooled to 45°, and a carbonate is added with the pure lactic ferment. Pure cultivations of the latter are made in barley wort to which calcium carbonate is added. The fermentation is carried out in vessels which are maintained at 45° by means of steam coils or hot-water pipes; the vessel should either be hermetically closed and furnished with a gas siphon, or covered with a double cloth in order to allow the escape of carbonic anhydride and prevent entrance of dust; a tube is also arranged by which filtered air is introduced to the base of the vessel once or twice during the day in order to agitate the liquor. The fermentation is complete after a lapse of five or six days.

The resulting solution of calcium lactate is freed from nitrogenous matters by the addition of tannic acid or of a tannin extract, and crystalline calcium lactate is obtained on evaporation of the filtrate. T. G. N.

Dehydracetic Acid. By D. TIVOLI (*Gazzetta*, 21, 414—420).—When a mixture of dry dehydracetic acid (50 grams) and lime (250 grams) is distilled, a brown oil (20 grams) is obtained, which on redistillation from lime and fractionation yields acetone, mesityl oxide, and parametaxyleneol, $C_6H_3Me_2 \cdot OH$, melting at 62.5° and boiling at 225° (compare *Abstr.*, 1878, 411; 1884, 737).

The formation of an aromatic compound directly from dehydracetic acid, in this manner, being difficult to understand, the author suggests that the xylenol may be a condensation product of the acetone. By the action of lime on acetone, Fittig (*Annalen*, 110, 32; 112, 311) obtained a substance melting at 28° and boiling at 210—220° to which he assigned the formula $C_9H_{14}O$, and the name phorone. The author, on preparing this substance, only obtained it in very small quantity, but suspects it to be xylenol. W. J. P.

Homologues of Malic Acid. By A. MICHAEL and G. TISSOT (*Ber.*, 24, 2544—2546).—In a recent paper, Bischoff states that Fittig has obtained ethylmethylmaleic anhydride by the action of pyruvic acid on pyrotartaric acid. The authors, in the course of their work on the homologues of malic acid, have also obtained this compound synthetically, and therefore communicate part of their results, although the investigation is not yet completed.

In order, first of all, to settle the question of the constitution of citramalic acid, the authors have prepared methoxysuccinic acid, which, according to Morris (*Abstr.*, 1880, 6) and Bredt (*Abstr.*, 1882, 162), is not identical with the first-named acid. They find, contrary to Bredt's statement, that the acid may be readily obtained by the action of nascent hydrogen cyanide on ethyl acetoacetate, and that it melts at 119° instead of 106°. Citramalic acid prepared by Morawski's method also melted at 119°, and behaved in exactly the same manner as methoxysuccinic acid, so that the two acids must be identical.

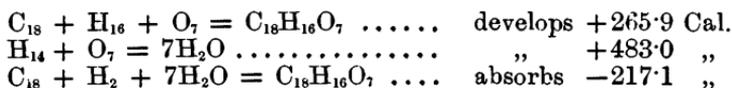
Symmetrical ethylmethylmalic acid may be readily obtained in a similar manner from ethyl ethylacetoacetate, and forms hygroscopic prisms, melts at 132°, and yields well crystallised salts. When

heated, it passes almost quantitatively into ethylmethylmaleïc anhydride, which boils without decomposition at 226°, dissolves only slightly in water, and yields salts of ethylmethylmaleïc acid with alkalis. On the addition of acids to aqueous solutions of the salts, the anhydride is reprecipitated as an oil.

Pyrocinchonic anhydride may be obtained in like manner from ethyl methylacetacetate, and the authors are at present engaged on the further investigation of this compound. They also find that the β - γ -dicarboxyl- γ -valerolactone described by Rach (Abstr., 1886, 1012) may be readily obtained from the products of the hydrolysis of the cyanhydrin of ethyl acetosuccinate, and that the tribasic potassium salt obtained by boiling it with potash loses water on heating at 150° in a vacuum, forming an acid which may be identical with cinchonic acid.

H. G. C.

Thermochemistry of Humic Acid from Sugar. By BERTHELOT and ANDRÉ (*Compt. rend.*, 112, 1237—1245).—Humic acid from sugar (this vol., p. 1089), prepared by separation from its alkali salts, and dried rapidly at a low temperature, had a composition agreeing with the formula $2C_{18}H_{16}O_7 + C_{18}H_{14}O_6$. Its heat of combustion was 5880 cal. at constant volume; consequently the heat of formation at constant pressure is 731 cal. for 1 gram. If the oxygen united with the hydrogen to form water, and the latter combined with the carbon and the surplus of hydrogen, the formation of the humic acid would absorb 628 cal.



Now $C_6 + C_6H_2O = C_6H_{12}O_6$ absorbs -109.1 Cal., and hence the conversion of $3C_6H_{12}O_6$ into $C_{18}H_{16}O_7$ is accompanied by the liberation of about $+110$ Cal.

Humic acid dried at about 100° swells up, forms a pasty mass in contact with water, but dissolves to a very slight extent only. There is, however, a considerable development of heat; $C_{18}H_{14}O_6 + H_2O = C_{18}H_{16}O_7$ develops $+13.7$ Cal., the heat of hydration of acetic anhydride being $+13.9$. It is remarkable that the acid tends to lose water and pass into the anhydride even at the ordinary temperature.

Humic acid is tribasic; neutralisation by the first equivalent of potassium hydroxide develops $+18$ Cal., and the salt formed is insoluble and highly stable. Addition of a second and third equivalent of alkali develops a further quantity of $+6$ Cal., with formation of bi-basic and tribasic salts. Freshly precipitated humic acid, when left in contact with its mother liquor, rapidly passes into the same condition as the air-dried acid.

Humic compounds, similar to those which exist in soils, attain their maximum degree of hydration in presence of alkalis, being dehydrated in presence of acids.

C. H. B.

A Furfurallevulinic Acid. By A. LUDWIG and E. A. KEHRER (*Ber.*, 24, 2776—2778).—When a solution of levulinic acid (2.3.2

grams) in water (300 c.c.) and one of sodium hydroxide (16 grams) in water (160 c.c.) are successively added to furfuraldehyde (19.2 grams) dissolved in 99 per cent. alcohol (200 c.c.), and the mixture is heated for five minutes at 60°, then cooled with ice and carefully acidified with hydrochloric acid, a precipitate is produced which is found to consist of a crystalline and a pulverulent compound; these are mechanically separated. The former is purified by crystallisation from hot ether, and forms faintly yellowish-coloured prisms, having the composition of a *furfurallevulinic acid*, $C_{10}H_{10}O_4$; it is very sparingly soluble in cold water and boiling light petroleum, readily soluble in hot alcohol or ether, and very easily in chloroform and benzene. The *silver salt*, $C_{10}H_9O_4Ag$, is not very sensitive towards light; the *calcium salt*, $(C_{10}H_9O_4)_2Ca + 2H_2O$, crystallises in yellow needles. The acid melts at 113° without perceptible decomposition, but after resolidification at 8—9° lower, having in fact then the same melting point as the above-mentioned pulverulent compound, which appears to be an isomeride, and seems also to be produced when the furfurallevulinic acid is crystallised from boiling water; this may be due to the fact that in the latter operation the acid melts prior to dissolving. Further experiments are in progress. A. R. L.

Decomposition Products of α -Hydroxy-acids. By H. v. PECHMANN (*Annalen*, 264, 261—309).—An exhaustive investigation of coumalinic acid, a compound obtained by treating malic acid with concentrated sulphuric acid (compare Abstr., 1884, 1124), has proved conclusively that it is a derivative of an unsaturated lactone (coumalin), and that its constitution is expressed by the formula



Coumalinic acid is best prepared by heating anhydrous malic acid (50 grams) on the water-bath with a mixture of concentrated sulphuric acid (75 grams) and 10—12 per cent. anhydrosulphuric acid (75 grams); when the evolution of carbonic oxide ceases, which is usually the case in $1\frac{1}{2}$ —2 hours, the solution is carefully mixed with ice (200 grams), kept over night, the precipitated acid separated by filtration, washed with ice-cold water until almost free from sulphuric acid, and then dried on porous plates; the acid in the mother liquors and washings is extracted by shaking six times with ether. The total yield of the crude product is about 80 per cent. of the theoretical, but it contains fumaric acid and traces of trimesic acid; it can be purified by dissolving it in water at 70—80°, shaking the solution with animal charcoal, and then extracting the acid with ether. It crystallises from methyl alcohol and glacial acetic acid in colourless prisms, turns reddish at 200°, and melts at 205—210° with decomposition; it boils at about 218° under a pressure of 120 mm. with partial decomposition, and when heated carefully it gives a sublimate the edges of which have a characteristic rose-colour. It is insoluble in chloroform, benzene, and light petroleum, and only sparingly soluble in cold water, ether, acetone, and ethyl acetate, but moderately easily in methyl alcohol, glacial acetic acid, and alcohol;

its solution in water and dilute acids undergoes decomposition on boiling, with evolution of carbonic anhydride and formation of crotonaldehyde, the solution turning brown. When boiled with barium hydroxide, it is decomposed into formic acid and glutaric acid (m. p. 132—134°). It is decomposed by cold alkalis, and it reduces Fehling's solution and ammoniacal silver nitrate solution (in presence of soda) on boiling; with boiling acetic anhydride, it gives an intense, brownish-red coloration. Small quantities of coumalinic acid are most easily detected by converting the acid first into the methyl salt, and then into the characteristic anil (m. p. 140°) previously described (*loc. cit.*); this reaction can be carried out with as small a quantity as 0.02 gram of the acid, if it is not very impure. All the salts of coumalinic acid are decomposed on boiling with water, yielding a carbonate and crotonaldehyde. The *magnesium* salt, $(C_6H_3O_4)_2Mg + 6H_2O$, crystallises from warm water in colourless prisms; the *zinc* salt (+ $6H_2O$) also crystallises very well. The *barium* salt, $(C_6H_3O_4)_2Ba + 2H_2O$, is a slightly coloured, crystalline powder, more readily soluble than the salts just described. The *silver* salt is colourless, but turns black on exposure to light in a dry condition. The *mercurous* salt is a colourless, granular compound. The salts of the alkalis are very readily soluble in water, but more sparingly in alcohol. A 5 per cent. solution of the barium salt gives precipitates with ferric chloride and with bismuth nitrate, but not with solutions of copper, cadmium, lead, manganese, or mercuric salts. The methyl salt (*loc. cit.*) boils at 178—180° under a pressure of 60 mm., and at 250—260° under the ordinary atmospheric pressure without appreciable decomposition; it crystallises well from hot water, &c., melts at 73—74°, and is decomposed by water and alkaline carbonates (see below). The *ethyl* salt, $C_6H_3O_4Et$, prepared by treating the acid with alcohol and sulphuric acid, melts at 36°, boils at 262—265°, and resembles the methyl salt in its behaviour with solvents; when treated with aniline, it is converted into a yellow, crystalline *anil*, which melts at 121°. The *chloride*, $C_6H_3O_2 \cdot COCl$, is formed when crude coumalinic acid is moistened with phosphorus oxychloride, and then warmed with phosphorus pentachloride on the water-bath, an energetic reaction taking place; it boils at about 180° under a pressure of 80 mm., and the distillate solidifies on cooling to a mass of crystals, which could not, however, be obtained free from phosphorus.

The formation of coumalinic acid from malic acid is due to the intermediate production of formylacetic acid; this is proved by the fact that ethyl sodioformylacetate (compare Wislicenus, *Abstr.*, 1888, 129) is readily converted into coumalinic acid on treatment with concentrated sulphuric acid. The sodium derivative just referred to is without doubt a derivative of ethyl formylacetate, as, when treated with resorcinol in presence of sodium ethoxide, it yields umbelliferon, just as resorcinol and ethyl acetoacetate give β -methylumbelliferon.

β -Nitrosopropionic acid (oximidoformylacetic acid),



is obtained when dilute (1 : 5) soda (140—150 c.c.) is gradually added

to a well-cooled mixture of coumalinic acid (20 grams), hydroxylamine hydrochloride (20 grams), and water (100 c.c.), and the solution then carefully warmed on the water-bath for 10—20 minutes; after cooling, sulphuric acid is added until the solution colours tropæoline paper violet, and the product is then extracted with ether. It separates from ether in colourless crystals, melts at 117—118° with decomposition, and is readily soluble in water and alcohol, but only sparingly in ether, and insoluble in chloroform, benzene, and light petroleum; it is decomposed by sodium carbonate and by boiling water, with evolution of carbonic anhydride, and it reduces Fehling's solution and ammoniacal silver nitrate solution on warming. In its aqueous solution, copper acetate produces a light-blue, crystalline precipitate, and ferric chloride a reddish-brown coloration; when warmed with acetic chloride in ethereal solution, it is converted into a compound which crystallises in colourless prisms, melts at 144—145° with decomposition, and gives a wine-red coloration with an alcoholic solution of ferric chloride. When the acid is kept for a long time, it is transformed into a porous, hygroscopic substance, which is insoluble in ether and alcohol. The molecular weight of β -nitrosopropionic acid was determined by Raoult's method, and found to be in accordance with the molecular formula given above; that it has the constitution assigned to it is proved by the following facts:—1. When boiled with dilute sulphuric acid, it is decomposed into hydroxylamine, acetaldehyde, and carbonic anhydride. 2. On reduction, it is converted into β -amidopropionic acid (β -alanine), which can be easily isolated in the form of the sulphone described below.

The most plausible explanation of the formation of β -nitrosopropionic acid from coumalinic acid is that the latter is first converted into formylglutaconic acid, $\text{COOH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{CHO})\cdot\text{COOH}$, by direct combination with 1 mol. H_2O ; this hypothetical intermediate product probably undergoes intramolecular change into a compound of the constitution $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{CHO})\cdot\text{COOH}$, which is then decomposed into 2 mols. of formylacetic acid by combination with a second molecule of water.

Benzenesulphone- β -alanine, $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, is obtained when β -nitrosopropionic acid is reduced with sodium amalgam, and the crude product shaken with soda and benzenesulphonic chloride; it crystallises from water in colourless plates or prisms, melts at 111—112°, and is readily soluble in most ordinary solvents except cold water.

Methyl dihydrogen trimesate, $\text{C}_{10}\text{H}_8\text{O}_6$, is easily obtained by treating methyl coumalinate with dilute soda (1 mol.) at the ordinary temperature, and then acidifying the solution; on keeping for a long time, the product is deposited in colourless prisms, and can be recrystallised from boiling water. The yield is 30—40 per cent. of the methyl coumalinate employed. It crystallises with 1 mol. H_2O , which is expelled at 105°, melts at 205—208°, and is readily soluble in alcohol and ether. When methyl coumalinate is kept for some days in contact with water, it is partially transformed into methyl dihydrogen trimesate; free coumalinic acid, on the other hand, seems not to give trimesic acid, even on treatment with alkalis. Trimesic

acid melts at about 345—350° (in an air-bath); its ethyl salt crystallises in long, lustrous prisms melting at 133°, and the methyl salt in slender, lustrous needles melting at 144°.

Coumalin, $\text{CH} \left\langle \begin{array}{l} \text{CH} \cdot \text{CO} \\ \text{CH} : \text{CH} \end{array} \right\rangle \text{O}$, can be obtained by the dry distillation of mercurous coumalinate in an atmosphere of hydrogen; the yield is about 30 per cent. of the theoretical. It is a colourless oil of sp. gr. 1.20006, 19.5°/4°, but it gradually darkens on exposure to the air; it solidifies on cooling to a mass of crystals which melt at 5°. It boils at 120°, under a pressure of 30 mm. without decomposition, and under the ordinary atmospheric pressure (717 mm.) at 206—209° with slight decomposition; it is miscible with all ordinary solvents, but it separates from its aqueous solution on the addition of potassium carbonate. It is not acted on by boiling water, but it is decomposed by alkalis with formation of crotonaldehyde and carbonic anhydride.

F. S. K.

Orthocyanobenzyl Chloride and Orthocyanobenzal Chloride.

By A. DROY (Ber., 24, 2563—2574).—Gabriel and Day (Abstr., 1890, 1249), by the action of concentrated sulphuric acid on orthocyanobenzyl thiocyanate, have obtained a compound, $\text{C}_6\text{H}_5\text{NS}$, which behaves both like a mercaptan and like a base. The author has examined the corresponding selenium compounds.

Orthocyanobenzyl selenocyanate, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{SeCN}$, is obtained by mixing an alcoholic solution of orthocyanobenzyl chloride with an alcoholic solution of potassium selenocyanate, and heating the mixture in a reflux apparatus for $\frac{1}{4}$ — $\frac{1}{2}$ hour. It crystallises from benzene in compact, colourless, rhombohedra or prisms, melts at 121°, completely decomposes at 200°, and is soluble in methyl and ethyl alcohol, ether, petroleum, carbon bisulphide, acetone, and benzene.

Selenophthalimidine (orthocyanobenzyl selenomercaptan), $\text{C}_6\text{H}_5\text{NSe}$, is obtained by gradually adding orthocyanobenzyl selenocyanate (10 grams) to concentrated sulphuric acid (75 c.c.). Carbonic anhydride is evolved, and a clear solution is obtained. The mixture is poured into iced water, excess of sodium carbonate added, and the resulting emulsion extracted with ether. The product is a yellow oil, has a nauseous odour, partially solidifies on remaining in a closed vessel and melts again at 30°. It is soluble in chloroform, petroleum, benzene, alcohol, and ether, decomposes on exposure to air, yielding orthocyanobenzyl diselenide, and cannot be distilled without decomposition. It dissolves completely in acids, is precipitated from solution by alkalis, and is again dissolved by excess of alkali. The salts of selenophthalimidine crystallise well from alcohol in prismatic needles, and are decomposed on evaporating the aqueous solution on the water-bath. The *hydrochloride* is sparingly soluble in water and alcohol, and is obtained in long, flat, prismatic needles by evaporating an aqueous solution in a vacuum over sulphuric acid. The *platinichloride* is precipitated as an orange-yellow, insoluble, and infusible powder. The *picrate* is obtained as an intensely yellow, crystalline precipitate, is sparingly soluble in alcohol, and decomposes at 170° without melting. The *hydrobromide* crystallises in colourless, prismatic needles, and melts at 264°. The *sulphate* crystallises from

water in slender, silky needles, melts at 145—150° with frothing, and, on boiling its aqueous solution, decomposes yielding selenophthalide.

Selenophthalimidine periodide, $C_8H_8NSeI_2$, is obtained by heating orthocyanobenzyl selenocyanate (5 grams) with hydriodic acid (20 c.c.; sp. gr. = 1.70) for five hours at 100°. The product is washed with ether and crystallised from alcohol. It crystallises in slender, dark-violet needles, melts at 223° with decomposition, and is sparingly soluble in boiling alcohol, and almost insoluble in all other solvents.

Orthocyanobenzyl methyl selenide, $CN \cdot C_6H_4 \cdot CH_2 \cdot SeMe$, is obtained by the action of methyl iodide (2 grams) on a solution of selenophthalimidine hydrochloride (4 grams) in alcoholic potash. The product is distilled with steam and extracted with ether. It is a yellowish-brown oil, has an unpleasant odour, and distils at 180—200° without decomposition.

Orthocyanobenzyl diselenide, $(CNC_6H_4 \cdot CH_2)_2Se_2$, is obtained when a solution of a salt of the compound C_8H_7NSe is treated with sodium hydroxide and extracted with ether. It crystallises in needles, melts at 108—110° with decomposition, and is soluble in methyl and ethyl alcohol, benzene, chloroform, and carbon bisulphide.

Selenophthalide, $C_6H_4 \langle \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix} \rangle Se$, is obtained on allowing an alcoholic solution of selenophthalimidine to remain with excess of potash in a warm place; ammonia is slowly evolved, and on distilling the mixture in a current of steam an emulsion is obtained which deposits short, nacreous needles of selenophthalide. It crystallises from alcohol in short, colourless leaflets, melts at 58°, and is soluble in alcohol, ether, and benzene.

When orthocyanobenzyl chloride is heated to boiling in a reflux apparatus with copper nitrate and water, the blue colour of the solution remains unaltered; the chloride, however, completely dissolves, and on extracting the solution with ether, phthalide is obtained. Silver nitrate has the same action. Gabriel and Otto, however, obtained phthalide by the action of water alone on orthocyanobenzyl chloride (Abstr., 1887, 1035), and the author points out that as the colour of the above copper solution remains unaltered, the metallic salts are probably without action, and the water alone is necessary.

Orthocyanobenzyl bromide, $CN \cdot C_6H_4 \cdot CH_2Br$, is obtained by leading bromine vapour, by means of a stream of carbonic anhydride, into boiling orthotolunitrile. It is easily soluble in alcohol, ether, benzene, petroleum, &c., sparingly in water, is volatile with steam, melts at 76°, distils without decomposition, and crystallises in the monosymmetric system, $a : b : c = 1.5363 : 1 : 0.9642$; $\beta = 78^\circ 5'$.

Orthophthalaldehydic acid (m. p. 96°) is obtained when orthocyanobenzal chloride (2 grams) is heated in a reflux apparatus with silver nitrate (4 grams) and water (150 c.c.).

Orthocyanotriphenylmethane is obtained as follows:—Aluminium chloride (7 grams) is gradually added to a mixture of orthocyanobenzal chloride (10 grams), and benzene (40 grams), and the mixture heated on the water-bath as long as hydrogen chloride is evolved. The mixture is then treated with dilute hydrochloric acid, and the layer of benzene which contains the product diluted with ether, separated,

dried with calcium chloride, and distilled. After the ether, benzene, and benzal chloride have distilled, an oil is obtained which distils at 270—285° under 20—30 mm. pressure. It is dissolved in absolute alcohol, decolorised with animal charcoal, and allowed to crystallise. It forms slender, white needles, melts at 89°, and is soluble in methyl and ethyl alcohol, ether, chloroform, acetic acid, and benzene, insoluble in petroleum and water. When hydrolysed with 25 per cent. alcoholic potash, it yields *triphenylmethaneorthocarboxylic acid*; this crystallises from acetic acid in slender, white needles, softens at 158°, and melts at 162°.

Orthocyanocinnamic acid, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$, is obtained by heating cyanobenzal chloride (2 parts) with dry sodium acetate (1 part) and acetic anhydride (10 parts) for 10 hours at 180°. The product is neutralised with sodium carbonate, the unaltered benzal chloride removed by distilling with steam, and the filtered solution precipitated with hydrochloric acid. It crystallises from alcohol in slender, colourless needles, melts at 252°, is soluble in alcohol, ether, acetic acid, chloroform, and benzene, but insoluble in water.

E. C. R.

Preparation of 1 : 2 : 4- and 1 : 3 : 4-Dichlorotoluenes. By H. ERDMANN (*Ber.*, **24**, 2769—2771).—1 : 2 : 4-Dichlorotoluene [$\text{Me} : \text{Cl}_2 = 1 : 2 : 4$] is best prepared from metatolylenediamine by Sandmeyer's method. A solution of 200 grams of cupric chloride in a litre of hydrochloric acid (sp. gr. = 1.175) is boiled with 150 grams of copper turnings until decolorised, then mixed with a solution of 1 kilo. of metatolylenediamine in a litre of hydrochloric acid diluted with a litre of water, and, without cooling, treated with about 9 litres of a 10 per cent. sodium nitrite solution added in a thin stream with constant stirring. The dichlorotoluene, which separates as a heavy, black oil, is steam-distilled, and freed from phenols and azo-derivatives by washing with aqueous soda, drying over solid potash, and afterwards distilling. The yield amounts to 45 per cent. of the theoretical. Pure 1 : 2 : 4-dichlorotoluene boils at 196—197.5° (compare Lellmann and Klotz, *Abstr.*, 1886, 452).

1 : 3 : 4-Dichlorotoluene [$\text{Me} : \text{Cl}_2 = 1 : 3 : 4$] can be prepared from metachloracetoparatoluidide by converting it into the crude hydrochloride (this vol., p. 1466), and treating this by Sandmeyer's method. The yield of dichlorotoluene from 1 kilo. of paratoluidine by this method was found to be 320 grams.

W. P. W.

Artificial Mineral Lubricating Oil. The Condensation Products of Allyl Alcohol with Methylbenzenes. By G. KRAEMER and A. SPILKER (*Ber.*, **24**, 2785—2793).—In a previous communication (this vol., p. 206), the authors have described the compounds obtained by the condensation of cinnamene with toluene, xylene, and pseudocumene, and were led to regard them as derivatives of propane. The investigations of Koenigs (this vol., p. 208), and of Liebermann and Hartmann (this vol., p. 1484), however, make it more probable that the compounds in question are ethane derivatives, the methyl radicles in the benzene ring taking no part in the condensation. Xylene-

cinnamene, previously described as phenyltolnylpropane, must, therefore, be regarded as phenylxylylethane, $\text{CHMePh}\cdot\text{C}_6\text{H}_3\text{Me}_2$. At the time the paper on the condensation of cinnamene with xylene was read, the hope was expressed that some light would soon be thrown on the obscure problem of the formation of lubricating oils from petroleum, on account of the resemblance between these oils and cinnamene derivatives, as evidenced not only by the behaviour towards chemical reagents, but also by the fact that cinnamene derivatives containing methyl radicles in the benzene ring exhibit the property of viscosity in a marked degree. For example, phenylxylylethane has a viscosity of 2.1, compared with the value 15 for a medium lubricating oil from Alsatian petroleum, and a value 35 for a good lubricating oil from Caucasian petroleum.

The present paper deals with the condensation of methylbenzenes with allyl alcohol in the presence of sulphuric acid. To bring about the condensation, a mixture of 100 c.c. of pure concentrated sulphuric acid and 50 c.c. of fuming sulphuric acid is gradually added, with vigorous shaking, to a mixture of 100 c.c. of anhydrous allyl alcohol with 1000 c.c. of pseudocumene (xylene, &c.), and precautions are taken against rise of temperature during the reaction. After remaining for some time, the sulphuric acid is carefully separated from the oil, and the latter mixed with a few drops of water to remove the remainder of the acid, and afterwards successively washed with dilute acid, three to four times with water in quantities of 100 c.c., then with 5 per cent. aqueous soda to alkaline reaction, and finally with water until neutral. During the washing, a difficulty arises from the tendency of the two layers to form a stable, white emulsion—a well-known and dreaded occurrence in the manufacture of lubricating oil; this can, however, be overcome by the addition of ether. The oil, after washing, is freed from pseudocumene (xylene, &c.) by a current of steam at $110\text{--}120^\circ$; the temperature is then raised, and at $200\text{--}220^\circ$ a thick, colourless oil passes over with the steam, leaving a yellowish-brown, resinous substance, which very slowly distils with steam at 250° , and can be purified by fractionally distilling with steam, extracting with ether, &c.

The thick, colourless oil obtained from pseudocumene can be purified by again distilling with steam at about 200° , or better by distillation in a vacuum. It has the composition $\text{C}_{21}\text{H}_{28}$, giving by Raoult's method numbers which agree well with this formula, and is probably a *dimethyladicumylmethane*. In the pure state it boils above 300° at the ordinary pressure, without appreciable decomposition, and in the viscosimeter gives at 15° the value 775 (water = 1), whilst the best Russian lubricating oil gives the value 40 in the same apparatus. The resinous product of the reaction has the composition $(\text{C}_{21}\text{H}_{28})_n$, and by Raoult's method gives as a mean of two determinations the value 763 for the molecular weight. The yields from 100 c.c. of allyl alcohol were 122 grams of oil and 90 grams of resin, and from 50 c.c. of alcohol, 52 grams of oil and 50 grams of resin.

The oily product of the condensation of allyl alcohol with xylene has the composition $\text{C}_{15}\text{H}_{24}$, as confirmed by a determination of the molecular weight by Raoult's method. It is significantly less viscous

than the corresponding product (containing two additional methyl radicles) from pseudocumene, and gives the value 8.1 in the same viscosimeter. The yield from 100 c.c. of allyl alcohol amounted to 88 grams of oil and 50 grams of resin.

As a necessary consequence, it would follow that all high boiling fractions of petroleum are free from oxygen, and that the lubricating oils are poorer in hydrogen than the less viscous paraffin oils. These conclusions are borne out by analyses of a commercial lubricating oil of Caucasian origin, and a paraffin oil (viscosity = 15) from Alsatian petroleum. The investigation is being continued, but on account of the difficulty of characterising the products, rapid progress is not to be expected.

W. P. W.

Artificial Musk. By A. BAUR (*Ber.*, **24**, 2832—2843).—The artificial musk described in a previous communication (*Abstr.*, 1890, 1401) was regarded as trinitroisobutyltoluene. It is, however, a derivative, not of isoprimary but of tertiary butyltoluene, owing to the occurrence in the preparation of the hydrocarbon of an intramolecular change, corresponding with that observed by Schramm in the case of the condensation of benzene with isobutyl bromide by the Friedel-Crafts method (*Abstr.*, 1889, 127).

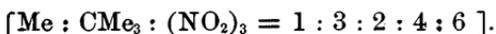
Tertiary butyltoluene is easily obtained by the action of tertiary butyl chloride on toluene in the presence of aluminium chloride. It boils at 185—187°, and agrees in properties with the so-called isobutyltoluene. The *sulphonic acid*, prepared by warming it with concentrated sulphuric acid, forms a *barium salt*, $(C_{11}H_{16}SO_3)_2Ba + H_2O$, which crystallises in white scales, and dissolves sparingly in cold water, but more easily in hot water, and in 50—60 per cent. alcohol. The *sulphonamide*, $C_{11}H_{16}SO_2NH_2$, crystallises from water in nacreous scales, and melts at 94—95°. Earlier determinations with the sulphonamide prepared from so-called isobutyltoluene gave 74—75° as the melting point, and this value is always obtained with the freshly-prepared substance; after being kept for some hours, the melting point is found to have risen to and remains constant at 94—95°. The trinitrobutyltoluene formed by the nitration of tertiary butyltoluene melts at 96—97°, and is identical with the product from so-called isobutyltoluene.

Nitrobutyltoluene, $CMe_3 \cdot C_6H_3Me \cdot NO_2$, is obtained by slowly adding fuming nitric acid to a solution of tertiary butyltoluene in acetic acid. It is a yellowish oil of a peculiar and slightly unpleasant odour, boils at 160—162° in a vacuum without decomposition, and is readily volatile with steam. On treatment with excess of nitric acid, it is converted into artificial musk.

Dinitrobutyltoluene, $CMe_3 \cdot C_6H_2Me(NO_2)_2$, is formed, together with the mononitro- and trinitro-derivatives when tertiary butyltoluene is dissolved in well-cooled nitric acid of sp. gr. 1.5. On distillation with steam, the mononitro-derivative passes over first, and then a mixture of the mononitro- and dinitro-derivatives distils over, leaving a residue of the trinitro-derivative mixed with a very small quantity of the dinitro-compound. A separation of the dinitrobutyltoluene can be more easily effected by crystallising out the greater part of the

trinitrobutyltoluene, repeatedly distilling the oil in a vacuum, and collecting the fraction boiling at 224—225°. Dinitrobutyltoluene is a brown oil of very unpleasant odour, and does not solidify in a freezing mixture. On further nitration, it is converted into artificial musk.

Trinitrobutyltoluene (artificial musk), $\text{CMe}_3\cdot\text{C}_6\text{HMe}(\text{NO}_2)_3$, is obtained when tertiary butyltoluene is slowly added in the cold to five times its weight of a mixture of 1 part of nitric acid (sp. gr. = 1.5) and 2 parts of 15 per cent. anhydrosulphuric acid, and the mixture afterwards heated for 8—9 hours on a water-bath. It crystallises from alcohol in yellowish-white needles, melts at 96—97°, is only very slightly volatile with steam, and has a powerful odour of musk. It is insoluble in water, but it dissolves readily in alcohol, ether, benzene, chloroform, and light petroleum. With naphthalene in alcoholic solution, it forms a compound $2\text{C}_{11}\text{H}_{13}(\text{NO}_2)_3\cdot\text{C}_{10}\text{H}_8$, which crystallises in large, yellowish scales, melts at 89—90°, and decomposes into its generators on warming with water. Trinitrobutyltoluene is not affected by treatment with alkalis or ammonia, and when warmed with an excess of aniline forms a compound $3\text{C}_{11}\text{H}_{13}(\text{NO}_2)_3\cdot 2\text{NH}_2\text{Ph}$, which crystallises from the excess of aniline in compact forms, and melts at 64°. Of the four possible formulæ for a trinitrometabutyltoluene, the author, on these grounds, excludes the three containing two nitro-radicles relatively in the ortho-position, and assigns to artificial musk the remaining formula



Amidobutyltoluene, $\text{CMe}_3\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$, is formed by the reduction of nitrobutyltoluene with tin and hydrochloric acid. It is a colourless oil, of pleasant, cummin-like odour, and boils at 245°. The acetyl derivative, $\text{C}_{11}\text{H}_{15}\cdot\text{NHAc}$, crystallises from alcohol in lustrous scales melting at 162°, and the benzoyl derivative in small, white needles melting at 167—168°. It is therefore identical with the amido-compound obtained by Effront (Abstr., 1884, 899; 1885, 152) by heating isobutyl alcohol with orthotoluidine hydrochloride at 280—300°, and must contain the amidogen in the para-position relatively to the tertiary butyl radicle.

Amidodinitrobutyltoluene, $\text{CMe}_3\cdot\text{C}_6\text{HMe}(\text{NO}_2)_2\cdot\text{NH}_2$, is obtained when trinitrobutyltoluene in alcoholic solution is reduced with the theoretical quantity of ammonium sulphide. It crystallises from alcohol in brownish-yellow needles, melts at 125—126°, and is insoluble in water. The *hydrochloride* crystallises in brown scales, and on treatment in alcoholic solution with ethyl nitrite, gives a *dinitrobutyltoluene*, which could not be crystallised.

Tertiary butylmetaxylene, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CMe}_3$ [$\text{Me}_2 : \text{CMe}_3 = 1 : 3 : 5$], can be prepared by boiling metaxylene either with isobutyl bromide or tertiary butyl bromide in the presence of aluminium chloride. It is a colourless liquid which boils at 200—202° under 747 mm. pressure, and on oxidation with nitric acid, yields mesitylenic acid, and with chromic acid, trimesic acid. The *trinitro*-derivative, $\text{CMe}_3\cdot\text{C}_6\text{Me}_2(\text{NO}_2)_3$, crystallises from alcohol in yellowish-white needles, melts at 110°, and has a strong, musk like odour; the *nitro*-derivative, $\text{CMe}_3\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NO}_2$,

formed by adding fuming nitric acid to a cold acetic acid solution of the hydrocarbon, crystallises from alcohol in white needles which melt at 85° , and have a cinnamon-like odour.

Butylethylbenzene, $C_6H_4Et \cdot CMe_3$, is formed by the condensation of ethylbenzene and isobutyl bromide in the presence of aluminium chloride, and is separated from the butyltoluene and butylbenzene produced in the reaction by fractional distillation at $200-205^{\circ}$. It resembles butyltoluene in properties, and yields a *trinitro*-derivative, $CMe_3 \cdot C_6H_4Et(NO_2)_3$, which is more soluble in alcohol than artificial musk, and has a strong, musk-like odour.

Among the secondary products of the reaction between pure toluene and pure isobutyl bromide in the presence of aluminium chloride, are butylbenzene, butylxylene, butylethylbenzene, dibutylbenzene, and dibutyltoluene, and these substances are present in the fraction $170-200^{\circ}$, which was formerly used instead of pure tertiary butyltoluene in the preparation of artificial musk. W. P. W.

Action of Chlorine on Acetoparatoluidide. Preparation of Metachloroparatoluidine. By H. ERDMANN (*Ber.*, **24**, 2766—2769).—Hitherto metachloracetoparatoluidide has been prepared by the action of chlorine on acetoparatoluidide, either suspended in water (Wroblewsky, *Annalen*, **168**, 196), or in dilute aqueous solution at 0° (Lellmann and Klotz, *Abstr.*, 1886, 452), and in both cases the yield was small and unsatisfactory. It can, however, be obtained in considerable quantity by dissolving acetoparatoluidide (100 grams) in hot acetic acid (100 c.c.), and passing a rapid stream of chlorine (160 grams) through the solution, which soon becomes boiling hot. To prevent loss of chlorine, three flasks placed in series, and containing the quantities given, are connected with the chlorine generator. The metachloracetoparatoluidide can be easily freed from accompanying resinous matters, and crystallises from alcohol, or from a mixture of chloroform and light petroleum, in needles melting at $111-112^{\circ}$.

Metachloroparatoluidine may be prepared directly from the chlorination product by distilling off the acetic acid, boiling the residue with 20 per cent. hydrochloric acid in a reflux apparatus for 3—4 hours, and afterwards distilling with steam to remove the small quantity of chlorinated cresol formed in the reaction. On cooling, the sparingly soluble hydrochloride separates as a crystalline mass, whilst the more soluble paratoluidine hydrochloride remains in the mother liquor. The crystalline hydrochloride is then decomposed with aqueous soda, and the base freed from the less volatile dichlorotoluidine by steam distillation. The yield, under these conditions, amounts to more than 400 grams from 1 kilo. of commercial paratoluidine, and the product is very fairly pure, boiling at $218-225^{\circ}$. Metachloroparatoluidine, purified by conversion into its sparingly soluble crystalline nitrate, is a colourless oil which boils at $223-224^{\circ}$ (corr.), and crystallises in a freezing mixture in lustrous, snow-white scales melting at 7° ; on exposure to air and light, it soon becomes coloured. W. P. W.

γ -Phenoxypropylamine. By J. LOHMANN (*Ber.*, **24**, 2631—2641).— γ -Bromopropyl phenyl ether, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$, is formed, together with a small proportion of trimethylene diphenyl ether, when an alcoholic solution of trimethylene bromide (41 grams) and sodium phenoxide (15 grams) is heated in a reflux apparatus for about four hours on a water-bath. After removal of the alcohol by distillation, the product is steam-distilled, and the distillate extracted with ether; the residue left after evaporation of the ether is freed from phenol by extraction with dilute aqueous soda, and from trimethylene bromide by fractional distillation. The yield amounts to about 40 per cent. of the theoretical. The ether is an oil which boils at $246\text{--}256^\circ$ with decomposition, and dissolves in most solvents except water.

γ -Phenoxypropylphthalimide, $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_3\text{H}_6\cdot\text{OPh}$, is obtained by heating equal weights of γ -bromopropyl phenyl ether and potassium phthalimide at 220° for an hour. It crystallises from alcohol in white needles, melts at 88° , and is easily soluble in most solvents. When heated with concentrated hydrochloric acid at $180\text{--}185^\circ$ for 4—5 hours, it is decomposed into a mixture of phthalic acid, phenol, and γ -chloropropylamine hydrochloride.

γ -Phenoxypropylphthalamic acid, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is obtained by boiling γ -phenoxypropylphthalimide with dilute aqueous potash until dissolved, pouring the solution into cold water, and acidifying with hydrochloric acid. It is a white, crystalline powder which melts at 134° , is insoluble in almost all solvents except alcohol, and regenerates the imide on boiling with alcohol. When heated with 5—6 times its weight of hydrochloric acid in a reflux apparatus for about an hour, it decomposes into phthalic acid and γ -phenoxypropylamine hydrochloride. γ -Phenoxypropylamine, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{NH}_2$, is a colourless oil which boils at $241\text{--}242^\circ$ under 766 mm. pressure, and readily absorbs carbonic anhydride from the air. The hydrochloride, $\text{C}_9\text{H}_{13}\text{NO}\cdot\text{HCl}$, crystallises from alcohol in lustrous, pale-yellow scales, and melts at 168° ; the picrate and platinochloride, $(\text{C}_9\text{H}_{13}\text{NO})_2\cdot\text{H}_2\text{PtCl}_6$, are crystalline. The benzoyl derivative,



crystallises from alcohol in white needles melting at 118° , and the carbamide, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{NH}\cdot\text{CONH}_2$, in silvery scales melting at 114° .

γ -Diphenoxypropylamine, $(\text{OPh}\cdot\text{C}_3\text{H}_6)_2\text{NH}$, is formed, together with a small quantity of γ -phenoxypropylamine when γ -bromopropyl phenyl ether (12 grams) is digested with 10 per cent. alcoholic ammonia (15—20 c.c.) at 100° for 2—3 hours. It is an oil boiling at above 300° . The hydrochloride, $\text{C}_{18}\text{H}_{23}\text{NO}_2\cdot\text{HCl}$, crystallises from alcohol in transparent needles, melts at 206° , and is very sparingly soluble in water. The nitrosamine, $\text{C}_{18}\text{H}_{24}\text{O}_2\text{N}\cdot\text{NO}$, crystallises from alcohol in pale-yellow, lustrous scales, melts at $60\text{--}61^\circ$, dissolves readily in most solvents except water, and decomposes into γ -diphenoxypropylamine and ammonia on reduction in alcoholic solution with zinc-dust.

γ -Phenoxypropylaniline, $\text{OPh}\cdot\text{C}_3\text{H}_6\cdot\text{NHPh}$, is prepared by heating γ -bromopropyl phenyl ether (12 grams) with aniline (15 grams) for about two hours on a water-bath, and subsequently removing the

excess of aniline by steam distillation. It is a brown oil of basic odour, and boils at above 300° , dissolves in most solvents with the exception of water, and on standing solidifies to a mass which melts at 32° . The *hydrochloride*, $C_{15}H_{17}NO, HCl$, crystallises from alcohol in needles, melts at 170° , and, when warmed with water, is partly dissolved and partly decomposed into the base and hydrochloric acid.

γ -*Phenoxybutyronitrile*, $OPh \cdot C_3H_6 \cdot CN$, is obtained when γ -bromopropyl phenyl ether (20 grams), alcohol (180 c.c.), and a solution of potassium cyanide (18 grams) in water (36 c.c.) are heated together for 3—4 hours in a reflux apparatus. It crystallises in white needles, melts at 45 — 46° , boils at 287 — 289° , and dissolves easily in the ordinary solvents. On hydrolysis with concentrated hydrochloric acid at 100° , it is converted into γ -*phenoxybutyric acid*, $OPh \cdot C_3H_6 \cdot COOH$, which crystallises from light petroleum in silvery scales, melts at 60° , and is insoluble in water, sparingly soluble in hydrochloric acid, light petroleum, and carbon bisulphide, and easily soluble in alcohol, ether, chloroform, and benzene. When dissolved in 5—6 times its weight of cold concentrated sulphuric acid, and left for 5—6 hours, the nitrile undergoes both hydrolysis and sulphonation with the production of *sulpho- γ -phenoxybutyramide*, $SO_3H \cdot C_6H_4 \cdot O \cdot C_3H_6 \cdot CONH_2$. This substance melts at 211° , can be crystallised from water, is insoluble in alcohol, benzene, chloroform, &c., and yields salts on treatment with carbonates.

Trimethylene diphenyl ether, $OPh \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OPh$, formed as a secondary product in the preparation of γ -bromopropyl phenyl ether, crystallises from alcohol in lustrous scales, melts at 61° , does not volatilise with steam, and is readily soluble in most solvents.

γ -*Phenoxypropyl alcohol*, $OPh \cdot C_2H_4 \cdot CH_2 \cdot OH$, prepared by treating a hot aqueous solution of γ -phenoxypropylamine hydrochloride with a hot solution of sodium nitrite, is an oily liquid boiling at 240 — 250° under 764 mm. pressure.

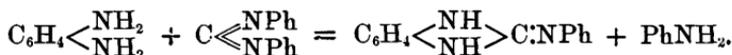
Trimethylene phenyl methyl ether, $OPh \cdot C_3H_6 \cdot OMe$, is obtained when γ -bromopropyl phenyl ether is boiled with the calculated quantity of sodium methoxide in methyl alcohol solution for 2—3 hours in a reflux apparatus. It is an oily liquid boiling at 230 — 231° .

Trimethylene phenyl ethyl ether, $OPh \cdot C_3H_6 \cdot OEt$, formed by boiling γ -bromopropyl phenyl ether with alcoholic potash for two hours in a reflux apparatus, is a colourless, oily liquid of pleasant odour, and boils at 328 — 330° under 760 mm. pressure. W. P. W.

Products of the Action of Aromatic Carbodiimides on Orthodiamines. By A. KELLER (*Ber.*, **24**, 2498—2525).—According to the investigations of Dahm and Gasiorowski (*Abstr.*, 1887, 247), and of Moore (*Abstr.*, 1889, 983; 1890, 246), orthodiamines combine with carbodiphenylimide and carbodiparatolyimide in molecular proportions. The author in continuing Moore's experiments has obtained results differing considerably from those of the latter investigator, and has therefore repeated the whole of the work with the following results:—

Carbodiphenylimide and orthophenylenediamine were heated

together in molecular proportion for five minutes at 210—220°, and the product, which smells strongly of aniline, distilled in a current of steam. The distillate contains aniline in considerable quantity, whilst the residue, after recrystallisation from benzene or alcohol, forms white needles or prisms, and melts at 190°. It has the composition $C_{13}H_{11}N_3$, and appears to be *phenylorthophenyleneguanidine*, its formation being represented as follows:—



It crystallises from alcohol, when the solution is allowed to evaporate slowly, in thick, apparently monosymmetric prisms, is almost insoluble in water and light petroleum, sparingly soluble in ether, and readily in alcohol. It distils with slight decomposition at 440—450°, but may be volatilised unchanged under 30 mm. pressure, and has then a vapour density corresponding with the above formula. It is a very stable substance, and is only attacked by hydrochloric acid at 300°. The *hydrochloride*, $C_{13}H_{11}N_3 \cdot HCl$, forms long, white, hair-like needles, and is soluble in water and alcohol; the *platinochloride*, $(C_{13}H_{11}N_3)_2 \cdot H_2PtCl_6$, is a pale-yellow, crystalline powder, almost insoluble in water; the *sulphate*, $(C_{13}H_{11}N_3)_2 \cdot H_2SO_4$, crystallises in long, hair-like needles, and is slightly soluble in cold, readily in hot water and in alcohol; the *acetyl* compound, $C_{13}H_{10}N_3Ac$, is unstable, and crystallises from benzene in fascicular aggregates of prisms melting at 160°; and the *dibenzoyl* compound, $C_{13}H_9N_3Bz_2$, crystallises in fascicular aggregates of white, lustrous needles, and melts at 171°. If the base is dissolved in acetic acid and mixed with an aqueous solution of potassium nitrite, a pale-yellow, crystalline precipitate of the *nitroso*-compound $C_{13}H_{10}N_3 \cdot NO$ is formed, which separates from all solvents as an oil, and shows Liebermann's reaction.

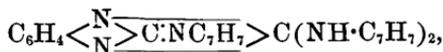
As the phenylorthophenyleneguanidine contains two imido-groups, it appeared probable that it would combine with phenyl isocyanate forming a double carbamide. This reaction does in all probability take place, but the product at once loses aniline, forming the compound $C_6H_4 \left\langle \begin{array}{c} N \\ N \end{array} \right\rangle C:NPh \begin{array}{c} CO \\ CO \end{array} \rangle NPh$, which crystallises from alcohol in thin, lustrous, white needles, melts at 264—266°, is insoluble in water and light petroleum, but soluble in alcohol and benzene.

According to Moore (*loc. cit.*), 2 mols. of carbodiphenylimide also unite directly with 1 mol. of orthophenylenediamine, forming the compound $C_6H_4 \cdot N_2 [C(NHPh)_2]_2$; the author finds, however, that the products of the reaction are aniline, phenylorthophenyleneguanidine, and triphenylguanidine (m. p. 144°). If, on the other hand, phenylorthophenyleneguanidine is treated with a second molecule of carbodiphenylimide at 210°, the compound *diphenylamidomethylenephenylorthophenyleneguanidine*, $C_6H_4 \left\langle \begin{array}{c} N \\ N \end{array} \right\rangle C:NPh \rangle C(NHPh)_2$, is formed, which crystallises from alcohol in white needles and melts at 188°; the yield is small, owing to the secondary reactions which take

place. If carbodiparatolyimide is substituted for carbodiphenylimide, the corresponding *paratoly* derivative is obtained; it crystallises in white needles and melts at 185—187°.

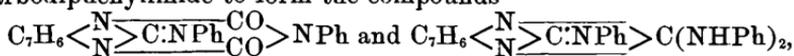
Paratolyorthophenyleneguanidine, $C_6H_4 \left\langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \right\rangle C \cdot N \cdot C_7H_7$, is obtained on heating together orthophenylenediamine and carbodiparatolyimide; it crystallises from alcohol in short, thick, slightly brownish tablets, melts at 209°, and dissolves readily in boiling alcohol and acetic acid, scarcely at all in water. The *hydrochloride*, $C_{14}H_{13}N_3 \cdot HCl$, forms white needles, soluble in hot water and cold alcohol; the *platinochloride*, $(C_{14}H_{13}N_3)_2 \cdot H_2PtCl_6$, is a pale-yellow, microcrystalline precipitate; the *sulphate*, $(C_{14}H_{13}N_3)_2 \cdot H_2SO_4$, crystallises in long, white needles; the *acetyl* compound, $C_{14}H_{12}N_3Ac$, forms unstable, white needles and melts at 152°; and the *dibenzoyl* compound, $C_{14}H_{11}N_3Bz_2$, crystallises in long, lustrous prisms, melting at 191°. The *nitroso*-compound, $C_{14}H_{12}N_3 \cdot NO$, forms yellow, crystalline flakes, and commences to decompose at 90°.

Paratolyorthophenyleneguanidine combines with phenyl isocyanate, forming the compound $C_6H_4 \left\langle \begin{smallmatrix} N \\ N \end{smallmatrix} \right\rangle \overline{C \cdot N \cdot C_7H_7} \begin{smallmatrix} CO \\ CO \end{smallmatrix} \right\rangle NPh$, which crystallises in small needles and melts at 252—254°. With carbodiparatolyimide, the base yields the compound



which separates from boiling alcohol in short needles melting at 187.5—188°.

Phenylorthotoluyleneguanidine, $C_7H_6 \left\langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \right\rangle C \cdot NPh$, is obtained together with aniline by heating orthotoluylenediamine with carbodiphenylimide in molecular proportion. It crystallises from alcohol in short, white needles, and from benzene in prisms, and melts at 166—167°; the *hydrochloride*, $C_{14}H_{13}N_3 \cdot HCl$, forms long, white, elastic, silky needles; the *platinochloride*, $(C_{14}H_{13}N_3)_2 \cdot H_2PtCl_6 + 3H_2O$, large, orange-yellow tablets; the *sulphate*, $(C_{14}H_{13}N_3)_2 \cdot H_2SO_4$, long, white, lustrous needles; the *acetyl* compound, $C_{14}H_{12}N_3Ac$, white needles, melting at 144—147°; the *dibenzoyl* compound fascicular aggregates of prisms, melting at 220—222°; the *nitroso*-compound, $C_{14}H_{12}N_3 \cdot NO$, is a flocculent precipitate, melting at 120—125° with decomposition. The base combines with phenyl isocyanate and carbodiphenylimide to form the compounds



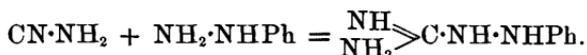
melting at 230—234° and 199—200° respectively. The *diparatoly* compound corresponding with the latter melts at 190—193°.

Paratolyorthotoluyleneguanidine, $C_7H_6 \left\langle \begin{smallmatrix} NH \\ NH \end{smallmatrix} \right\rangle C \cdot N \cdot C_7H_7$, is obtained by heating together orthotoluylenediamine and carbodiparatolyimide; it crystallises from alcohol in white prisms, and melts at 197—198°. The *hydrochloride*, $C_{15}H_{15}N_3 \cdot HCl$, forms long, white, silky needles; the *platinochloride*, $(C_{15}H_{15}N_3)_2 \cdot H_2PtCl_6$, orange-coloured tablets; the

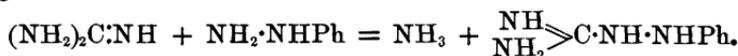
sulphate, $(C_{15}H_{15}N_3)_2, H_2SO_4 + 5H_2O$, lustrous, white needles; the *acetyl* compound, $C_{15}H_{14}N_3Ac$, long, white needles melting at $148-149^\circ$; the *dibenzoyl* compound, $C_{16}H_{13}N_3Bz_2$, fascicular aggregates of white needles melting at $198-201^\circ$; the *nitroso*-compound, $C_{15}H_{14}N_3 \cdot NO$, commences to decompose at 130° .

Tolyltoluyleneguanidine combines with phenyl isocyanate, yielding the compound $C_7H_6 \langle \overset{N}{\parallel} \overline{C \cdot NC_7H_7} \overset{CO}{\parallel} \rangle NHPH$, which crystallises from alcohol in small needles, and melts at $230-233^\circ$. With carbodiparatolyimide, it forms $C_7H_6 \langle \overset{N}{\parallel} \overline{C \cdot NC_7H_7} \rangle C(NH \cdot C_7H_7)_2$, which melts at $208-210^\circ$; the corresponding *diphenyl* compound melts at $174-176^\circ$.
H. G. C.

Anilguanidine. By G. PELLIZZARI (*Gazzetta*, **21**, 330-340).—Cyanamide reacts with phenylhydrazine hydrochloride to form anilguanidine hydrochloride,



The same product is obtained by the action of phenylhydrazine on guanidine,

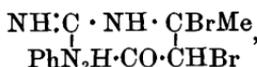
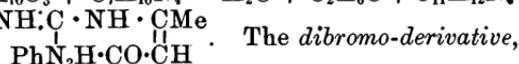


Anilguanidine hydrochloride, $C_7H_{10}N_4, HCl$, is obtained by boiling a solution of cyanamide (18 grams) and phenylhydrazine hydrochloride (60 grams) in alcohol (300 grams) for 12 hours; the greater part of the alcohol is then evaporated, very dilute hydrochloric acid added, and the solution allowed to cool after expulsion of the remaining alcohol. The salt separates in reddish crystals, which, on recrystallisation from water, form yellowish, acicular crystals, very soluble in hot alcohol and water, less so in hydrochloric acid. It melts with decomposition at 226° , and reduces ammoniacal silver nitrate solution. A yield of 50 per cent. is obtained by the above method; the mother liquors contain another base not yet studied. The hydrochloride may also be obtained by gradually heating guanidine carbonate with phenylhydrazine hydrochloride to 180° , the crude product being crystallised from dilute hydrochloric acid. The yield is, however, a poor one. *Anilguanidine platinochloride*, $(C_7H_{10}N_4)_2, H_2PtCl_4$, is precipitated in minute, yellowish, prismatic crystals frequently twined crosswise. It is soluble in hot water, but after a time is reduced with separation of metallic platinum. The *carbonate*, $(C_7H_{10}N_4)_2, H_2CO_3 + H_2O$, forms minute, white scales, which are slowly coloured red on exposure to the air. On heating, it loses ammonia and water, yielding a new base not yet investigated. The *acetate*, $C_7H_{10}N_4, C_2H_4O_2$, is obtained in small, colourless crystals which decompose at 195° ; it is very soluble in alcohol.

When concentrated potash is added to the solution of the hydrochloride, the free base separates in little drops, which soon solidify to

yellow, needle-shaped crystals. It changes spontaneously in air, and is obtained pure only with great difficulty.

Ethyl acetoacetate reacts with anilguanidine, forming a closed chain compound. A solution of anilguanidine hydrochloride (10 grams), ethyl acetoacetate (7 grams), and sodium carbonate (2.8 grams) in alcohol (50 c.c.) is boiled for seven hours, the alcoholic solution partly evaporated, dissolved in water, and acidified with acetic acid; on cooling, the new compound (8 grams) is obtained. By recrystallisation from alcohol, it may be obtained in white crystals of the composition $C_{11}H_{12}N_4O$, which on heating turn red and slowly decompose without melting. The reaction may be represented by the equation $C_6H_{10}O_3 + C_7H_{10}N_4 = H_2O + C_2H_6O + C_{11}H_{12}N_4O$; the product is probably



is obtained on bromination in glacial acetic acid solution, and consists of minute, colourless crystals, insoluble in water and alcohol, slightly soluble in acetic acid, and decomposing at 220—222°.

The *ethyl derivative*, $C_{13}H_{16}N_4O$, is obtained on treating anilguanidine hydrochloride with ethyl ethylacetoacetate in alcoholic solution, as spherical aggregates of short, thin, yellow prisms.

When a mixture of ethyl diethylacetoacetate and anilguanidine hydrochloride is treated as above, no reaction occurs even when the heating is continued for some days. W. J. P.

Halogenated Amines of the Fatty Series. By O. SEITZ (*Ber.*, 24, 2624—2631).—With the object of preparing chlorinated amines of the fatty series, the author has treated potassium phthalimide with various chlorobromides by Gabriel's method (*Abstr.*, 1888, 439) in the hope that the more reactive bromine would alone be eliminated with the production of chlorethyl- or chloropropyl-phthalimide. Trimethylene chlorobromide, however, yields a mixture of γ -chloropropyl- and γ -bromopropyl-phthalimide, and ethylene chlorobromide in like manner gives a mixture of chlorethyl- and bromethyl-phthalimide.

Chlorethylphthalimide, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CH_2Cl$, is obtained when potassium phthalimide is heated with five times its weight of ethylene dichloride at 180—190° for three hours. It crystallises from carbon bisulphide in colourless needles, melts at 79—81°, and, when heated with concentrated hydrochloric acid at 180° for four hours, yields phthalic acid and chlorethylamine hydrochloride. The latter can be crystallised from amyl alcohol, in which it is less soluble than in the ordinary solvents, and melts at 119—123°; the picrate and platinochloride of the amine have already been described (*loc. cit.*).

β -*Bromopropylphthalimide*, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CHBrMe$, is formed when a mixture of allylphthalimide (1.5 grams) with concentrated hydrobromic acid prepared at 0° (6 c.c.) is allowed to remain in a stop-

pered flask for 24 hours at the ordinary temperature. It separates from methyl alcohol as a silky, felted, crystalline mass, and melts at 105° .

β -Thiocyanopropylphthalimide, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CHMe \cdot SCN$, is prepared by heating β -bromopropylphthalimide with alcoholic potassium thiocyanate at 170° for four hours. It dissolves in methyl alcohol, cold benzene, and acetic acid, but less readily in light petroleum, and melts at $89-93^{\circ}$.

β -Mercaptopropylphthalimide, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CHMe \cdot SH$, is obtained when β -bromopropylphthalimide is heated with alcoholic potassium hydrosulphide in a pressure flask for one hour at 100° . After purification by conversion into its mercury salt, it crystallises from alcohol in aggregates melting at 88° . When oxidised by the addition of iodine to its alcoholic solution, it is converted into *β -diphthalimido-propyl bisulphide*, $(C_8H_4O_2 \cdot N \cdot CH_2 \cdot CHMe)_2S_2$, which crystallises in white needles and melts at $159-161^{\circ}$.

The action of aniline on β -bromopropylphthalimide is essentially different from that on the γ -compound (compare Goldenring, *Abstr.*, 1890, 976), and is by no means complete at 150° . When aniline (8 grams) and β -bromopropylphthalimide (9 grams) are heated together on a sand-bath for 20 minutes, a mixture of phthalanil, as chief product, with a relatively small proportion of *β -anilidopropylphthalimide*, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CHMe \cdot NPh$, is obtained. The latter crystallises from alcohol in beautiful yellow needles, melts at 93° , and on digestion with concentrated hydrochloric acid at 190° , is decomposed into phthalic acid and a base, probably β -anilidopropylenediamine, $NPh \cdot CH(CH_2 \cdot NH_2)_2$, boiling at $250-260^{\circ}$.

W. P. W.

Azoimide. By E. NOELTING and E. GRANDMOUGIN (*Ber.*, **24**, 2546—2547).—Curtius has shown (this vol., p. 56) that triazobenzene or diazobenzeneimide must be regarded as the phenyl salt of azoimide. In view of the stability of such aromatic salts, there appeared little likelihood of eliminating the phenyl group, but it seemed not improbable that the entrance of nitro-groups into the phenyl residue might render the elimination more easy, just as is the case with chlorobenzene.

An experiment with dinitrotriazobenzene has shown that such is really the case. The dinitro-compound was prepared from 1:2:4-dinitraniline by diazotising, converting into the perbromide, and treating this with ammonia; by the action of alcoholic potash, it is converted, apparently very readily, into dinitrophenol and azoimide.

H. G. C.

Orthohydroxyazo-dyes. By J. D. ZIBELL (*Chem. Centr.*, 1891, ii, 56; from *Schweiz. Wochenschr. Pharm.*, **29**, 186; compare *Abstr.*, 1884, 742 and 1146).—The author finds that diazobenzene chloride reacts with parahydroxybenzoic acid with separation of the carboxyl group, forming phenylazophenol and phenyldiazophenol. Diazosulphanilic acid reacts similarly, forming sodium phenolazosulphanilate. On the other hand, the azo-compounds obtained by employing ortho- and

meta-hydroxybenzoic acids behaved differently from one another when cotton was dyed with them, only that obtained from orthohydroxybenzoic acid adhering to the fibre.
J. W. L.

Thiocarbamides. By H. SALKOWSKI (*Ber.*, **24**, 2724—2729).—Symmetrical dibenzylthiocarbamide, $\text{CS}(\text{NH}\cdot\text{CH}_2\text{Ph})_2$, may be readily obtained by heating benzylamine benzylthiocarbamate at 125° until hydrogen sulphide ceases to be evolved; it melts at 148° , not at 114° as stated by Strakosch.

Benzylthiocarbamide, $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, is prepared by heating benzylamine thiocyanate at 110° for about 14 hours, and is identical with the product formed by the action of alcoholic ammonia on benzylthiocarbimide; it is soluble in 61 parts of 95 per cent. alcohol, crystallises in colourless, concentric needles, and melts at 164° . Paternò and Spica give the melting point as 101° , and state that the compound is readily soluble in water; they appear, however, to have mistaken benzylamine thiocyanate for benzylthiocarbamide, since the latter is almost insoluble in water, and the former melts, according to the author, at 95° .

Paternò and Spica have made a similar error regarding unsymmetrical dibenzylthiocarbamide, $\text{NH}_2\cdot\text{CS}\cdot\text{N}(\text{CH}_2\text{Ph})_2$, which they obtained by the evaporation of benzylamine hydrochloride and potassium thiocyanate solutions; the author failed to detect the formation of any thiocarbamide in this manner. *Dibenzylamine thiocyanate* is prepared by dissolving dibenzylamine in hot dilute thiocyanic acid; it crystallises in colourless, lustrous plates melting at 164 — 165° . On melting the compound and heating it at 140° for several hours, unsymmetrical dibenzylthiocarbamide is formed; this is insoluble in water, and is deposited from alcohol in small, yellow crystals which melt at 141° .

Contrary to the statement of Clermont, aniline thiocyanate is readily converted into phenylthiocarbamide by dissolving the salt in water, evaporating to dryness, and heating the residue for 2—3 hours on the water-bath. The conversion of methylamine thiocyanate into the corresponding thiocarbamide has not as yet been observed by the author.

Methylthiocarbamide, prepared from methylthiocarbimide and alcoholic ammonia, melts at 119 — 120° instead of below 100° as usually stated in text books.

The observations of O. Hecht regarding symmetrical dimethylthiocarbamide are confirmed.

The above results prove that, in certain cases at all events, the conversion of amine thiocyanates into the corresponding thiocarbamides is independent of the former compounds being in the nascent state.
J. B. T.

Derivatives of Bromopiperonal. By A. OELKER (*Ber.*, **24**, 2592—2596).—Bromopiperonal, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_4\text{Br}\cdot\text{COH}$, is obtained by adding the calculated quantity of bromine to a solution of piperonal in carbon bisulphide in the presence of a small quantity of iodine. The carbon bisulphide is distilled off and the mass boiled with alcohol.

On cooling, it separates in long, white needles, melts at 129—130°, and is identical with the compound obtained by Fittig and Mielk (*Annalen*, 152, 39).

Bromopiperonalphenylhydrazone is obtained in yellow, nacreous scales on adding phenylhydrazine to a solution of the above compound in dilute acetic acid. It melts at 136°, is insoluble in water, and easily soluble in alcohol, ether, and acetone.

Bromopiperonaldoxime is obtained by adding an aqueous solution of hydroxylamine hydrochloride to an alcoholic solution of bromopiperonal. It forms slender, white needles, crystallises from alcohol, melts at 168°, is insoluble in water, but easily soluble in alcohol, ether, and benzene.

Mononitrobromopiperonal, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{HBr}(\text{NO}_2) \cdot \text{COH}$, is obtained by adding twice the theoretical quantity of nitric acid (1.48) to a cold solution of bromopiperonal in acetic acid. Heat is developed, and the solution must be cooled below 50°, otherwise the action becomes too violent, and the bromopiperonal is decomposed. The mixture is poured into ice-cold water, and the product crystallised from alcohol. It crystallises in beautiful, bright-yellow needles, melts at 90°, and is soluble in all the ordinary solvents except water. When treated with acetone and caustic soda, the mixture becomes red, and an indigo-compound is not formed; hence the author is inclined to believe that the nitro-group is in the meta-position with respect to the aldehyde group. However, dinitrobromopiperonal, in which one nitro-group must be in the ortho-position relatively to the aldehyde group, behaves in a similar way, and does not yield an indigo compound with acetone and alkali. The red coloration is also produced by boiling the compound with alkalis alone, and disappears on the addition of hydrochloric acid.

Dinitrobromopiperonal is obtained by adding bromopiperonal in small portions to well-cooled nitric acid (sp. gr. 1.52), and pouring the solution into ice-cold water. It crystallises from alcohol and acetone in golden-yellow needles, melts at 173°, is insoluble in water, somewhat sparingly soluble in alcohol and ether, easily so in acetone and chloroform, and turns deep yellow on exposure to light.

Bromopiperonylacryl methyl ketone, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_2\text{Br} \cdot \text{CH} : \text{CH} \cdot \text{COMe}$, is formed, together with dibromodipiperonylacryl methyl ketone, by shaking bromopiperonal (5 grams) with acetone (15 c.c.) and 3 per cent. caustic soda (4—5 c.c.). It is separated by extracting the product with a small quantity of alcohol, in which it is easily soluble; it crystallises in white, lustrous needles, and melts at 152—154°. The *oxime* crystallises from alcohol in slender, white needles, melts at 210° with decomposition, and is sparingly soluble in alcohol and benzene, easily so in acetone and ether. The *phenylhydrazone* crystallises in large, yellow plates, melts at 158°, and is easily soluble in all the usual solvents.

Dibromodipiperonylacryl ketone, $(\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_2\text{Br} \cdot \text{CH} : \text{CH})_2\text{CO}$, is sparingly soluble or insoluble in most solvents, crystallises from acetic acid in slender, lemon-yellow needles, and dissolves in concentrated sulphuric acid forming an intense blue solution. Both ketones are sensitive to light.

Bromopiperonyllactyl methyl ketone,

is obtained as an intermediate product in the above condensation when bromopiperonal is dissolved in a large quantity of acetone. It is a yellowish-white, crystalline compound, melts at 110° , is insoluble in cold water, sparingly soluble in hot water, easily so in alcohol, ether, and benzene, and is converted into bromopiperonyllactyl methyl ketone (m. p. 152°) when boiled with acetic acid. E. C. R.

Isomeric Paranitrobenzaldoximes. By H. GOLDSCHMIDT and C. KJELLIN (*Ber.*, **24**, 2547—2556).— α -Paranitrobenzaldoxime was prepared according to the method described by Gabriel and Herzberg (*Abstr.*, 1883, 1104), and exhibited all the properties formerly assigned to it.

Carbanilido- α -paranitrobenzaldoxime, $\text{NHPH}\cdot\text{COO}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is obtained by warming equivalent quantities of the oxime and phenyl cyanate dissolved in benzene on the water-bath, and evaporating the solution in a vacuum. It crystallises from alcohol in yellowish-white scales, melts at 157° , and is easily soluble in hot alcohol and benzene, less so in ether, and only very sparingly in light petroleum. When warmed with soda, it is decomposed into the oxime, aniline, and carbonic acid.

α -Paranitrobenzaldoxime methyl ether, $\text{OMe}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, is obtained by the action of methyl iodide on a mixture of equivalent quantities of the α -oxime and sodium methoxide dissolved in methyl alcohol, and is purified by distillation with steam. It crystallises in white needles, melts at 101° , and is easily soluble in cold alcohol, benzene, light petroleum, chloroform, and ether.

α -Paranitrobenzaldoxime ethyl ether is obtained in a similar way to the methyl ether; the reaction does not, however, take place so easily, and it is necessary to heat the mixture for some time on the water-bath. It crystallises in colourless, tetragonal tablets, melts at 107 — 108° , is easily soluble in the ordinary solvents, and is volatile with steam. When it is heated with alcohol at 200° , paranitrobenzamide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$, is formed.

β -Paranitrobenzaldoxime is obtained by passing hydrogen chloride into a dry ethereal solution of the α -oxime, and then treating with a solution of soda the hydrochloride of the β -oxime, which separates in small, white needles, and melts at 116° with decomposition. It crystallises from ethyl acetate in small, lustrous tablets, melts at 170 — 176° , and is sparingly soluble in cold alcohol, benzene, and chloroform, more so in hot alcohol, and dissolves in alkalis with a yellowish-red coloration.

Carbanilido- β -paranitrobenzaldoxime is obtained in lemon-yellow needles on adding phenyl cyanate to an ethereal solution of the β -oxime. It melts at 94° with evolution of gas, is easily soluble in benzene, sparingly so in cold alcohol, and is decomposed on warming with alcohol. When warmed with sodium hydroxide, it yields β -paranitrobenzaldoxime, aniline, carbonic acid, paranitrobenzotrile, and a small quantity of diphenylcarbamide.

Methyl paranitroisobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{smallmatrix} \text{O} \\ \text{NMe} \end{smallmatrix}$, is obtained by the action of methyl iodide on the β -oxime and sodium methoxide dissolved in methyl alcohol. It crystallises from hot alcohol in lemon-yellow needles, melts at 205° , and is sparingly soluble in light petroleum, benzene, ether, and cold alcohol, fairly easily in hot alcohol. When boiled with hydrochloric acid, it yields paranitrobenzaldehyde and methylhydroxylamine, $\text{NHMe} \cdot \text{OH}$. When heated with strong hydriodic acid at 120° , it yields methylamine. A small quantity of the isomeric ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{OMe}$, is also formed in the above reaction, and is separated from the mother liquors by steam distillation.

Ethyl paranitroisobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{smallmatrix} \text{O} \\ \text{NEt} \end{smallmatrix}$, is obtained in a similar way to the methyl compound, together with a small quantity of the isomeric ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{OEt}$. It crystallises from hot alcohol in lemon-yellow needles, melts at 119 – 120° , is easily soluble in hot alcohol and benzene, sparingly in ether, and almost insoluble in light petroleum. When boiled with hydrochloric acid, it yields paranitrobenzaldehyde and a compound which reduces Fehling's solution, and is probably $\text{NHEt} \cdot \text{OH}$.

β -Paranitrobenzaloxime methyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{OMe}$, is obtained as follows:—The β -oxime is dissolved in the smallest quantity of soda, and silver nitrate added to the solution. The silver salt thus obtained is collected, suspended in ether, and methyl iodide added. The mixture is shaken from time to time and, after some hours, is filtered; the ethereal filtrate is washed with dilute soda, the ether distilled, and the residue crystallised from petroleum. It crystallises in spear-like needles, melts at 67 – 68° , and is easily soluble in the ordinary solvents.

β -Paranitrobenzaloxime ethyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{OEt}$, is obtained in a similar way to the methyl compound; it crystallises from petroleum in colourless needles, melts at 70 – 71° , and is easily soluble in the ordinary organic solvents. When heated with alcohol at 190 – 200° , a product melting at 145° is obtained; on further heating, paranitrobenzamide is obtained.

The last two β -compounds are easily converted into α -compounds by dissolving them in carbon bisulphide containing a little iodine, and heating the mixture on a water-bath.

A determination of the molecular weights of the above compounds gave results agreeing with the formula $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{NOR}$, both for the α - and β -compounds.

E. C. R.

Additive Compounds of Alkylisobenzaldoximes. By H. GOLDSCHMIDT and C. KJELLIN (*Ber.*, **24**, 2808–2817).—The compound $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} < \begin{smallmatrix} \text{O} \\ \text{NMe, NaI} \end{smallmatrix}$ separates when a methyl alcoholic solution of metanitroisobenzaldoxime is mixed with sodium ethoxide and methyl iodide in molecular proportion, and the mixture concentrated, whilst methylmetanitroisobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{OMe}$, melting at 72° (compare *Abstr.*, 1890, 1262) remains in the mother

liquor; the additive compound is likewise obtained when the above mixture is allowed to remain for a time, filtered from sodium iodide, evaporated to dryness, and the methylmetanitrosobenzaldoxime (m. p. 72°) extracted with ether from the residue; also when its components are heated together in a sealed tube at 100°. It forms large, yellow plates, melts at 180—185°, and is readily soluble in alcohol, but when dissolved in hot water, it is decomposed into methylmetanitrosobenzaldoxime (m. p. 117°; *loc. cit.*); benzene and ether also decompose it. It is unaltered when heated in a current of dry air at 160°, whilst at 190° methylamine passes over.

Ethylmetanitrosobenzaldoxime, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{O} \\ | \\ \text{N} \cdot \text{Et}' \end{array}$, is obtained from metanitrosobenzaldoxime, ethyl iodide, and sodium ethoxide; it crystallises from boiling water in yellowish needles, melts at 97°, and is only slightly soluble in cold water, sparingly in ether and light petroleum, readily in alcohol and hot benzene; the formation of a compound with sodium iodide was not observed here.

The two stereoisomeric *ethylmetanitrosobenzaldoximes*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{O} \\ | \\ \text{EtO} \cdot \text{N} \end{array}$ and $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \begin{array}{c} \text{O} \\ | \\ \text{N} \cdot \text{OEt}' \end{array}$, were also prepared; they are both oils.

The compound $\text{CHPh} \begin{array}{c} \text{O} \\ | \\ \text{NMe, NaI} \end{array}$ is produced from isobenzaldoxime, sodium ethoxide, and methyl iodide in methyl alcoholic solution; also by evaporating mixed aqueous solutions of methylisobenzaldoxime and sodium iodide in molecular proportion; it melts at 69—72°, dissolves readily in water and alcohol, is slowly decomposed by benzene and ether, and gives a brown precipitate which readily undergoes decomposition when treated with a concentrated aqueous solution of copper acetate. When an aqueous solution, to which common salt has been added, is extracted with ether, methylisobenzaldoxime, $\text{CHPh} \begin{array}{c} \text{O} \\ | \\ \text{NMe} \end{array}$, is obtained from the ethereal solution; on adding light petroleum to its solution in a little benzene, it separates in colourless plates; it melts at 82°, and is readily soluble in water, alcohol, and benzene, somewhat less so in ether; it decomposes when heated with dilute hydrochloric acid, and in addition to the above described sodium iodide compound, it appears to form a similar derivative with calcium chloride. Unlike isobenzaldoxime, it is not volatile, and as methyl derivatives are invariably more readily volatile than their parent substances, it would seem that isobenzaldoxime has not the constitution $\text{CHPh} \begin{array}{c} \text{O} \\ | \\ \text{NH} \end{array}$ previously ascribed to it.

Ethylisobenzaldoxime, $\text{CHPh} \begin{array}{c} \text{O} \\ | \\ \text{NEt}' \end{array}$, likewise yields a compound with sodium iodide; this melts at 67—70°.

When methylisobenzaldoxime (m. p. 82°) and phenyl cyanate are dissolved in benzene in molecular proportion, and the solution, after remaining for 24 hours, evaporated, the additive compound, $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$,

which crystallises from alcohol in white needles and melts at 119° , is obtained; when heated with concentrated hydrochloric acid in a sealed tube at 100° , carbonic anhydride, aniline, ammonia, and benzaldehyde are formed. The compound $C_{16}H_{15}N_2O_2$, melting at $116-117^{\circ}$, is prepared from ethylisobenzaldoxime and phenyl cyanate; when heated with concentrated hydrochloric acid at 100° , it yields the same decomposition products as the methyl derivative. In like manner the compound $C_{16}H_{15}N_3O_4$, melting at 148° , is formed from ethylmetanitroisobenzaldoxime (m. p. 67°) and phenyl cyanate. whilst the compound $C_{21}H_{17}N_3O_4$, melting at $158-159^{\circ}$, is produced from benzylmetanitrobenzaldoxime and phenyl cyanate.

A. R. L.

Homologues of Benzhydrylamine. By H. GOLDSCHMIDT and H. STÖCKER (*Ber.*, **24**, 2797—2808).—*Paratolhydrylamine*,



is prepared from paraditolyketoxime (Goldschmidt, *Abstr.*, 1890, 1412) as follows:—The ketoxime (5 grams) is treated in alcoholic solution with 2.5 per cent. sodium amalgam (105 grams) and acetic acid at 60° (compare *Abstr.*, 1887, 249). The product is poured into water, sodium hydroxide added, and the mixture extracted with ether; on distilling the ethereal solution, a white, crystalline mass is left, from which paratolhydrylamine is extracted by boiling with light petroleum, whilst paratoluic paratoluide (Goldschmidt, *loc. cit.*) remains undissolved. It separates from light petroleum in transparent tablets, melts at 93° , and is readily soluble in ether and alcohol. The *hydrochloride*, formed by passing hydrogen chloride into a solution of the base in light petroleum, separates from water in white needles, and melts at 235° ; whilst the *acetyl derivative*, $C_{15}H_{15} \cdot NHAc$, obtained by boiling the base with acetic anhydride, crystallises from alcohol in delicate, white needles, and melts at 159° . When a solution of potassium cyanate is added to a hot aqueous solution of the hydrochloride, *paratolhydrylcarbamide*, $CH(C_6H_4Me)_2 \cdot NH \cdot CO \cdot NH_2$, is produced; it separates from dilute alcohol in small, white needles, and melts at 152° .

Parahomobenzhydrylamine, $C_6H_4Me \cdot CHPh \cdot NH_2$, is obtained, together with paratoluic anilide, by reducing crude paratolylphenylketoxime (Hantzsch, *Abstr.*, 1890, 1273) as above, employing sodium amalgam (110 grams) and the ketoxime (5 grams). The product is thrown into water, acidified with hydrochloric acid, and extracted with ether to remove the anilide; it is then rendered alkaline and again extracted with ether; on distilling the second ethereal solution, parahomobenzhydrylamine is obtained as an oil having a faint basic odour and boiling at 296° (723 mm.); it is sparingly soluble in water, cannot be solidified, and absorbs carbonic anhydride from the air. The *hydrochloride* crystallises from boiling water in quadratic prisms, and melts at 252° ; the *platinochloride*, $(C_{14}H_{15}N)_2 \cdot H_2PtCl_6 + 2H_2O$, is a bright yellow, crystalline precipitate which dissolves sparingly in water, but more readily in alcohol, and melts at 119° ; whilst the *acetyl derivative*, $C_{14}H_{13} \cdot NHAc$, crystallises from alcohol in white needles, and melts at 131° . When a solution of potassium

cyanate is added to a hot aqueous solution of the hydrochloride, *parahomobenzhydrylcarbamide*, $C_6H_4Me \cdot CHPh \cdot NH \cdot CO \cdot NH_2$, separates; it crystallises from dilute alcohol in white needles, and melts at 158° . *Parahomobenzhydrylaminethiocarbamide*, $C_6H_4Me \cdot CHPh \cdot NH \cdot CS \cdot NH_2$, is obtained by treating an aqueous solution of the hydrochloride with the theoretical quantity of potassium thiocyanate, evaporating to dryness, extracting with absolute alcohol, and again evaporating; the oil thus obtained soon solidifies to reddish needles, which are rendered colourless by washing with ether; it melts at $100-101^\circ$. *Parahomobenzhydrylphenylcarbamide*, $C_6H_4Me \cdot CHPh \cdot NH \cdot CO \cdot NHPh$, is formed when phenyl cyanate is added to an ethereal solution of the base; it separates from boiling alcohol in small, white needles, and melts at 206° . Parahomobenzhydrylamine contains an asymmetric carbon atom, but, as might be anticipated, since it is a synthetic product, is optically inactive. The authors were not, however, successful in resolving it into two optically active isomerides by crystallisation of either the monodextrotartrate or of the normal salt; they also find that the same base is formed by reducing pure α -paratolylphenylketoxime (Hantzsch, *loc. cit.*) instead of the crude ketoxime, together also with paratoluic anilide. The *monodextrotartrate*, $C_{14}H_{15}N, C_4H_6O_6$, forms small, white needles, and melts at 157° ; whilst the normal *dextrotartrate*, $(C_{14}H_{15}N)_2, C_4H_6O_6$, which is only produced when concentrated solutions of the acid and base are mixed in the requisite proportion, separates in white, microscopic needles, and melts at $72-73^\circ$.

Orthotolyl phenyl ketone, $C_6H_4Me \cdot COPh$, prepared from orthotoluic chloride by the method described by Elbs (Abstr., 1886, 461), for the preparation of aromatic ketones, boils at 295° (722 mm.); compare Ador and Rilliet (*Ber.*, 12, 2301). The *oxime* forms white needles, and melts at $95-98^\circ$; it is probably a mixture of two stereochemical isomerides.

Orthohomobenzhydrylamine, $C_6H_4Me \cdot CHPh \cdot NH_2$, is formed, together with orthotoluic anilide, by reducing orthotolylphenylketoxime with sodium amalgam; the two products are isolated in the same manner as those of the para-series (see above). The new base is a colourless oil which boils at 299° (721 mm.), absorbs carbonic anhydride from the air, and is somewhat soluble in water. The *hydrochloride* begins to darken at 220° , melts at 249° , and is readily soluble in water; whilst the *acetyl* derivative crystallises from alcohol in small, white prisms, and melts at 124° .

Metatolyl phenyl ketone, prepared from metatoluic chloride, boils at $311-313^\circ$ (723 mm.); compare Ador and Rilliet (*loc. cit.*); the *oxime* melts at $100-101^\circ$, and is perhaps a mixture of two stereochemical isomerides.

Metahomobenzhydrylamine, $C_6H_4Me \cdot CHPh \cdot NH_2$, is a colourless oil closely resembling its isomerides; it boils at 299° (724 mm.); the *hydrochloride* forms delicate, white needles, commences to darken at 220° , melts completely at 243° , and is fairly soluble in water; whilst the *acetyl derivative* crystallises from alcohol in colourless needles, and melts at 97° .

A. R. L.

Conversion of Gallic Acid and Tannin into Benzoic Acid.

By C. E. GUIGNET (*Compt. rend.*, **113**, 200—201).—When a warm solution of gallic acid is added to a warm mixture of zinc powder and ammonia solution, the gallic acid is completely converted into benzoic acid after heating for some hours at 60°. A similar result is obtained by heating gallic acid with zinc and dilute sulphuric acid, except that in this case the benzoic acid remains undissolved.

Under similar conditions, tannin is first converted into gallic acid, and finally into benzoic acid. C. H. B.

Hydrogenation of Benzoic Acid. By O. ASCHAN (*Ber.*, **24**, 2617—2622; compare this vol., p. 1053).—*Hexahydrobenzoic acid* is obtained, together with benzoic acid, when the product of the action of hydrogen bromide on tetrahydrobenzoic acid (*loc. cit.*) is reduced with sodium amalgam. In the pure and anhydrous form, it melts at 28°, and boils at 224° under 725 mm. pressure. The *amide*, $C_6H_{11}\cdot CONH_2$, crystallises from water in large, flat prisms melting at 184°, and the *methyl* salt boils at 175—176° under 719 mm. pressure, and has a density of 1.014 at 0°/0°, and 0.9927 at 20°/20°. The acid is not affected by heating with concentrated hydrochloric acid at 170—250°, and does not seem to be identical with the author's hexanaphthenecarboxylic acid (*Abstr.*, 1890, 737).

α-Bromhexahydrobenzoic acid, $C_6H_{10}Br\cdot COOH$, is prepared by heating the mixture of phosphorus oxychloride and the acid chloride, produced by the action of phosphorus pentachloride on hexahydrobenzoic acid, with the calculated quantity of bromine at 100—120°, and extracting the product with formic acid (sp. gr. = 1.2). It crystallises from formic acid in large, silvery scales or flat prisms, melts at 63°, has an odour of iodoform, and is unstable in the presence of boiling water and alkalis.

Δ^1 -*Tetrahydrobenzoic acid* is obtained when *α*-bromhexahydrobenzoic acid is treated with alcoholic potash at the ordinary temperature and the product is distilled with steam. It is a colourless oil which boils at 235—236° under 718 mm. pressure, and, when cooled below 0°, solidifies to a crystalline mass melting at about 8°. Bromination takes place only slowly and incompletely when the acid is treated with bromine, and leads to the production of the two stereometric dibromides, which could not be satisfactorily separated, although they differ in solubility and crystalline form, the less soluble substance crystallising in prisms, and the more soluble in lamelliform rhombohedra. If, however, the mixture of acid chloride and phosphorus oxychloride formed by the action of phosphorus pentachloride on the acid is treated with the calculated quantity of bromine, and the brominated acid chloride converted into the acid by prolonged boiling with excess of formic acid (sp. gr. = 1.2), the less soluble dibromide of Δ^1 -tetrahydrobenzoic acid is the sole product. This crystallises from concentrated formic acid, dilute acetic acid, or a mixture of benzene and light petroleum in small, prismatic forms, melts at 142°, and regenerates the tetrahydro-acid when boiled with alkalis or alkaline carbonates, or if treated in the cold with alcoholic potash.

Δ^1 -Tetrahydrobenzamide crystallises from ether in octahedra, and melts at 127—128°.

The tetrahydrobenzoic acid obtained by the reduction of benzoic acid with sodium amalgam (*loc. cit.*), is most probably the Δ^2 -acid, since, on the one hand, it yields the Δ^1 -acid by boiling with strong, aqueous potash, and, on the other, its methyl salt is converted into methyl benzoate by atmospheric oxygen, reactions which, according to v. Baeyer's experience, are characteristic of hydrophthalic acids containing a "double bond" in the Δ^2 -position. The action of bromine on this acid leads to the formation of only one dibromide, further examination having shown that the supposed isomeride is nothing but benzoic acid, which is almost always present in small quantity in the crude tetrahydro-acid. The pure dibromide crystallises from dilute acetic acid in lustrous, colourless scales, and melts at 166°, not at 163°. Δ^2 -Tetrahydrobenzamide forms white, nacreous scales or prisms, melts at 144°, and is more soluble in water and ether than the amide of the Δ^1 -acid.

A dihydrobenzoic acid, possibly the $\Delta^{1,3}$ -acid, is formed by the action of concentrated alcoholic potash on the dibromide of the Δ^2 -tetrahydro-acid at the ordinary temperature. It crystallises from its concentrated aqueous solution, by slow evaporation in the cold, in large, hard prisms which melt at 73°. W. P. W.

β -Dichlorhydrin Metahydroxybenzoate. By C. GÖTTIG (*Ber.*, 24, 2741—2743; compare this vol., p. 707).—Metahydroxybenzoic acid is dissolved in 10 parts of glycerol, the solution heated at 85°, and treated with hydrogen chloride for five hours; two compounds are formed, and may be separated by solution in hot water. The one is amorphous, and has not been further investigated; the second consists of β -dichlorhydrin metahydroxybenzoate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{OC}_2\text{H}_4\text{Cl}$, and crystallises in long, slender needles which melt at about 90°. The constitution of the compound is proved by the fact that on hydrolysis with soda or potash, metahydroxybenzoic acid and epichlorhydrin are formed as the sole products. If the etherification of the metahydroxybenzoic acid is conducted at temperatures above 85°, the yield of the amorphous compound is proportionately increased.

J. B. T.

Optically Active Phenylbromolactic Acids and Phenoxyacrylic Acids. By E. ERLÉNMEYER, Jun. (*Ber.*, 24, 2830—2831).—Optically inactive phenylbromolactic acid can be easily separated into its optically active constituents by conversion into the cinchonine salt and crystallisation from alcohol. The salt of the dextrorotatory acid crystallises almost completely from the solution when a certain concentration is reached, and the remainder can be separated by the addition of ether. The salt of the levorotatory acid is left as a viscid mass after evaporation of the alcoholic mother liquor, and can be obtained in the solid form by repeated treatment with pure ether. The optically active acids, obtained from the salts by treatment with dilute hydrochloric acid and extraction with ether, closely resemble the optically inactive acid in properties; the melting points, however, are not identical.

The sodium salts of the optically active phenoxyacrylic acids are formed when the optically active phenylbromolactic acids are treated with aqueous caustic soda. The aqueous solutions of these salts exhibit a greater rotatory power than the solutions of the phenylbromolactic acids, and, moreover, the salt derived from dextrorotatory phenylbromolactic acid rotates to the left, whilst that from the levorotatory acid rotates to the right. On treatment with sulphuric acid, both salts are converted into phenylethylaldehyde. A detailed account of the physical properties of these optically active isomerides is reserved for a later communication. W. P. W.

Diiodocinnamic Acid. By C. LIEBERMANN and H. SACHSE (*Ber.*, **24**, 2588—2589).—*Diiodocinnamic acid*, $\text{C}_6\text{H}_4\text{I}_2\text{COOH}$, is obtained by allowing a solution of molecular proportions of phenylpropionic acid and iodine in carbon bisulphide to remain exposed to sunlight in a stoppered bottle. The iodine is very slowly absorbed, and is still visible after a month. The mixture deposits beautiful leaflets having a silvery lustre. It is purified by dissolving in alcohol and precipitating with water, and melts at 171° . The *sodium* salt is obtained in beautiful needles by dissolving the acid in dilute sodium carbonate, and then adding excess of the reagent. The *barium* salt is soluble; the *lead* salt forms a white precipitate. With sodium amalgam, it yields hydrocinnamic acid.

Methyl diiodocinnamate is obtained from methyl phenylpropiolate in a similar way. It is easily soluble in alcohol, and is precipitated, on the addition of water, in scales of silvery lustre, and melts at 77° .

E. C. R.

Nitration of Cinnamic Acid and Phenylmethacrylic Acid in the Side Chain. By H. ERDMANN (*Ber.*, **24**, 2771—2775).—The author has previously obtained phenylnitroethylene in small quantity by the action of red fuming nitric acid on phenylisocrotonic acid (*Abstr.*, 1884, 906). Phenylnitroethylene is also formed in very small quantity when cinnamic acid is stirred into warm, red fuming nitric acid; in larger quantity when an ethereal solution of the acid, cooled in a bath of ice and salt, is saturated with nitrous gas obtained by the action of arsenious anhydride on nitric acid, and to the extent of 15 per cent. of the theoretical, when a mixture of the acid (20 grams) with 10 per cent. aqueous sodium nitrite (100 c.c.) is distilled with steam.

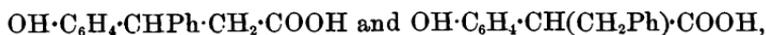
Phenylnitropropylene is obtained when a cold, ethereal solution of phenylmethacrylic acid is treated with nitrous gas, and a volatile product of aromatic odour is formed in very small quantity from phenylangelic acid under like conditions.

Two stereometric forms of phenylnitroethylene are conceivable, and the author is of opinion that the formula $\text{Ph}\cdot\overset{\text{H}}{\underset{\text{H}\cdot\text{C}\cdot\text{NO}_2}{\text{C}}}$ is the more probable for the compound produced in the above reactions. This view seems to derive some confirmation from the fact that all attempts to reduce orthonitrophenylnitroethylene to cinnoline have been fruitless.

W. P. W.

Condensation of Allocinnamic Acid with Phenols. By C. LIEBERMANN and A. HARTMANN (*Ber.* **24**, 2582—2587).—The following method of condensation is employed:—Finely powdered allocinnamic acid (10 grams) is dissolved in phenol (10 grams) and acetic acid (5 c.c.); the mixture cooled and mixed with strong sulphuric acid (10 c.c.) diluted with acetic acid (5 c.c.). After remaining four days, the viscid mass is poured into water, and extracted with ether. The ethereal solution is shaken with water to get rid of acetic acid, and then extracted with soda, and finally the ether is distilled off. An oil is thus obtained which has a phenolic odour, and gradually solidifies; it is then spread on porous plates to remove adhering oil. If a crystal of the substance thus obtained be added to the oil from later experiments, it at once solidifies. The substance is phenylhydrocoumarin. The soda solution contains hydroxydiphenylpropionic acid.

Hydroxydiphenylpropionic acid, $C_{15}H_{14}O_3$, is obtained from the above soda solution by acidifying and extracting with ether. It is very soluble in alcohol, crystallises from benzene in plates, and melts at 151° . The ammonium salt loses ammonia on evaporation of its solution. Lead acetate and silver nitrate cause white precipitates when added to solutions of the ammonium salt. The calcium and barium salts are very soluble. The author puts forward two formulæ for the compound,



of which he considers the former to be the more probable. The acid is not converted into phenylhydrocoumarin when heated at 160° .

Phenylhydrocoumarin, $C_{15}H_{12}O_2$, an indifferent compound, is insoluble in soda, dissolves easily in alcohol, and on the addition of water is obtained in beautiful, colourless needles; it crystallises from light petroleum in rosettes of needles, melts at 82° , and distils at 237° under a pressure of 30 mm., for the most part without decomposition. When boiled with alkali, it dissolves, and on adding an acid to the solution a white compound is precipitated, which is only partly soluble in soda, as it rapidly changes into phenylhydrocoumarin.

Phenylhydroxyhydrocoumarin, $C_{15}H_{12}O_3$, is obtained by condensation of allocinnamic acid with resorcinol by the method described above. It is easily soluble in most solvents, almost insoluble in light petroleum, and quite so in water, gives a yellow solution with soda or ammonia, and a yellow lead salt on the addition of lead acetate to the ammoniacal solution.

The condensation of cinnamic acid with phenol does not give good results under the above conditions. The condensation was effected by heating cinnamic acid (5 grams), phenol (5 grams), sulphuric acid (7 grams), and acetic acid (7 grams) on the water-bath for an hour. From the product, phenylhydrocoumarin was obtained, identical with that obtained from allocinnamic acid. The condensation takes place very slowly in the cold.

E. C. R.

Amidobenzoic Derivatives of Ethyl Acetoacetate. By G. PELLIZZARI (*Gazzetta*, **21**, 340—345).—It has been shown by Knorr (*Abstr.*, 1887, 159) and Conrad and Limpach (*Abstr.*, 1887, 679;

Ber., **22**, 78) that aromatic amines generally react in two ways with ethyl acetoacetate according to the conditions of the experiment. The author investigates these reactions in the case of amidobenzoic acid.

Ethyl hydrogen ac-metacrotonamidobenzoate, $C_{15}H_{15}NO_4$, is obtained by boiling a solution of metamidobenzoic acid (10 grams) and ethyl acetoacetate (10 grams) in 96 per cent. alcohol (20 grams) for one hour; on cooling, the whole solidifies to a crystalline mass, which, after recrystallisation from alcohol, is obtained in beautiful, colourless prisms melting at 137° . It is very soluble in alcohol and ether, and on prolonged heating in aqueous solution breaks up into its constituents, the yield of amidobenzoic acid being quantitative. It has probably the constitution $COOEt \cdot CH : CMe \cdot NH \cdot C_6H_4 \cdot COOH$. Attempts to eliminate alcohol and obtain a quinoline derivative, as may be done in analogous cases, did not succeed.

ac-Acetylacetometamidobenzoic acid, $COMe \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot COOH$, is obtained by directly heating a mixture of equivalent proportions of metamidobenzoic acid and ethyl acetoacetate; the semi-fluid mass is extracted with ether to remove the unaltered constituents, and recrystallised from alcohol; it is then obtained in colourless crystals very soluble in hot alcohol and acetic acid, moderately so in water, and melting with decomposition at $172-173^\circ$. The *silver salt* is a white powder. On endeavouring to prepare a quinoline derivative by heating the acid with concentrated sulphuric acid, nothing but amidobenzoic acid sulphate was obtained. *Acetylacetorthamidobenzoic acid* is obtained in a manner quite analogous to the meta-acid as white needles melting with decomposition at 160° . It is moderately soluble in hot alcohol and water, less so in benzene, and only sparingly in ether.

W. J. P.

Action of Phthalic Chloride on Phenols. By R. MEYER (*Ber.*, **24**, 2600; see also this vol., p. 1029).—Ethereal salts of phthalic acid are usually formed by the action of phthalic chloride on phenols, and not phthaleins or their anhydrides; for instance, phenyl phthalate has been prepared by this method. Paracresol and pseudocumenol also yield the corresponding ethereal salts, which are very well crystallised compounds. β -Naphthol and phthalic chloride yield, as the chief product, naphthyl phthalate, together with a compound which melts above 200° , dissolves in sulphuric acid with an intense reddish-yellow fluorescence, and is evidently the anhydride of β -naphtholphthalein. The author reserves a full description of the compounds for a future communication.

E. C. R.

Relationship between Ethyl Succinosuccinate and Phloroglucinol. By A. v. BAEYER (*Ber.*, **24**, 2687—2690).—The author and Kochendörfer have previously shown that phloroglucinol combines with 2 mols. of phenylhydrazine yielding a dihydrazine derivative (*Abstr.*, 1889, 1162); the formation of this compound may be explained by assuming that the triketohexamethylenedihydrazone first produced undergoes intramolecular change.

Ethyl succinosuccinate shows a behaviour similar to that exhibited

by phloroglucinol, and with phenylhydrazine gives a hydrazine derivative of dihydroterephthalic acid (compare following abstracts). Now, since diketohexamethylene, the parent substance of succinosuccinic acid, behaves like a true diketone (compare Baeyer and Noyes, *Abstr.*, 1889, 1147), its conversion into a phenol, analogous to phloroglucinol, in the reaction just referred to, must be due to the presence of the carboxyethyl groups. The fact that a hydroxy-derivative of dihydrobenzene, which shows all the properties of a phenol, can be obtained by simple substitution in the nucleus is of fundamental importance with regard to the benzene theory; for, if in dihydrobenzene the double binding which, on the introduction of a hydroxyl-group, is converted into a single binding with formation of a ketone (in accordance with Erlenmeyer's rule), attains the character of the double binding in phloroglucinol simply owing to the presence of a carboxyethyl group, there is no reason to deny the probability of other substitutions or other changes in the molecule giving a stability to the double binding similar to that observed in the case of benzene derivatives. The objection might be raised that the stability of the double binding in ethyl succinosuccinate is due to the fact that the substituting groups are in the para-position to one another; such a view is negated by the observation of Baeyer and Tutein (*Abstr.*, 1889, 1180) that hydroxytetrahydroterephthalic acid behaves just like succinosuccinic acid.

F. S. K.

Phenylhydrazine Derivatives of Ethyl Succinosuccinate.

By A. v. BAEYER, R. JAY, and L. JACKSON (*Ber.*, 24, 2690—2691).—*Ethyl parabenzenedihydrazo- $\Delta^{2:5}$ -dihydroterephthalate*, $C_{24}H_{28}N_4O_4$, is formed, together with the isomeric $\Delta^{1:4}$ -compound, when finely divided ethyl succinosuccinate (5 grams) is warmed with phenylhydrazine (4.2 grams) and alcohol (15 grams) until solution is complete; after keeping the mixture for 3 to 4 days, the crystals are separated by filtration, and extracted with boiling alcohol, from which, on cooling, the $\Delta^{2:5}$ -derivative is deposited in colourless needles. It turns yellow at 135—140°, sinters together at 145°, melts at 165° with decomposition, and is soluble in 15 parts of boiling alcohol; it is unstable towards acids and alkalis, and dissolves in cold, concentrated mineral acids, and in acetic acid and formic acid yielding red solutions; its solution in propionic acid has a reddish hue, but it dissolves in valeric acid yielding a colourless solution which, on heating, suddenly turns yellow, crystals of the $\Delta^{1:4}$ -compound being deposited. When heated alone or in alcoholic solution, it is converted into the isomeride described below.

Ethyl parabenzenedihydrazo- $\Delta^{1:4}$ -dihydroterephthalate (Knorr and Bülow's ethyl diphenylzinsuccinosuccinate), $C_{24}H_{28}N_4O_4$, prepared as described above, is very sparingly soluble in all ordinary solvents and can be easily purified by extraction with boiling alcohol; it is a yellow, microscopic, crystalline powder, melts at 208°, and behaves like the $\Delta^{2:5}$ -derivative on treatment with acids and alkalis.

F. S. K.

Constitution of the Phenylhydrazine Derivatives of Ethyl Succinosuccinate. By A. v. BAEYER and G. v. BRÜNING (*Ber.*, 24,

2692—2699).—*Ethyl benzenebiazo- $\Delta^{2:5}$ -dihydroterephthalate*, $C_{24}H_{24}N_4O_4$, can be obtained in yellow needles by gradually adding a hot, saturated alcoholic solution of normal copper acetate (7 grams), acidified with a little acetic acid, to a boiling alcoholic solution of the $\Delta^{2:5}$ -hydrazo-compound described in the preceding abstract, and then dropping the filtered solution on to ice; it melts at 155° , is readily soluble in alcohol and other ordinary solvents, and dissolves in concentrated hydrochloric acid and concentrated sulphuric acid, yielding red solutions. It is much more stable than the $\Delta^{2:5}$ -hydrazo-compound; on reduction, it is converted into the $\Delta^{1:4}$ -hydrazo-derivative, intramolecular change taking place.

Ethyl benzenebiazoterephthalate, $C_{24}H_{22}N_4O_4$, is formed, with liberation of hydrogen bromide, when bromine is added to an alcoholic solution of the preceding compound; it crystallises from alcohol in long, lustrous, orange-red needles and melts at 126° . It resembles the dihydrazo-derivative in appearance, but is more readily soluble in alcohol and much more stable. The corresponding acid, $C_{20}H_{14}N_4O_4$, prepared by hydrolysing the ethyl salt with boiling concentrated potash, crystallises from a mixture of glacial acetic acid, water, and alcohol in orange-red needles, melts above 250° , and is readily soluble in alcohol and other organic solvents, but insoluble in water. The silver salt, $C_{20}H_{12}N_4O_4Ag_2$, is a dark-red, crystalline powder.

Ethyl benzenebiazo- $\Delta^{1:4}$ -dihydroterephthalate, $C_{24}H_{24}N_4O_4$, is formed when the corresponding dihydrazo-compound (compare preceding abstract) is oxidised with copper acetate as described above, but the solution must be boiled for a much longer time, owing to the insolubility of the hydrazo-compound; the $\Delta^{1:4}$ -biazo-derivative is also formed, together with varying quantities of the corresponding $\Delta^{2:5}$ -compound, from which it is produced by intramolecular change, when the $\Delta^{2:5}$ -dihydrazo-derivative is oxidised with copper acetate in presence of water. It crystallises from alcohol in light-yellow needles, melts at 180° , and is more sparingly soluble than its isomeride; it dissolves in hydrochloric acid with a red coloration, and, on reduction, it is converted into the $\Delta^{1:4}$ -dihydrazo-compound. When treated with bromine in chloroform solution, the colour of the mixture changes from brown to red and crystals of a bromo-derivative, melting at 253 — 254° , are deposited; if, however, a solution of the azo-compound in concentrated sulphuric acid is treated with bromine, ethyl benzenebiazoterephthalate, identical with the compound described above, is obtained.

The isomerism of the two compounds obtained by the action of phenylhydrazine on ethyl succinosuccinate is caused by a difference in the constitution of the dihydroterephthalic acids of which they are derivatives. It has been previously shown that, on careful reduction, terephthalic acid is first converted into the readily soluble $\Delta^{2:5}$ -dihydro-acid, which, when boiled with soda, is transformed into the sparingly soluble, stable $\Delta^{1:4}$ -dihydro-derivative; in an exactly analogous manner, ethyl succinosuccinate gives, in the first place, the colourless, unstable hydrazo-derivative, which is readily converted into the yellow, stable, insoluble isomeride.

Now, in accordance with theory, three isomeric benzenebihydrazo-

dihydroterephthalic acids, namely the $\Delta^{2:5}$, $\Delta^{1:5}$, and $\Delta^{1:4}$ -compounds, differing from one another only as regards the position of the double linking, can be derived from a hydrazone of the constitution $\text{COOEt}\cdot\text{CH}\left\langle\begin{array}{c} \text{C}(\text{N}_2\text{HPh})\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{C}(\text{N}_2\text{HPh}) \end{array}\right\rangle\text{CH}\cdot\text{COOEt}$, the hypothetical primary product of the action of phenylhydrazine on ethyl succinosuccinate; since the $\Delta^{2:5}$ -compound may, theoretically, exist in two forms, the maleinoid and the fumaroid, a fourth isomeride is also capable of existence. The only two isomerides which have yet been obtained show the same relation to one another as that existing between the fumaroid $\Delta^{2:5}$ and the $\Delta^{1:4}$ -dihydroterephthalic acids; it may be assumed, therefore, at any rate provisionally, that they have the constitutions assigned to them above.

This investigation affords an interesting contribution to the question of the relation between colour and constitution; the above facts show that, by a slight change in the position of the double linking, a yellow compound may become colourless, and *vice versa*.

F. S. K.

Sulphonation of Parachloronitrobenzene and Parachloraniline. By A. CLAUS and C. MANN (*Annalen*, 265, 87—95).—*Chloronitrobenzenesulphonic acid* [$\text{Cl} : \text{SO}_3\text{H} : \text{NO}_2 = 1 : 2 : 4$] is best prepared by adding parachloronitrobenzene to 10—12 per cent. anhydrosulphuric acid (6 parts) and then heating the mixture at 120—130° until it is completely soluble in dilute alkali; no other sulphonic acid is formed even when the conditions of the experiment are altered. It separates from water in well-defined, almost colourless, asymmetric crystals, $a : b : c = 0.8584 : 1.08520$, containing 2 mols. H_2O , both of which are expelled at 110°; it is readily soluble in water, but only very sparingly in alcohol. The *ammonium* salt, with $1\text{H}_2\text{O}$, *sodium* salt, with $1\text{H}_2\text{O}$, and the *potassium* salt (anhydrous) are crystalline compounds, readily soluble in water, but only sparingly in alcohol. The *barium* salt (anhydrous), *calcium* salt, with $8\text{H}_2\text{O}$, *copper* salt, with $5\text{H}_2\text{O}$, and *lead* salt, with $7\text{H}_2\text{O}$, are readily soluble in hot water and crystallise well. The *chloride*, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO}_2\text{Cl}$, crystallises from ether in yellowish prisms melting at 89—90° (uncorr.). The *amide*, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{SO}_2\cdot\text{NH}_2$, crystallises in colourless, lustrous needles and prisms, melts at 185—186° (uncorr.), and is readily soluble in ether, chloroform, alcohol, and hot water.

Chloramidobenzenesulphonic acid [$\text{Cl} : \text{SO}_2\text{H} : \text{NH}_2 = 1 : 2 : 4$], prepared by reducing the preceding compound with tin and boiling dilute hydrochloric acid, crystallises from hot water in colourless, prismatic needles. The *barium* salt, with $6\text{H}_2\text{O}$, is almost insoluble in alcohol, but very readily soluble in hot water, from which it separates in small needles. The *stannochloride* crystallises in large, lustrous prisms.

Two isomeric sulphonic acids are formed when parachloraniline sulphate is mixed with 15 per cent. anhydrosulphuric acid (8 parts), the mixture heated on the water-bath for 6—8 hours, and then poured into a large volume of water; the yield of the mixed products is small. On fractionally crystallising the mixture of acids from hot

water, a chloramidobenzenesulphonic acid, identical with the compound just described, is first deposited, and from the mother liquors the isomeride $[\text{Cl} : \text{SO}_3\text{H} : \text{NH}_2 = 1 : 3 : 4]$ is obtained in short, oblong, efflorescent prisms, containing 2 mols. H_2O . F. S. K.

Sulphonation of Metachloronitrobenzene and Metachloraniline. By A. CLAUS and H. BOPP (*Annalen*, **265**, 95—107).—The authors can confirm the statement of Post and Meyer (*Ber.*, **14**, 1605), that two isomeric sulphonic acids are obtained on heating metachloronitrobenzene with anhydrosulphuric acid at 125° for several hours. Post and Meyer's α -acid, isolated in the manner described by them, has the constitution $[\text{SO}_3\text{H} : \text{NO}_2 : \text{Cl} = 1 : 3 : 5]$, and is formed in larger quantities the more concentrated the anhydro-acid employed. The corresponding *chloride*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SO}_2\text{Cl}$, is an oil; the *amide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SO}_2 \cdot \text{NH}_2$, crystallises from alcohol and water in small, colourless plates melting at 164 — 165° (uncorr). The constitution of this acid was proved to be that given above by first reducing it to the corresponding chloramidodisulphonic acid described by Post and Meyer (*loc. cit.*); this compound was then converted into metachlorobenzenesulphamide by first eliminating the amido-group and then treating the product with phosphorus pentachloride and anhydrous ammonia consecutively. Another portion of the chloramidodisulphonic acid was treated with sodium amalgam to eliminate the chlorine, and the resulting amidodisulphonic acid transformed into the corresponding chlorosulphonic acid by means of the diazo-compound; this substance was finally converted into the sulphamide, which was found to be identical with the metachlorobenzenesulphamide obtained in the first case.

The second acid, obtained by sulphonating metanitrochlorobenzene as described above, has the constitution $[\text{SO}_3\text{H} : \text{NO}_2 : \text{Cl} = 1 : 2 : 6]$; its *chloride*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SO}_2\text{Cl}$, crystallises from ether in yellow prisms, melts at 180° , and is sparingly soluble in chloroform; the corresponding *amide*, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Cl} \cdot \text{SO}_2 \cdot \text{NH}_2$, crystallises from water in long, colourless needles, and decomposes at a high temperature, but without melting. The constitution of this sulphonic acid was determined by the same methods as those employed in the case of the isomeride.

At least two, possibly four, isomeric sulphonic acids are formed when metachloraniline sulphate is heated for 10—12 hours on the water-bath with anhydrosulphuric acid (3—4 parts); on treating the product with water, and precipitating the sulphuric acid with barium hydroxide, there remains in solution a mixture of barium salts which cannot be easily resolved into its constituents, but from which, by fractionally crystallising the free acids from water, pure metachloranilinesulphonic acid $[\text{SO}_3\text{H} : \text{NH}_2 : \text{Cl} = 1 : 2 : 4]$ and an impure isomeride can be obtained. The former has been previously described by Post and Meyer; its constitution was determined by the authors by the same methods as those used in the case of the nitrochlorobenzenesulphonic acids. The impure isomeride has, most probably, the constitution $[\text{SO}_3\text{H} : \text{Cl} : \text{NH}_2 = 1 : 2 : 4]$. F. S. K.

Sulphonation of Orthotoluidine. By A. CLAUS and F. IMMEL (*Annalen*, **265**, 67—87).—Orthotoluidinemetasulphonic acid



is formed in considerable quantity, together with the isomeride $[\text{NH}_2 : \text{Me} : \text{SO}_3\text{H} = 1 : 2 : 4]$, when orthotoluidine sulphate (1 part) is mixed with 50 per cent. anhydrosulphuric acid (2 parts) cooled below 0° , and the mixture kept at this temperature with frequent shaking until it has become a thick, brown mass; the product is then treated with ice-cold water, the cold solution neutralised with barium carbonate, and the barium salts in the filtered solution separated by fractional crystallisation from water. With regard to the 1 : 2 : 4-acid, it may be remarked that the statements of Gerver on this subject are incorrect, but those of Neville and Winther (*Ber.*, **13**, 1941) correct; when treated with bromine (1 mol.) in glacial acetic acid solution, it is converted into a crystalline bromo-derivative



the barium salt of which crystallises with 3 mols. H_2O ; when this bromo-acid is treated with bromine (1 mol.) in aqueous solution, it yields dibromotoluidine (m. p. 50°), the platinochloride of which crystallises with $1\frac{1}{2}$ mols. H_2O . Orthotoluidinemetasulphonic acid, prepared from the barium salt, is very readily soluble in water, from which it crystallises in colourless, transparent needles, containing 1 mol. H_2O ; it is doubtless identical with the acid obtained by the reduction of nitrotoluenesulphonic acid (compare Hayduck, *Annalen*, **172**, 204). The sodium salt, with $3\text{H}_2\text{O}$, crystallises in needles, and is very readily soluble in water and alcohol. The barium salt, with $2\frac{1}{2}\text{H}_2\text{O}$, crystallises in rhombic plates, and is more readily soluble in water than the corresponding salt of the isomeric acid referred to above. The calcium salt, with $6\text{H}_2\text{O}$, the cobalt salt, and the nickel salt are crystalline and readily soluble in water. When the acid is treated with bromine in aqueous solution, it is converted into a dibromo-derivative $[\text{NH}_2 : \text{Me} : \text{Br}_2 : \text{SO}_3\text{H} = 1 : 2 : 4 : 6 : 5]$, which crystallises from boiling water in long, colourless needles, containing 1 mol. H_2O (compare Hayduck, *loc. cit.*); the barium salt of this bromo-acid crystallises from hot water with $8\frac{1}{2}$ mols. H_2O .

Tribromotoluenesulphonic acid $[\text{Br}_3 : \text{Me} : \text{SO}_3\text{H} = 1 : 4 : 6 : 2 : 5]$ can be obtained by decomposing the diazo-derivative of the dibromo-acid just described with cuprous bromide (compare Hayduck, *Annalen*, **174**, 354); it crystallises from hot water in small, colourless prisms, and, when treated with highly superheated steam in concentrated sulphuric acid solution, it is readily decomposed into tribromotoluene (m. p. 53°).

Paratoluidinemetasulphonic acid $[\text{NH}_2 : \text{SO}_3\text{H} : \text{Me} = 1 : 3 : 4]$ is formed in large quantities when paratoluidine is sulphonated under the conditions described in the case of the corresponding ortho-compound; the product is washed with cold water to free it from small quantities of the orthosulphonic acid, and then crystallised from hot water, from which it separates in well-defined rhombohedra containing 1 mol. H_2O . It is insoluble in alcohol, reduces am-

moniacal silver nitrate solution, and gives a red coloration on warming with ferric chloride; when boiled with excess of bromine in aqueous solution, it yields a *tribromoparatoluidine*, $[\text{NH}_2 : \text{Br}_3 : \text{Me} = 1 : 2 : 3 : 6 : 4]$, which crystallises in colourless needles melting at 83° (uncorr.).

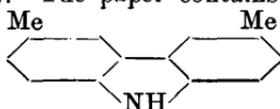
When aniline sulphate is sulphonated in the cold in the manner described above, the parasulphonic acid alone is obtained; ortho-bromaniline also gives but one sulphonic acid, which is identical with the compound $[\text{NH}_2 : \text{Br} : \text{SO}_3\text{H} = 1 : 2 : 5]$ described by Andrews (*Ber.*, **13**, 2126). F. S. K.

Bromisatin-blue. Compounds of Mono- and Di-bromisatin with Piperidine. By C. SCHOTTEN (*Ber.*, **24**, 2604—2607).—*Dipiperidylbromisatin*, $\text{C}_{18}\text{H}_{24}\text{BrN}_3\text{O}$, is obtained by warming an alcoholic solution of bromisatin with twice the molecular proportion of piperidine. It crystallises in colourless needles, is very sparingly soluble in alcohol, and closely resembles dipiperidylisatin in its behaviour with acids, alkalis, and on warming (compare this vol., p. 928).

Bromisatin-blue is formed when dipiperidylbromisatin is warmed with several times its weight of acetic anhydride, and, on the addition of water to the blue solution is precipitated as a microcrystalline powder. It resembles isatin-blue (*loc. cit.*) in its behaviour with solvents, acids, and alkalis.

Piperidinedibromisatin, $\text{C}_{13}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2$, is obtained by adding piperidine to dibromisatin suspended in warm, absolute alcohol. It crystallises in short, pale-yellow prisms, melts at 152° , dissolves sparingly in alcohol, but more easily in ether, and is insoluble in water. It is not affected by boiling with dilute mineral acids or alkalis, or with acetic acid or acetic anhydride, but decomposes with the regeneration of dibromisatin when heated with a mixture of hydrochloric and acetic acids. W P. W.

Dimethylcarbazole. By E. TÄUBER and R. LOEWENHERZ (*Ber.*, **24**, 2597—2599).—The paper contains a further account of the di-

methylcarbazole  formerly described by the

authors (this vol., p. 834). Dimethylcarbazole can be prepared in two ways, from diamidodimethylcarbazole, and by heating orthodiamidoditolyl with a mineral acid above 200° . The first method gives very bad results; the second method is also disadvantageous owing to the difficulty of preparing large quantities of orthodinitroditolyl.

Orthodinitroditolyl is best obtained as follows:—Well dried metadinitrotolidine is made into a paste with a little absolute alcohol and the calculated quantity of 100 per cent. sulphuric acid (for 2 mols.), poured into 15 times as much absolute alcohol, and amyl nitrite (2 mols.) added to the mixture at 10° . The mixture is then heated for some hours to boiling, diluted with water, and the orthodinitroditolyl extracted with high boiling petroleum. The nitro-product is

reduced with tin and hydrochloric acid, and the diamido-hydrochloride (m. p. 83°) thus obtained is converted into dimethylcarbazole by heating it with six times the quantity of hydrochloric acid (18 per cent.) in a sealed tube at 230° for 20 hours.

Dimethylcarbazole crystallises from benzene in colourless needles, melts at 219°, is easily soluble in hot benzene, toluene, and alcohol, somewhat easily in ether and carbon bisulphide, and sparingly so in light petroleum, and is very like ordinary carbazole. The *picric acid compound* crystallises in reddish-brown needles, and melts at 192°. The *nitroso-compound* crystallises from alcohol in pure, yellow needles, and melts at 106°. The *acetyl compound* crystallises from alcohol in needles, and melts at 129°. A wood splinter soaked in an alcoholic solution of dimethylcarbazole is coloured red by hydrochloric acid; with isatin, its solution in sulphuric acid gives an indigo-blue. It is distinguished from carbazole by not giving a blue dye on fusion with oxalic acid. When shaken with quinone in acetic acid solution containing a few drops of concentrated sulphuric acid, it gives a deep, indigo-blue solution, and this, on the addition of water, deposits greyish-blue flocks, which dissolve in ether with a bluish-violet colour. Carbazole, under the same treatment, gives a magenta solution, which, on the addition of water, yields reddish-brown flocks, soluble in ether to a red liquid. A table is given of the properties of carbazole and dimethylcarbazole.

E. C. R.

Preparation of Hydrobenzoin and of Deoxybenzoin. By P. JUILLARD and G. TISSOT (*Chem. Centr.*, 1891, ii, 166; from *Arch. sci. phys. nat. Genève*).—The authors recommend the following method for the preparation of hydrobenzoin; the product is very pure, but the amount is small: 100 grams of benzaldehyde is reduced with 100 grams of zinc-dust in 500 grams of glacial acetic acid and 10 grams of anhydrous acetic acid. After the zinc-dust has been gradually added, the mixture is heated at 100° for 1½ hours. The resulting liquid is diluted with 4—5 volumes of water and the hydrobenzoin precipitated with sodium carbonate. It crystallises in beautiful plates, and melts at 134°. The yield is 5—10 per cent. From the oily residue, a few white crystals separated at the end of a few days; the remainder was principally benzyl alcohol and deoxybenzoin. If dilute acetic acid be employed for the reduction, the product consists chiefly of benzyl alcohol.

Deoxybenzoin is prepared by the reduction of benzoin or acetylbenzoin as follows:—40 grams of benzoin and 40 grams of zinc are treated with 200 grams of glacial acetic acid, and the reduction is almost perfect. Neither hydrobenzoin nor acetylhydrobenzoin is found among the products. Acetylbenzoin was prepared by heating 2 grams of benzoin with 10 grams of anhydrous acetic acid for four hours in a tube at 150°, whereby the theoretical quantity was obtained. It crystallises in white needles, and melts at 83°.

J. W. L.

Derivatives of Deoxybenzoin. By J. EPHRAIM (*Ber.*, 24, 2820—2827).—*Deoxybenzoinorthodicarboxylic acid*,



is obtained by heating 1 : 2-carboxyphenylacetic acid (10 parts) with an equal weight of phthalic anhydride, and sodium acetate (1 part) in an oil-bath at 180—190°, the reagents being anhydrous, treating the dark-coloured melt with hot water, dissolving in cold sodium hydroxide solution, precipitating the filtrate with hydrochloric acid, treating the precipitate with cold alcohol, and crystallising from glacial acetic acid; it forms white needles and melts at 238—239°; the *silver salt* separates in white, feathery needles on adding silver nitrate to a solution of the ammonium salt. When the acid (2 grams) is heated with fuming hydriodic acid (5 c.c.) and amorphous phosphorus (1 gram) in a sealed tube at 160° for 2—3 hours, and the melt extracted with sodium carbonate solution, dibenzylorthodicarboxylic acid, $C_2H_4(C_6H_4 \cdot COOH)_2$, melting at 225°, separates on the addition of hydrochloric acid. The *acid*, $C_{16}H_{11}O_3N$, is formed when deoxybenzoïnorthodicarboxylic acid (1 gram) is heated with concentrated alcoholic ammonia in a sealed tube for 12 hours; it crystallises from alcohol in white rhombohedra, and its constitution is represented either by $COOH \cdot C_6H_4 \cdot CH \cdot C \left\langle \begin{array}{c} NH \\ C_6H_4 \end{array} \right\rangle CO$ or by $COOH \cdot C_6H_4 \cdot C \left\langle \begin{array}{c} CH \\ NH \cdot CO \end{array} \right\rangle C_6H_4$. This, when heated on the water-bath with twice its weight of phosphorus oxychloride, yields the *compound*, $C_6H_4 \left\langle \begin{array}{c} CO \cdot N \cdot CO \\ C \cdot CH \end{array} \right\rangle C_6H_4$.

When deoxybenzoïnorthodicarboxylic acid is dissolved in absolute alcohol, the cooled solution saturated with hydrogen chloride, and water added, the *anhydride*, $O \left\langle \begin{array}{c} CO \cdot C_6H_4 \cdot CH_2 \\ CO \cdot C_6H_4 \cdot CO \end{array} \right\rangle$, is precipitated; it crystallises from alcohol in white needles, melts at 260°, and is insoluble in cold alkalis. The *oximidolactone*, $C_6H_4 \left\langle \begin{array}{c} CH_2 \\ COO \cdot N \end{array} \right\rangle C \cdot C_6H_4 \cdot COOH$ or $CO \left\langle \begin{array}{c} C_6H_4 \\ O \cdot N \end{array} \right\rangle C \cdot CH_2 \cdot C_6H_4 \cdot COOH$, is produced when the acid is dissolved in alkali and treated with hydroxylamine; it crystallises from alcohol in delicate, rose-coloured needles, and melts at 229—230°; the *lactone*, $COOH \cdot C_6H_4 \cdot CH_2 \cdot CH \left\langle \begin{array}{c} C_6H_4 \\ O \end{array} \right\rangle CO$ or $COOH \cdot C_6H_4 \cdot CH \left\langle \begin{array}{c} CH_2 \\ O \cdot CO \end{array} \right\rangle C_6H_4$, is obtained when the acid is treated with five times the calculated quantity of sodium amalgam in alkaline solution; it separates from alcohol in monosymmetric crystals, $a : b : c = 0.8962 : 1 : 0.7478$; $\beta = 61^\circ 43'$, and melts at 201°. The *barium salt* of the bibasic acid, $COOH \cdot C_6H_4 \cdot CH_2 \cdot CH(OH) \cdot C_6H_4 \cdot COOH$, is formed when the lactone is boiled with barium hydroxide, and, on adding the silver nitrate to the resulting solution, the *silver salt* is precipitated.

The author has separated a small quantity of a bye-product, $C_{16}H_{10}O_4$, in the preparation of deoxybenzoïnorthodicarboxylic acid by the above-described method; it crystallises from glacial acetic acid in white needles, melts at 250°, and is not identical with deoxybenzoïnorthodicarboxylic anhydride. It yields an acid, $C_{16}H_{12}O_5$, melting at 196°, which thus appears to be isomeric with deoxybenzoïnorthodicarboxylic acid.

A. R. L.

Synthesis of Hydroxyxanthenes. By B. NESSLER (*Chem. Centr.*, 1891, ii, 61; from *Schweiz. Wochenschr. Pharm.*, 29, 186).—Similarly to the formation of xanthone from orthohydroxybenzoic acid, hydroxyxanthenes may be prepared from dihydroxy-acids. From dihydroxybenzoic acid, dihydroxyxanthone is formed; from a mixture of salicylic and dihydroxybenzoic acids, a monohydroxyxanthone is obtained; and the phenols, resorcinol, orcinol, quinol, and phoroglucinol unite with hydroxy-acids with formation of corresponding hydroxyxanthenes.

J. W. L.

Derivatives of Lapachic Acid. By E. PATERNÒ and L. CABERTI (*Gazzetta*, 21, 374—381).—Monobromolapachic acid may be reduced by suspending it in very dilute caustic potash and treating with zinc dust; after half an hour, the solution is filtered, saturated with carbonic anhydride, and, as soon as the resin is deposited, the liquid is filtered and acidified with hydrochloric acid, when a flocculent precipitate of lapachic acid falls. This shows Hooker and Green's opinion, that monobromolapachic acid is a derivative of lapachone (Abstr., 1889, 999), is incorrect.

Paternò and Minunni (Abstr., 1890, 1310) showed that lapachic acid, when treated with thiophen and sulphuric acid, yields a condensation product; the authors find that the reaction occurs between the thiophen and lapachone formed by the action of sulphuric acid on the lapachic acid. Lapachone (1 part) and thiophen (1 part) are dissolved in glacial acetic acid (1 vol.) and concentrated sulphuric acid (1 vol.) added; after five hours, the emerald-green solution is poured into much water, the bulky, blue precipitate collected and washed, first with water, then with a mixture (equal parts) of alcohol and water, and finally dried. The substance is now of an intense, sky-blue colour, and is soluble in strong alcohol, ether, chloroform, and light petroleum, yielding a blue solution; it dissolves in acetic acid and in sulphuric acid, from which it is precipitated by water, a part being resinified. In solution this substance seems to be unaltered by hydrochloric acid or sodium amalgam, but is slowly oxidised by nitric acid and at once decolorised by chlorine-water. It contains sulphur, but could not be obtained sufficiently pure for quantitative analysis.

On passing dry hydrogen chloride through a solution of lapachic acid in glacial acetic acid, the solution becomes brownish-red, and, on pouring it into water, yields lapachone and a trace of another substance, probably the compound obtained when lapachic acid is treated with nitric acid. If a solution of lapachone and thiophen in glacial acetic acid is saturated with dry hydrogen chloride and allowed to remain for some days, the blue compound described above is obtained. A solution of lapachic acid (1 part) in glacial acetic acid, on treatment with fused zinc chloride (10 parts), yields nothing but pure lapachone after remaining for 18 hours. Zinc chloride also effects the condensation of lapachone with thiophen, but much resinous matter is produced at the same time. Lapachic acid is partially converted into lapachone by calcium chloride, but is seemingly unaltered by stannous chloride in alcoholic solution.

An improved process for the preparation of lapachic acid is the fol-

lowing:—The crude product (100 grams), obtained by boiling the shavings or sawdust of lapacho wood with sodium carbonate, and decomposing the solution with hydrochloric acid, is boiled with baryta-water (30—35 grams barium hydrate in 15 litres of water). On filtration and precipitation with hydrochloric acid, the lapachic acid is generally pure enough to be at once recrystallised from alcohol.

W. J. P.

Melting Points of Binary Systems of Hydrocarbons. By L. VIGNON (*Compt. rend.*, 113, 133—136).—The hydrocarbons employed were naphthalene, diphenyl, phenanthrene, triphenylmethane, and anthracene, which were mixed in pairs in various proportions.

The mixtures may be divided into two groups, namely, (a) those that contain anthracene and have a melting point which rises as the proportion of anthracene increases, but is always higher than the mean calculated melting point; and (b) those that contain no anthracene. In the latter group, the melting point is always lower than the mean calculated melting point, and the curves have a characteristic form, showing a point of reversal which corresponds in the various cases to the following mixtures: naphthalene, 2 mols., and diphenyl, 1 mol.; naphthalene, 2 mols., and phenanthrene, 1 mol.; naphthalene, 1 mol., and triphenylmethane, 1 mol.; diphenyl, 2 mols., and phenanthrene, 1 mol.; diphenyl, 2 mols., and triphenylmethane, 1 mol.

C. H. B.

Truxillic Acids. By J. HOMANS, R. STELTZNER, and A. SUKOW (*Ber.*, 24, 2589—2592).—When α -truxillic acid is treated with a small quantity of fuming nitric acid (1.52), it dissolves, and two isomeric mononitro-acids are formed. The one acid (b) crystallises from the solution on cooling, the other (a) is obtained by diluting with water and is purified by crystallisation from alcohol.

a-Nitro- α -truxillic acid, $[C_9H_7(NO_2)O_2]_2$, forms small prisms, melts at 228—229°, and is easily soluble in alcohol, ether, and acetic acid, sparingly in benzene. It is not attacked by potassium permanganate in alkaline solution, and is thus distinguished from nitrocinnamic acid. The salts do not crystallise. *Ethyl a-nitro- α -truxillate* crystallises from alcohol in yellow needles and melts at 138°.

b-Nitro- α -truxillic acid is insoluble, or only sparingly soluble, in all solvents, melts at 290° with decomposition, and does not reduce permanganate. The *silver* salt forms a white, granular precipitate. The *barium* salt is easily soluble in water and crystallises in bright-yellow needles.

β - and γ -truxillic acids each yield only one mononitro-acid.

Nitro- β -truxillic acid is, when first obtained, an oil which is purified with difficulty by recrystallisation from alcohol. It melts at 216°, is easily soluble in ether, acetic acid, and chloroform, sparingly in benzene, and does not reduce potassium permanganate.

Nitro- γ -truxillic acid forms small prisms, melts at 293°, is easily soluble in alcohol and acetic acid, insoluble in benzene, and slowly reduces potassium permanganate.

The amido-derivatives of α -truxillic acid are obtained by reducing the nitro-derivatives with tin and hydrochloric acid, precipitating the

tin with sulphuretted hydrogen, and concentrating the filtrate in a vacuum on the water-bath.

a-Amido- α -truxillic acid is obtained, in scales of silvery lustre, by precipitating a solution of the hydrochloride with sodium acetate, and is purified by precipitation from acetone by petroleum. The *hydrochloride* forms very soluble needles.

b-Amido- α -truxillic acid crystallises from water in needles. The *hydrochloride* forms needles, and is less soluble than the *a-amido-acid*. The *sulphate* is obtained in beautiful, sparingly soluble needles on adding the theoretical quantity of sulphuric acid to a solution of the hydrochloride.

b-Diazo- α -truxillic acid nitrate, $[C_9H_7(N_2NO_3)O_2]_2$, is obtained in pale-yellow needles by adding sodium nitrite (1.84 grams) to an ice-cold solution of the hydrochloride of the amido-acid (5 grams) in a small quantity of water and nitric acid (5 c.c.). It is easily soluble in water, and yields a ponceau-red dye with sodium β -naphtholdisulphonate, which does not, however, dye cotton directly.

b-Hydroxy- α -truxillic acid is obtained by adding the calculated quantity of sodium nitrite to a solution of the amido-hydrochloride in concentrated sulphuric acid. The mixture is diluted with water and heated to boiling, when the hydroxy-acid is obtained as a yellow precipitate. It crystallises from alcohol in colourless flocks, is sparingly soluble in most solvents, does not melt at 360° , dissolves in cold soda, and is precipitated by acids. The *calcium* salt is obtained by boiling the acid with calcium carbonate, is easily soluble in water, and is precipitated on the addition of alcohol.

b-Acetylhydroxy- α -truxillic acid is obtained by the action of acetic anhydride and sodium acetate on the hydroxy-acid; it crystallises from acetic acid in tufts of needles, and melts at 244° . E. C. R.

Essence of Lemons. By V. OLIVERI (*Gazzetta*, 21, 318—330).—Recently prepared essence of lemons is a canary-yellow, oily liquid, of a pungent acid taste. Its sp. gr. is 0.860 at 16° , and its specific rotatory power $[\alpha]_D$ at 16° varies from $+69.75^\circ$ to $+75.10^\circ$.

On distilling essence of lemons which has been steam-distilled and dried over fused potassium carbonate, three principal fractions are obtained. The first portion, boiling at 170 — 170.5° , constitutes about one-fifteenth part of the whole, and has a sp. gr. of 0.8867 at 0° and a specific rotatory power $[\alpha]_D = +64.82^\circ$ at 16° . It is a colourless, mobile liquid, having the characteristic odour of the essence, and has the composition of a terpene, $C_{10}H_{16}$.

Limonene Tetrabromide, $C_{10}H_{16}Br_4$.—This is obtained when the limonene (1 vol.) is dissolved in a mixture of alcohol (4 vols.) and ether (4 vols.), and bromine (0.7 vol.) dropped into the solution cooled to 0° . The product, after washing with cold alcohol and dissolving in boiling ethyl acetate, is obtained as an oil which, after a time, solidifies to a crystalline mass melting at 31° . The *dihydrochloride*, $C_{10}H_{18}Cl_2$, is prepared by passing excess of hydrogen chloride through a mixture of equal weights of ether and the limonene; the ether is evaporated, and the product dried on a porous plate and recrystallised from alcohol. It forms small, colourless, six-sided tables melting at

50°; it agrees in properties with the dihydrochloride prepared by Wallach.

The second fraction from lemon oil boils between 176° and 178° and includes about nine-tenths of the whole; it is a mobile, colourless liquid having a sp. gr. of 0·8990 at 0° and a specific rotatory power $[\alpha]_D = +76\cdot75^\circ$. Vapour density determinations and analyses show it to have the composition $C_{10}H_{16}$. The *tetrabromide*, $C_{10}H_{16}Br_4$, prepared as above, melts at 102—103°; the *dihydrochloride*, $C_{10}H_{18}Cl_2$, crystallises in scales soluble in alcohol, and melts at 50°.

The third fraction boils at 240—242°; in fresh lemon oil, the proportion is very small, but much larger quantities are obtained from old oil, along with polyterpenes boiling at 250—340°. The portion boiling at 240—242° consists of a sesquiterpene, $C_{15}H_{24}$; it is a viscous, yellowish liquid, of sp. gr. = 0·9847 at 0°, very slowly volatile with steam, and optically inactive. It is soluble in ether, and sparingly soluble in alcohol. The *tetrabromide*, $C_{15}H_{24}Br_4$, is a heavy, colourless oil, which does not solidify at -20°. The *dihydrochloride*, $C_{15}H_{26}Cl_2$, separates from its cooled alcoholic solution as an oil.

Detection of Oil of Turpentine as an Adulterant in Essence of Lemons.—The sophistication of essence of lemons by turpentine oil is difficult to detect, owing to the percentage composition of the two oils being identical and their boiling points and densities being almost the same.

The author finds that the readiest method of detecting the fraud is to observe the specific rotatory power. As the adulterant most frequently employed is French turpentine oil, having a specific rotatory power of $[\alpha]_D = -27\cdot0^\circ$ about, its presence in lemon oil, having a specific rotation $[\alpha]_D = +60\cdot0^\circ$, is at once betrayed; the amount of the adulterant may be easily calculated, as the rotatory power of the mixture is the algebraic sum of the rotatory powers of its constituents taken in the proportions in which they are present. Even when the adulterant is a dextrorotatory oil, such as Russian or English turpentine, the change in the rotatory power is so great as to at once betray its presence.

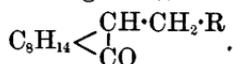
The author gives tables for calculating the percentage of the adulterant present from its rotatory power. W. J. P.

Hygroscopic Behaviour of Camphor and Thymol. By G. CLAUTRIAU (*Ber.*, 24, 2612—2614).—In the course of the physiological investigation of the irritability of a fungus, Errera arrived at the conclusion that camphor has a considerable hygroscopic capacity which is not shared by thymol. This view is confirmed by the author's experiments. A small, tared vessel containing camphor was supported in the middle of a glass receiver of 3 litres capacity, which was closed by a cover smeared with camphorated lard. To avoid loss of camphor by evaporation, the walls of the receiver were completely covered with a layer of camphor, and the water employed to keep the air moist was also saturated with camphor. Similar precautions were adopted in the case of thymol. After deducting the weight of water found to condense on the tared vessel in a blank experiment, numbers were obtained indicating that 10 grams of camphor absorbed 0·022

and 0.032 gram of water in two experiments, whilst thymol showed no appreciable increase in weight. Dry camphor, although it attracts a comparatively small amount of water, does so with such energy that its weight increases even in air containing but little moisture. On the other hand, the condensed water is readily removed, even under the influence of less moist camphor. W. P. W.

Compounds of Camphors with Aldehydes. By A. HALLER (*Compt. rend.*, 113, 22—26).—If the constitution of camphor is correctly represented by the formula $C_8H_{14} \left\langle \begin{array}{l} CH_2 \\ | \\ CO \end{array} \right.$, it may be expected to form, with aldehydes, condensation products having the general formula $C_8H_{14} \left\langle \begin{array}{l} C:CH \cdot R \\ | \\ CO \end{array} \right.$.

After various unsuccessful or only partially successful attempts to verify this idea, it was found that many aldehydes react with sodium-camphor according to the general equation $C_8H_{14} \left\langle \begin{array}{l} CHNa \\ | \\ CO \end{array} \right. + R \cdot CHO = C_8H_{14} \left\langle \begin{array}{l} C:CH \cdot R \\ | \\ CO \end{array} \right. + NaOH$, and that the substances thus obtained furnish reduction products having the general formula



Benzalcamphor, $C_{10}H_{14}O \cdot CHPh$, is obtained by treating sodium-camphor with benzaldehyde. Camphor (150 grams) dissolved in toluene (400 grams) is heated with sodium (15 grams) in a reflux apparatus until the metal is dissolved, and the benzaldehyde (105 grams) is added to the cooled and washed product. The resulting liquid is washed with water and dried, the toluene is distilled off, and the residue is heated as long as camphor volatilises. The benzalcamphor separates from the alcoholic extract in brilliant prisms. It melts at 95—96°, and is soluble also in ether, benzene, and toluene. It exists in three physically isomeric modifications, dextrorotatory and lævorotatory, prepared respectively from dextrorotatory and lævorotatory camphor, and racemic, prepared by mixing equal proportions of the active varieties. The racemic modification melts at 78°. Benzalcamphor, when reduced with sodium amalgam, yields *benzylcamphor*, $C_{10}H_{15}O \cdot CH_2Ph$, which resembles, optically, the modification from which it is prepared.

Cuminalcamphor, $C_{10}H_{14}O \cdot CH \cdot C_6H_4Pr$, prepared in a similar way from cumaldehyde, forms long, brittle prisms, soluble in the same menstrua as benzalcamphor. It melts at 62°, and is dextrorotatory. On reduction, it yields *cuminylcamphor*, $C_{10}H_{15}O \cdot CH_2 \cdot C_6H_4Pr$, a yellow, oily liquid which boils between 280° and 290° under a pressure of 50 mm.

Cinnamalcamphor, $C_{10}H_{14}O \cdot CH \cdot CH \cdot CHPh$, was obtained as a yellowish, viscous, uncrystallisable liquid, boiling at 280° under a pressure of 50 mm.

Methylsalicylalcamphor, $C_{10}H_{14}O \cdot CH \cdot C_6H_4 \cdot OMe$, separates from alcohol in beautiful crystals melting at 92—94°. On reduction, it

yields *methylsaligenylcamphor*, $C_{10}H_{16}O \cdot CH_2 \cdot C_6H_4 \cdot OMe$, which crystallises from alcohol in white, rhomboïdal plates, and melts at 49° . The corresponding ethyl compounds were also prepared. JN. W.

Derivatives of Cyanocamphor. By A. HALLER (*Compt. rend.*, **113**, 55—59).—Sodiumcyanocamphor, $C_8H_{14} \left\langle \begin{array}{l} CNa \cdot CN \\ | \\ CO \end{array} \right.$ (*Compt. rend.*, **112**, 1477), reacts with alkyl iodides and acid chlorides to form derivatives having the general formula $C_8H_{14} \left\langle \begin{array}{l} CR \cdot CN \\ | \\ CO \end{array} \right.$

To prepare the alkyl derivatives, cyanocamphor (1 mol.) is mixed in a reflux apparatus with the alkyl iodide (rather more than 1 mol.); potash (1 mol.), dissolved in its own weight of water, is then gradually added from a tap funnel, and the whole is heated for an hour. The excess of the iodide having been distilled off, the upper oily layer of the residual liquid is treated with aqueous potash to dissolve any undecomposed cyanocamphor, and is then extracted with ether. The dry ethereal solution is evaporated, and the residual, oily product is rectified in a vacuum.

To prepare the acid derivatives, an alcoholic solution of sodium cyanocamphor is treated in the cold with the theoretical amount of an ethereal solution of the acid chloride, and the reaction is completed with the aid of heat. The product is then taken up with water and extracted with ether, and the ethereal solution is washed with aqueous potash, dried, and allowed to evaporate. The residue consists of a solution of the acid derivative in the ethyl salt of the acid, from which crystals of the former separate after a time.

The alkyl and acid derivatives of cyanocamphor thus obtained are colourless, oily liquids, or crystalline solids, soluble in alcohol, ether, and hydrocarbons, but insoluble in water and alkalis.

Methylcyanocamphor is a liquid, which smells of grass, and boils at 170 — 180° under a pressure of 36 mm. Its molecular rotatory power is $[\alpha]_D = +107.69^\circ$. (The determinations of the rotatory power of the various derivatives were made on toluene solutions containing $\frac{1}{2}$ gram-mol. per litre.)

Ethylcyanocamphor is a liquid, which smells of grass and hydrocyanic acid, and boils at 163 — 165° under a pressure of 21 mm. Its molecular rotatory power is $[\alpha]_D = +120.71^\circ$.

Normal propylcyanocamphor crystallises in needles and has an aromatic smell and fresh taste. It melts at 46° , and boils at 150° under a pressure of 20 mm. Its molecular rotatory power is $[\alpha]_D = +126.16^\circ$.

Benzylcyanocamphor melts at 58 — 59° . Its molecular rotatory power is $[\alpha]_D = +93.62^\circ$.

Ortho-nitrobenzylcyanocamphor melts at 104 — 105° . Its molecular rotatory power is $[\alpha]_D = +68.37^\circ$.

Benzoylcyanocamphor crystallises in thin, rectangular plates, and melts at 105° . It is decomposed by strong aqueous potash into potassium-cyanocamphor and potassium benzoate.

Ortho-toluylcyanocamphor forms hard crystals, which are larger than those of its homologue. JN. W.

Methyl and Ethyl Methylcamphocarboxylates. Preparation of Methylcamphor. By J. MINGUIN (*Compt. rend.*, **112**, 1369—1372).—The methyl camphocarboxylate used was a colourless oil boiling at 155—160° under a pressure of 15 mm. Its rotatory power in alcohol $[\alpha]_D = +61.90^\circ$.

Methyl Methylcamphocarboxylate.—Methyl camphocarboxylate (30 grams) and methyl iodide (25 grams) are boiled together for about two hours in a reflux apparatus with the addition of five or six portions of 20—30 c.c. of methyl alcohol in which 3.2 grams of sodium has been dissolved. Water is added and the precipitate taken up with ether. The ethereal solution, on evaporation, yields colourless crystals, soluble in alcohol, but more so in ether. The yield is about 15 grams of the pure product. There remains an oily liquid distilling at the same temperature as the camphocarboxylate and still containing, after distillation, a certain quantity of this solid. Methyl methylcamphocarboxylate melts at 85°; its rotatory power in alcohol ($\frac{1}{2}$ mol. per litre) is $[\alpha]_D = +17.25^\circ$.

Ethyl methylcamphocarboxylate is similarly prepared. It is a crystalline substance melting at 60—61°, soluble in alcohol and ether, and has a rotatory power $[\alpha]_D = +13.8^\circ$.

Methylcamphor, $C_8H_{14} \begin{matrix} < \\ \text{CO} \end{matrix} \begin{matrix} \text{CHMe} \\ \text{CO} \end{matrix}$.—The methylcamphocarboxylates described above are not hydrolysed by treatment during four days with alcoholic potash in a reflux apparatus, but the change is readily brought about by heating in sealed tubes at 130—140°. Water is added to the contents of the tubes and the precipitate taken up with ether. The wash water contains potassium carbonate; the ethereal solution washed, dried, and evaporated, gives a crystalline substance having the odour of camphor and melting at 37—38°. Its rotatory power (1 mol. in 1 litre of alcohol) is $[\alpha]_D = 270.65$.

The oily residue is hydrolysed in a reflux apparatus, when the camphocarboxylic ether is readily converted into camphor and a further quantity of the substituted ethers is obtained. W. T.

Reduction of Apione. By G. CIAMICIAN and P. SILBER (*Ber.*, **24**, 2608—2612).—Dibromapione (Abstr., 1888, 1100) is best prepared by rapidly adding the calculated quantity of bromine to a warm solution of apiolic acid in acetic acid, and immediately pouring the product into water. After addition of some sulphurous acid, the dibromapione is filtered, and purified by crystallisation from alcohol. The yield amounts to 20 grams from 13 grams of apiolic acid.

Apione (Abstr., 1888, 848) can be prepared with advantage by reduction of dibromapione, and as a small proportion of the phenol obtained by reducing apione is also formed in the reaction, the two reductions can be carried on in the same operation. Dibromapione is dissolved in 20 parts of alcohol and the boiling solution gradually saturated with sodium. The product is then diluted with twice its volume of water, distilled on a water-bath to remove alcohol, and the recovered apione again treated with sodium and boiling alcohol, the process being repeated several times until all is reduced. The alkaline

liquors from each reaction are shaken out with ether to remove any dissolved apione, then acidified, and the reduction product extracted with ether, which is subsequently removed by distillation. The reduction product of apione, a dimethoxyhydroxybenzene, $C_6H_3(OMe)_2 \cdot OH$, is a thick oil, which slowly solidifies in a freezing mixture, melts at 24° , boils at $251-252^\circ$, and has a pronounced phenolic odour. With concentrated soda and potash solutions, it forms salts which crystallise in needles and dissolve easily in water. The acetyl derivative, $C_6H_3(OMe)_2 \cdot OAc$, crystallises from alcohol in large, colourless forms, and melts at 68° . When heated with hydrochloric acid at 100° , charring occurs, and methyl chloride is obtained, together with a crystalline compound which forms an acetyl derivative melting at about 166° . On methylation in the usual way, the reduction product is converted into a trimethoxybenzene, $C_6H_3(OMe)_3$, boiling for the most part at 248° ; this, although it solidifies but slowly in a freezing mixture, melts at 14° , and, moreover, does not seem to yield a nitro-derivative, is regarded by the author as possibly identical with Will's 1 : 2 : 4-trimethoxybenzene (Abstr., 1888, 457). Further experiments to decide this question are promised. W. P. W.

Adonin, a Glucoside from *Adonis amurensis*. By Y. TAHARA (Ber. 24, 2579—2582).—The author has prepared the glucoside from *Adonis amurensis* in order to compare it with adonidin, the glucoside from *Adonis vernalis*. The following method of extraction was used. The air-dried root (1.7 kilograms) was cut fine and extracted five times with 90 per cent. alcohol. On distilling off the alcohol, a brown mass was obtained which dissolved in water. The concentrated aqueous solution was made strongly alkaline and extracted with chloroform, the chloroform distilled off, and the residue dissolved in alcohol and fractionally precipitated with ether. In this way a yellowish, gummy mass was obtained which yields a white powder. The yield amounts to 1.94 per cent. on the material extracted. This glucoside the author calls adoniu. On analysis, it gave numbers corresponding with the formula $C_{24}H_{40}O_9$.

Adonin is easily soluble in water, alcohol, chloroform, and acetic acid, insoluble in ether. The aqueous solution has a very bitter taste. It dissolves in concentrated nitric acid with an indigo blue colour; the same coloration is obtained on adding nitric acid to the acetic acid solution; with concentrated sulphuric acid it gives a deep red, with hydrochloric acid a rose-red. In aqueous solution, it is easily decomposed by mineral acids, and a few drops of hydrochloric acid in the cold convert it into a sugar and a resinous substance easily soluble in ether. Acetic acid and alkalis do not, however, decompose it. The aqueous solution is precipitated by gallic acid, picric acid, Meyer's reagent, gold chloride, &c. On shaking with benzoic chloride and potassium hydroxide, it gives a benzoyl derivative. Its toxic action is similar to that of adonidin, but is weaker. E. C. R.

Action of Methyl Alcohol on Pyrroline. By M. DENNSTEDT (Ber., 24, 2559—2563).—The author has examined the products obtained when a mixture of methyl alcohol and pyrroline is passed over

heated zinc dust. The product consists of an oil together with a small quantity of a compound which crystallises in the cooler parts of the tube, and is probably a tripyrrolmethane derivative; the latter dissolves in alcohol and acetic acid to a dark-red solution, and dyes wool and silk brown. The oil was fractionally distilled, the different fractions heated in sealed tubes with acetic anhydride and sodium acetate at 180—190°, and the products examined. The fraction boiling below 135° contained unaltered pyrroline, aldehydic and ketonic condensation products of methyl alcohol, and a very small quantity of 1-methylpyrroline. The fractions 137—140° and 142—143° gave a mixture of acetylmethylpyrrolines which distils at 230—240° and is partially solid. The solid compound which is the main product melts at 86°, and on condensation with benzaldehyde gives 2-methylpyrrol cinnamyl ketone melting at 193—194°. The oily product yields 3-methylpyrrol cinnamyl ketone melting at 148—149°. The greater part of the product is contained in the fraction boiling at 147—149°, and consists of 2-methylpyrroline, which yields the acetyl compound melting at 86°. From the last fractions, a compound was obtained which the author believes to be 2:3-dimethylpyrroline, together with a trimethylpyrroline.

Ethyl alcohol and pyrroline yield as chief product the ethylpyrroline boiling at 163—165°.

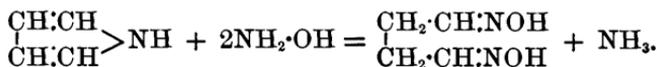
The author has also prepared the dimethylindole from the methylpyrroline boiling at 147—148°, and finds that it readily yields an acetyl compound when heated with acetic anhydride and sodium acetate at 190°. This *acetyldimethylindole* crystallises from dilute alcohol, melts at 215—217°, and is not altered by boiling with dilute alkali. The author thinks that the formation of this acetyldimethylindole is evidence that the methylpyrrol boiling at 147—148° is 3-methylpyrroline.

E. C. R.

Action of Hydroxylamine on the Pyrrolines. By G. CIAMICIAN and C. U. ZANETTI (*Gazzetta*, 21, 231—247).—*Succinazone* (*succinodiphenyldihydrazone*), $C_2H_4(CH:N_2HPh)_2$, prepared by treating a boiling aqueous solution of the oxime with an acetic acid solution of phenylhydrazine, crystallises from boiling alcohol in yellow scales, and melts at 124—125°.

Diphenyldipyridazine, $C_{20}H_{20}N_4$, is prepared by treating the previous compound (6 grams) in the cold with concentrated hydrochloric acid (100 c.c.) and precipitating the solution with water. It crystallises from ethyl acetate in tufts of white or yellowish needles, and melts at 184—185° with decomposition. It dissolves readily in benzene and boiling ethyl acetate, sparingly in ethyl alcohol, and is almost insoluble in light petroleum. It is a feeble base and dissolves in concentrated acids without decomposition, but is reprecipitated from its solutions by water. On treating its sulphuric acid solution with a crystal of potassium dichromate, an intense blue coloration is obtained. It probably has a constitution analogous to that of Ach's dimethyldiphenyldipyridazine (*Annalen*, 253, 44). On treating an alcoholic solution of 1-ethylpyrroline with hydroxylamine hydrochloride and sodium carbonate, succinaldixime and ethylamine are

formed. From this, the authors conclude that the action of hydroxylamine on pyrroline may be rigorously represented by the equation



α-Methyllevulindioxime, $\begin{array}{c} \text{CHMe}\cdot\text{CH:NOH} \\ | \\ \text{CH}_2\cdot\text{CMe:NOH} \end{array}$, prepared by boiling an alcoholic solution of 2:4'-dimethylpyrroline with hydroxylamine hydrochloride and sodium carbonate, crystallises when pure from ether in pale-yellowish needles or prisms, melts at 87–90°, dissolves in water and alcohol, and sparingly in ether, and has the general properties of an oxime. It readily reduces an alkaline copper solution and ammoniacal silver nitrate. The sodium derivative, $\text{C}_7\text{H}_{10}\text{Na}_2\text{N}_2\text{O}_2$, is a whitish powder which deliquesces in the air.

αβ'-Dimethyltetramethylenediamine,



is obtained by reducing a solution of *α*-methyllevulindioxime in absolute alcohol with metallic sodium. It is a colourless, fuming liquid with a penetrating disagreeable odour, and boils at 175°. The *oxalate*, $\text{C}_4\text{H}_6\text{Me}_2(\text{NH}_2)_2\cdot\text{H}_2\text{C}_2\text{O}_4$, crystallises in slender needles melting at 244°, with decomposition. It is hygroscopic and very soluble in water. The *platinochloride*, $(\text{C}_6\text{H}_{16}\text{N}_2)_3\text{H}_2\text{PtCl}_6$, forms small, orange-coloured crystals very soluble in boiling water. The *aurochloride* crystallises in tufts of yellow needles.

Acetophenoneacetonedioxime, $\text{CPh}(\text{NOH})\cdot[\text{CH}_2]_2\text{CMe:NOH}$, prepared by the action of hydroxylamine on 2:5'-methylphenylpyrroline, crystallises when pure in small, white needles, melts at 108°, and dissolves in alcohol, acetic acid, and ethyl acetate, but is almost insoluble in water and light petroleum. It is readily soluble in solutions of the alkalis, but is reprecipitated by dilute acids.

S. B. A. A.

Pyridyl Ketones. By C. ENGLER (*Ber.*, **24**, 2525–2527).—The ketone derivatives of pyridine have been little studied hitherto, on account of the difficulty experienced in obtaining them in quantity; in view, however, of the close relations existing between these compounds and the alkaloids, the author has subjected them to further investigation. The results obtained up to the present are given in the following abstracts.

H. G. C.

Methyl *α*-Pyridyl Ketone. By C. ENGLER and P. ROSUMOFF (*Ber.*, **24**, 2527–2529).—All attempts to obtain this ketone by the action of acetic chloride on pyridine in presence of aluminium chloride were without success. It was therefore prepared by distilling calcium picolinate with a slight excess of calcium acetate; a portion of the crude distillate was treated with phenylhydrazine or its sulphonic acid, the condensation product reconverted into the ketone, and the boiling point of the latter determined. The remainder of the crude product was then purified by fractional distillation.

Methyl α -pyridyl ketone, $C_5NH_4 \cdot COMe$, is a colourless liquid, which boils at 192° (uncorr.), has a very characteristic odour, and becomes yellow in the air. The *hydrochloride* and *sulphate* form deliquescent masses, the *platinochloride* is a sparingly soluble crystalline powder, and the *dichromate* forms orange-yellow crystals. The *picrate* crystallises from alcohol in yellow needles melting at 131° , the *mercurochloride* melts at 150° , the *methiodide* at 161° , the *ethiodide* at 205° , and the *chloriodo-additive product* at 116° .

The *oxime*, $C_5NH_4 \cdot CMe \cdot NOH$, is obtained by mixing the ketone with fused hydroxylamine hydrochloride, adding aqueous soda, and gently warming. It crystallises from a mixture of ether and light petroleum in white needles, and melts at 120° . The *phenylhydrazone*, $C_5NH_4 \cdot CMe \cdot N_2HPh$, forms beautiful, yellow crystals, and melts at 155° ; the *phenylhydrazonesulphonic acid* is obtained as a yellow precipitate by boiling the ketone with an aqueous solution of phenylhydrazinesulphonic acid, and is purified by repeated solution in ammonia and reprecipitation by acids; it does not melt at 300° and is insoluble in neutral solvents. To reconvert it into the ketone, it must be boiled with hydrochloric acid, mixed with ferric chloride to oxidise the hydrazine, and saturated with caustic soda, the solution being then extracted with ether.

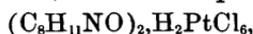
On reduction with sodium amalgam, the ketone yields a solid pinacone, and a liquid pyridinalkine. The products of the action of sodium have not been isolated.

H. G. C.

Ethyl α -Pyridyl Ketone and its Conversion into Pseudoconhydrine. By C. ENGLER and F. W. BAUER (*Ber.*, **24**, 2530—2536). —*Ethyl α -pyridyl ketone* is obtained in a manner similar to the methyl base by distilling a mixture of calcium picolinate and propionate, and is a characteristic smelling liquid, which boils at 205° (uncorr.) and quickly becomes brown in the air; it is soluble in alcohol, ether, and acids, but almost insoluble in water. It yields a deliquescent *hydrochloride*, a crystalline *platinochloride*, and also an *aurochloride*, a *chromate*, and a *picrate*. The *mercurochloride*, $C_5H_9NO, HgCl_2$, may be crystallised from mercuric chloride solution; the *methiodide* and *ethiodide* are obtained by heating the base with the alkyl iodide and alcohol in a sealed tube, the latter compound melting at 160° ; the *chloriodo-additive product* melts at 124° . The *oxime*, $C_5NH_4 \cdot CEt \cdot NOH$, forms needles melting at 106° , and yields an *acetyl* and a *benzoyl* derivative melting at 46° and 69° respectively. The *phenylhydrazone*, $C_5NH_4 \cdot CEt \cdot N_2HPh$, crystallises in pale-yellow needles, and melts at 142° ; the *phenylhydrazonesulphonic acid* forms yellow or reddish crystals, and melts at 268° .

By the action of sodium amalgam, the ketone yields a mixture of two products; one of these separates in crystalline flakes, which increase in quantity on the addition of water, and may be recrystallised from alcohol. It consists of the *pinacone of ethyl α -pyridyl ketone*, $C_2Et_2(C_5NH_4)_2(OH)_2$; this forms white needles, melts at 135 — 136° , and yields a *platinochloride*, $C_{16}H_{20}N_2O_2, H_2PtCl_6 + H_2O$, which readily loses its water of crystallisation. The filtrate from the pinacone, after further treatment with sodium amalgam at 30 — 40° ,

yields the second product of the reduction, which may be extracted with ether, and consists of α -ethylpyridylalkine, $C_5NH_4 \cdot CHEt \cdot OH$; it is a thick, yellowish oil which boils at 213 — 216° , very readily undergoes oxidation in the air, and forms a *platinochloride*,



crystallising in yellow prisms.

Different results are obtained by reducing the ketone with sodium in amyl alcohol solution. The fractions of the crude product boiling between 190 — 250° all solidify more or less on cooling, and the solid compound, after freeing from adhering oil and recrystallising from light petroleum, forms white needles which melt after sublimation at 99 — 100° ; it has the composition $C_8H_{17}NO$, and from its mode of preparation must be α -ethylpiperylalkine, $C_8NH_{10} \cdot CHEt \cdot OH$. It has in all its properties the strongest possible resemblance to the *pseudoconhydrine* obtained by Merck from *Conium maculatum*, and further examined by Ladenburg and Adam (this vol., p. 1119). There is indeed a difference of 2° in the melting point, but this may be due to the fact that the synthetical compound is an optically inactive variety. On further reduction, it is converted into coniine.

The light petroleum mother liquors from α -ethylpiperylalkine contain another crystalline substance which melts at 68 — 69° , and is being further examined.
H. G. C.

Propyl α -Pyridyl Ketone. By C. ENGLER and H. MAJMON (*Ber.*, **24**, 2536—2538).—*Propyl α -pyridyl ketone*, $C_5NH_4 \cdot COPr^a$, is obtained by distilling a mixture of calcium picolinate and butyrate, and is a colourless liquid, which boils at 216 — 220° , does not solidify at -20° , and assumes a greenish colour on exposure to air. Its salts are mostly deliquescent; the *platinochloride* forms yellow, crystalline plates almost insoluble in water and alcohol, the *mercuriochloride* melts at about 78° , the *methiodide* at 79° , and the *chlorido-additive product* at 85° . The *oxime*, $C_5NH_4 \cdot CP_1^a \cdot NOH$, crystallises from light petroleum in long, white needles, melts at 48° , and yields a *benzoyl* derivative melting at 56 — 57° (uncorr.). The *phenylhydrazone* forms yellowish-white, lustrous needles, and melts at 82° , and the *phenylhydrazonesulphonic acid* beautiful, yellow needles melting at 251° (uncorr.).

Sodium amalgam readily acts on the ketone, and yields a mixture of the *pinacone*, $C_{18}H_{24}N_2O_2$, and of α -propylpyridylalkine,



The former crystallises from alcohol in white, lustrous needles, and melts at 146° (uncorr.); the latter was only obtained in small quantity, and is an oil, the boiling point of which lies between 212° and 224° .
H. G. C.

β -Ketone Derivatives of Pyridine. By C. ENGLER (*Ber.*, **24**, 2539—2542).—*Ethyl β -pyridyl ketone*, $C_5NH_4 \cdot COEt$, is prepared by distilling a mixture of calcium nicotinate with a slight excess of calcium propionate. It is isolated from the crude distillate by means of phenylhydrazine, the hydrazone being decomposed by boiling hydrochloric acid, the precipitated hydrochloride filtered off, and the re-

maining phenylhydrazine destroyed by the careful addition of potassium nitrite. The liquid is then saturated with alkali, extracted with ether, the ethereal solution evaporated, and subjected to fractional distillation. The ketone is thus obtained as a pale-yellow liquid which boils at 230—232°, and darkens on remaining in the air. The *platinochloride* forms golden-yellow crystals, and the *picrate* yellow needles; the *mercuriochloride*, $C_8H_9NO, HgCl_2$, may be crystallised from a dilute mercuric chloride solution, and melts at 130°. The *oxime*, $C_8NH_4 \cdot CEt \cdot NOH$, crystallises in white needles, and melts at 115°; the *hydrazone*, $C_8NH_4 \cdot CEt \cdot N_2HPh$, in yellow needles melting at 145° (uncorr.), and the *hydrazonesulphonic acid* in pale-yellow needles melting at 235° (uncorr.).

Propyl β-pyridyl ketone, $C_8NH_4 \cdot COPr^a$, is obtained in a similar manner from calcium nicotinate and butyrate, and is an almost colourless liquid boiling at 246—252°, the odour of which resembles that of coniine. The *hydrazone* melts at 182°, the *hydrazonesulphonic acid* at 283°, the *mercuriochloride* at 173°, and the *ethiodide* at 192°. The *picrate* and *platinochloride* also crystallise well, and the *oxime* forms a white, crystalline powder.

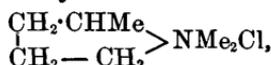
H. G. C.

Behaviour of "Dimethylpiperidine" and Allied Bases towards Hydrogen Chloride.

By G. MERLING (*Annalen*, 264, 310—351).—The tertiary base obtained by Hofmann (*Ber.*, 14, 659) by the dry distillation of dimethylpiperidylammonium hydroxide, and named by him dimethylpiperidine, is an unsaturated compound of the constitution $CH_2 \cdot CH \cdot [CH_2]_3 \cdot NMe_2$, and is termed by the author butallylcarbindimethylamine (methyl = carbin, methylamine = carbinamine). When this base is heated in a stream of hydrogen chloride, it is converted into methyl- α -methylpyrrolidine, and not into methylpiperidine, as was supposed by Hofmann. The experiments on which these statements are based, and others of a like nature, are described below.

Hydrochlorobutallylcarbindimethylamine, $CHClMe \cdot [CH_2]_3 \cdot NMe_2$, is obtained in the form of its hydrochloride when Hofmann's "dimethylpiperidine" is heated in a stream of hydrogen chloride at 130—160°, and also when "dimethylpiperidine hydrochloride" is treated with an aqueous solution of hydrogen chloride saturated at 0°. This salt is a crystalline substance readily soluble in water; when melted in a stream of dry hydrogen, it gradually loses hydrogen chloride. The free base is a colourless oil. The *aurochloride*, $C_8H_{10}Cl \cdot NMe_2, HAuCl_4$, crystallises from hot concentrated hydrochloric acid in large, golden plates.

Dimethyl- α -methylpyrrolidylammonium chloride,

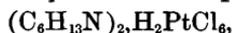


is formed when hydrochlorobutallylcarbindimethylamine is heated at 150°, and the product freed from butallylcarbindimethylamine by heating it in a stream of hydrogen; it is a colourless, crystalline, deliquescent compound. The *platinochloride*, $(C_7H_{16}NCl)_2PtCl_4$, crystallises in orange-red octahedra, and is sparingly soluble in water.

The *aurochloride*, $C_7H_{16}NCl, AuCl_3$, is sparingly soluble in water, from which it crystallises in golden needles. The corresponding *ammonium iodide*, $C_7H_{16}NI$, prepared by treating methyl- α -methylpyrrolidine with methyl iodide in methyl alcoholic solution, crystallises from alcohol in small, colourless octahedra and cubes, turns yellow on exposure to light, and is very readily soluble in alcohol.

Methyl- α -methylpyrrolidine, $\begin{matrix} CH_2 \cdot CHMe \\ | \\ CH_2 - CH_2 \end{matrix} > NMe$, is formed with evolution of methyl chloride when the ammonium chloride just described is heated strongly; it is a colourless, basic oil, of sp. gr. 0.799 at 15° ; it boils at $96-97^\circ$, is miscible with water, and has an odour of piperidine. The *platinochloride*, $(C_6H_{13}N)_2, H_2PtCl_6$, crystallises from hot water in flat, orange-yellow needles or prisms, and melts at about 225° with decomposition. The *aurochloride*, $C_6H_{13}N, HAuCl_4$, is sparingly soluble in cold water, and crystallises from hot water in golden needles melting at $215-217^\circ$ with decomposition.

Butallylmethylcarbinamine, $CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot NH_2$, can be obtained by reducing the hydrazone of allylacetone with sodium amalgam in warm, alcoholic glacial acetic acid solution; it is a colourless, mobile liquid, having an odour of piperidine and a strong alkaline reaction; it is miscible with water, boils at $117-118^\circ$, and its sp. gr. is 0.779 at 15° . The *hydrochloride* and the *hydrobromide* are deliquescent, crystalline compounds. The *platinochloride*,



crystallises in yellow needles and is moderately easily soluble in cold water; the *aurochloride* is a yellow, crystalline compound.

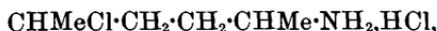
Butallylmethylcarbintrimethylammonium iodide,



is obtained when the preceding compound is treated with methyl iodide and methyl alcoholic potash; it crystallises from alcohol in well-defined prisms, and melts at $199-200^\circ$. The corresponding *chloride*, prepared by treating the iodide with moist silver chloride, is a hygroscopic, crystalline compound.

Butallylmethylcarbindimethylamine, $CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot NMe_2$, is formed, together with various other products, when the dry ammonium chloride just described is heated at $150-180^\circ$ in a stream of air; it is a colourless oil of sp. gr. 0.780 at 15° , boils at $138-140^\circ$, and has a strong odour recalling that of piperidine. The *platinochloride*, $(C_6H_{11}NMe_2)_2, H_2PtCl_6$, is an orange-yellow, crystalline substance readily soluble in water; the *aurochloride* is also crystalline.

Hydrochlorobutallylmethylcarbinamine hydrochloride,



is formed when hydrogen chloride is passed into butallylmethylcarbinamine heated at 130° ; it is a colourless, hygroscopic, crystalline substance. The *platinochloride*, $(C_6H_{14}NCl)_2, H_2PtCl_6$, is a pale-yellow, crystalline compound, and is decomposed by boiling water; the *aurochloride* is also crystalline, but the free base is a colourless oil. When hydrochlorobutallylmethylcarbinamine is heated on the

water-bath, it is converted into $\alpha\alpha_1$ -dimethylpyrrolidine hydrochloride, identical with the compound recently described by Tafel (Abstr., 1888, 1015; 1890, 1000). Dimethyl- $\alpha\alpha_1$ -dimethylpyrrolidylammonium iodide crystallises in transparent cubes and octahedra, and decomposes at about 400° , but without melting (Tafel gives $255-256^\circ$ as the melting point of this compound).

Hydrochlorobutallylmethylcarbindimethylamine hydrochloride,

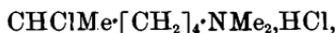


prepared by passing hydrogen chloride into butallylmethylcarbindimethylamine heated at 130° , is a colourless, hygroscopic, crystalline substance. The *platinochloride*, $(\text{C}_6\text{H}_{12}\text{Cl}\cdot\text{NMMe}_2)_2, \text{H}_2\text{PtCl}_6$, is a yellow, crystalline compound; it melts at $91-93^\circ$, and is decomposed by boiling water. The *aurochloride* is a yellow powder melting at $76-77^\circ$. The free base is a colourless oil which, when heated on the water-bath, is readily converted into *dimethyl- $\alpha\alpha_1$ -dimethylpyrrolidylammonium chloride*; on further heating, methyl chloride is evolved and methyl- $\alpha\alpha_1$ -dimethylpyrrolidine, identical with Tafel's trimethylpyrrolidine (*loc. cit.*) is formed.

Dimethyl- α -pipercolylammonium iodide, $\text{C}_8\text{H}_{18}\text{NI}$, is formed when α -pipercoline, prepared by Ladenburg's method, is treated with methyl iodide and potash in methyl alcoholic solution; it crystallises from hot alcohol in long, white crystals, and is sparingly soluble in cold alcohol.

Pentallylcarbindimethylamine, $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_4\cdot\text{NMe}_2$, is obtained when the ammonium iodide just described is treated with moist silver oxide, and the hydroxide thus formed gradually heated to 140° ; it is a colourless oil, of sp. gr. 0.767 at 15° , boils at $143-143.5^\circ$, and has an odour of piperidine; it has a strongly alkaline reaction, and is not miscible with water. The *platinochloride* is an oil, and the *aurochloride* an unstable, crystalline compound.

Hydrochloropentallylcarbindimethylamine hydrochloride,



can be obtained by passing hydrogen chloride into pentallylcarbindimethylamine heated at 160° ; it is a very hygroscopic, crystalline substance. The *platinochloride* and the *aurochloride* are oils.

Methyl- α -pipercoline, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}\rangle\text{NMe}$, is formed when the preceding compound is decomposed with soda, the colourless, oily base thus obtained heated first at 120° to convert it into dimethyl- α -pipercolylammonium chloride, and then at a higher temperature to eliminate methyl chloride; it can also be obtained by heating dimethyl- α -pipercolylammonium chloride prepared directly from α -pipercoline. It is a colourless oil, of sp. gr. 0.826 at 15° , boils at $126-128^\circ$, and is not miscible with water. The *platinochloride*, $(\text{C}_7\text{H}_{15}\text{N})_2, \text{H}_2\text{PtCl}_6$, separates from hot water in compact, orange-red crystals melting at $180-185^\circ$.

Pentallylcarbintrimethylammonium iodide, $\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_4\cdot\text{NMe}_3\text{I}$, is formed when pentallylcarbindimethylamine is treated with methyl iodide in methyl alcoholic solution; it separates from alcoholic other

in colourless plates melting at 126—129°; when treated with moist silver oxide, it is converted into a strongly alkaline hydroxide, which is decomposed, on heating at about 160°, into water, trimethylamine, diallyl (b. p. 60—61°), and a hydrocarbon (b. p. 80—83°) isomeric with diallyl.

The *hydrocarbon*, boiling at 80—83°, is a colourless, refractive oil, of sp. gr. 0·727 at 15°, and has an odour like that of diallyl; it combines readily with bromine, yielding a *tetrabromide* $C_6H_{10}Br_4$, which crystallises from hot glacial acetic acid in lustrous plates melting at 160—162°; on oxidation with chromic acid, it yields carbonic anhydride and acetic acid.

When butallylmethylcarbintrimethylammonium iodide (m. p. 199—200°) is digested with moist silver oxide, it is converted into the corresponding hydroxide; this substance decomposes at about 160° into water, trimethylamine, diallyl, and a hydrocarbon (b. p. 80—83°) identical with that obtained from pentallylcarbintrimethylammonium iodide in like manner.

F. S. K.

Formation of Bases of the Quinoline Series. By E. LELLMANN and W. LIPPERT (*Ber.*, **24**, 2623—2624).—It is known that either aniline or nitrobenzene yields quinoline when heated with glycerol and sulphuric acid, and that in the one case oxidation, in the second reduction, must occur. Azobenzene occupies an intermediate position between aniline and nitrobenzene, and, if found to react with acraldehyde, might, therefore, be expected to do so without either oxidation or reduction being necessary. This conclusion is confirmed by experiment, since the authors find that azobenzene (compare Claus and Stegelitz, *Abstr.*, 1887, 173) and its derivatives yield bases of the quinoline series when heated with glycerol and sulphuric acid. Azobenzene and paratoluene give, respectively, quinoline and toluquinoline, whilst amidoazobenzene forms a mixture of quinoline and pseudophenanthroline. The yield in each case was small.

W. P. W.

Preparation of Amidoquinoline. By J. EPHRAIM (*Ber.*, **24**, 2817—2820).— *α -Phenylhydrazoquinoline*, $C_9NH_6 \cdot NH \cdot NHPh$, is prepared by carefully heating a mixture of α -chloroquinoline (1 mol.) and phenylhydrazine (2 mols.) in a reflux apparatus, over a free flame, extracting the uncombined portion of the reagents, and the phenylhydrazine hydrochloride produced, with boiling water, and crystallising from absolute alcohol. It then separates in white needles, melts at 191° with decomposition, and is readily soluble in glacial acetic acid and chloroform, almost insoluble in ether; it gives a violet colour with concentrated sulphuric acid, which, on diluting with water, becomes rose-coloured. The yield is equal to that of the chloroquinoline employed.

α -Phenylazoquinoline, $C_9NH_6 \cdot N_2Ph$, is formed by oxidising the hydrazo-compound, best as follows:—The hydrazo-derivative is dissolved in glacial acetic acid, an excess of ferric chloride added, and after a while the mixture diluted with water, when the azo-derivative separates in delicate, red needles; it melts at 93°, and is readily soluble

in glacial acetic acid, alcohol, and ether; it exhibits the same colour reaction with concentrated sulphuric acid as the hydrazo-derivative.

α -*Amidoquinoline*, $C_9NH_8NH_2$ [$NH_2 = 2'$], is obtained by heating α -phenylhydrazoquinoline (1 gram) with hydriodic acid (1.7 grams) and amorphous phosphorus (0.5 gram) in a sealed tube at 180° for an hour, rendering the product alkaline, driving over the aniline with a current of steam, and extracting the residual solution with ether, from which the new base is obtained as a violet, crystalline mass, which, when crystallised from light petroleum, melts at 114° , and is readily soluble in alcohol, ether, chloroform, and benzene; the *picrate* and the *platinochloride* are sparingly soluble compounds. A *hydrazo-derivative* melting at 197° is obtained from α -chlorolepidine.

A. R. L.

Tetrahydro-derivatives of β -Naphthaquinoline and β -Naphthaquinaldine. By E. BAMBERGER and R. MÜLLER (*Ber.*, **24**, 2641—2647).— β -Naphthaquinoline (Skraup and Cobenzl, *Abstr.*, 1883, 1010) is most readily purified by pouring the product of the Skraup reaction into water, neutralising partially with caustic soda, filtering from tarry matters, and, with the object of removing all resinous matters from solution, heating the filtrate on a water-bath with sodium nitrite until it gives the reactions of nitrous acid. The pure base separates in the solid form on the addition of excess of alkali to the filtrate. It boils at 349.5 — 350° (thermometer in vapour) under 721 mm. pressure.

Tetrahydro- β -naphthaquinoline, $C_{13}H_{13}N$, is obtained when β -naphthaquinoline (20 grams), dissolved in concentrated hydrochloric acid, is gradually added to a boiling mixture of tin (80 grams) and hydrochloric acid (500 grams), and heated until the metal is dissolved. The crystalline stannochloride, which separates on cooling, is decomposed by aqueous soda, and the base purified by distillation with steam and subsequent crystallisation from light petroleum. It crystallises in lustrous, silvery-white needles or scales, melts at 93.5° , and dissolves readily in the ordinary organic solvents, but only sparingly in water. The solutions in indifferent solvents are destitute of fluorescence, but those in mineral acids show a beautiful blue fluorescence, resembling that of anthracene. Ferric chloride or potassium dichromate, added to the acid solution, produces a deep, reddish-brown coloration, rapidly changing to dark brown. The *hydrochloride*, $C_{13}NH_{13}HCl$, crystallises in silvery-white prisms, melts at 230.5 — 231° , and dissolves easily in water, but only sparingly in strong hydrochloric acid; the *sulphate* forms lustrous, white needles, and is very soluble in water. The *acetyl* derivative, $C_{13}H_{12}NAc$ [$Ac = 1''$], crystallises in white prisms, melts at 77° , and is sparingly soluble in water, but readily in most other solvents. The *nitroso-derivative*, $C_{13}NH_{12}NO$, crystallises from alcohol in silvery-white prisms or scales, melts at 105.5° , and dissolves easily in benzene, chloroform, ether, &c.

1''-Benzeneazotetrahydro- β -naphthaquinoline, $C_{13}NH_{12}N_2Ph$ [$N_2Ph = 1''$], prepared by the action of diazobenzene chloride on tetrahydro- β -naphthaquinoline in the presence of sodium acetate, crystallises from light petroleum in yellow needles of golden lustre, melts at 96.5 — 97° , and dissolves easily in the ordinary organic solvents.

When warmed with mineral acids, it decomposes into the tetrahydro-base, phenol, and nitrogen.

Tetrahydro-β-naphthaquinaldine is obtained by reducing β-naphthaquinaldine by the method just described. It crystallises from light petroleum in hard, thick, glassy prisms, melts at 51·5—52°, dissolves readily in the ordinary organic solvents, but only sparingly in water, forming fluorescent solutions which lose their blue fluorescence on the addition of a mineral acid. Ferric chloride or potassium dichromate added to an acid solution produces a reddish-brown coloration, which becomes brighter and eventually greenish-yellow when the mixture is warmed. The *hydrochloride*, $C_{14}NH_{15}HCl$, crystallises in white prisms, melts at 239—240°, and is readily soluble in water, but sparingly in hydrochloric acid. The *acetyl* derivative, $C_{14}H_{14}NAc$, forms white needles, melts at 86—86·5°, and dissolves easily in organic solvents. The *nitroso-derivative*, $C_{14}NH_{14}NO$ [$NO = 1''$], crystallises from alcohol in straw-yellow, lustrous scales, and melts at 69—69·5°. The *benzeneazo-compound* has not yet been obtained in crystalline form.

W. P. W.

Octohydro-derivatives of β-Naphthaquinoline. By E. BAMBERGER and R. MÜLLER (*Ber.*, **24**, 2648—2661).—The first part of this paper is devoted to a restatement of the effect of reduction on the properties of β-naphthaquinoline, for which a previous paper may be consulted (*Abstr.*, 1890, 1303). When β-naphthaquinoline (10 grams) is reduced with sodium (30 grams) and amyl alcohol (250 grams) in the usual way, a mixture of the “alicyclic” and “aromatic” octohydrides is obtained. The relative proportion of the two bases varies slightly in different experiments, but the “aromatic” derivative is always the chief product, the average yield of the “alicyclic” base being about 3 per cent. of the naphthaquinoline employed. To separate the bases, the fluorescent amyl alcohol layer is acidified, the alcohol removed by steam distillation, the residue rendered alkaline, and the bases distilled with steam. The solid distillate is extracted with light petroleum to free it from a very small quantity of a third base insoluble in that solvent, and the “alicyclic” constituent separated as carbonate by treating the filtrate with moist carbonic anhydride. The carbonate is freed from small quantities of the “aromatic” base, which adhere to it even after washing with light petroleum, either by repeating the precipitation with carbonic anhydride several times, or by adding nitrous acid to the cold dilute aqueous solution and extracting the resulting “aromatic” nitrosamine with ether.

ac.-Octohydro-β-naphthaquinoline, $C_{13}NH_{17}$, crystallises from dilute aqueous soda in long, silky, matted needles, or from alcohol in long, glassy prisms, melts at 91°, boils at 321° under 727 mm. pressure, has a basic odour, and is volatile with steam. It gives no colour reactions with ferric chloride, potassium dichromate, or diazotised bases, and in its properties resembles the “alicyclic” tetrahydronaphthylamines; its physiological action, for example, being, according to Filehne, very similar to that of those bases (compare *Abstr.*, 1889, 737), and in no sense like that of quinoline. The *hydrochloride*, $C_{13}NH_{17}HCl$, crystallises in thick, glassy, monoclinic prisms, melts at 252°, and is readily soluble in water and alcohol, but only sparingly in hydrochloric

acid; the *platinochloride* crystallises in golden-yellow, serrated, thin prisms, melts at 250° with blackening, and dissolves very sparingly in cold water; the *nitrate* forms lustrous prisms, somewhat sparingly soluble in cold water; the *nitrite* crystallises from water in short, thick, glassy prisms, melts at 238°, and is not decomposed by boiling water or cold mineral acids. The *acetyl* derivative, $C_{13}H_{16}NAc$, crystallises from light petroleum in strongly refractive, glassy prisms, from water in small needles, and dissolves readily in the ordinary solvents. The *benzeneazo*-compound, $C_{13}NH_{16} \cdot N_2Ph$ [$N_2Ph = 1''$], obtained by the action of diazobenzene chloride on the base in the presence of sodium acetate, crystallises from aqueous alcohol in silvery-white, flat needles, melts at 95°, is readily soluble in the ordinary organic solvents, and yields a *picrate*, $C_{13}H_{21}N_3 \cdot C_6H_2(NO_2)_3 \cdot OH$, crystallising in lustrous, golden-yellow needles. The *nitroso*-derivative, $C_{13}NH_{16} \cdot NO$, prepared by heating a solution of the base in excess of acid with the calculated quantity of sodium nitrite at 110–120° for 5 hours, crystallises from alcohol in lustrous, flat, serrated, silvery-white prisms, melts at 122.5°, and dissolves readily in ether, chloroform, benzene, and boiling alcohol.

ar.-*Octahydro-β-naphthaquinoline*, $C_{13}NH_{13}$, exhibits a remarkable power of crystallisation. From its solution in light petroleum, it usually separates in large, transparent, colourless prisms, whose length seems to be conditioned only by the size of the containing vessel. If, however, the concentrated solution is slowly cooled, it forms pale yellow, shorter prisms an inch in thickness, belonging either to the monoclinic, or more probably, the triclinic system; exact crystallographic measurements could not be made, since the crystals, on removal from the solvent, became white and opaque in a few seconds, owing to volatilisation of the light petroleum crystallised with the base. The mother liquor of these efflorescent crystals solidifies after a few minutes to a mass of long, thin, silky needles, which do not alter on exposure to the air. The base melts at 60.5°, boils at 325° under 727 mm. pressure, has a neutral reaction, and dissolves easily in organic solvents, but only sparingly in water. In its reactions, it resembles the "aromatic" tetrahydronaphthylamines; thus it reduces alcoholic silver nitrate in the cold and platinic chloride on warming, reacts with diazotised sulphanilic acid forming a dark claret colouring matter, and gives a yellowish coloration on warming its acid solution with ferric chloride or potassium dichromate. The *hydrochloride*, $C_{13}NH_{17} \cdot HCl$, crystallises either in silvery-white scales or long, glassy prisms, melts at 219°, and is soluble in alcohol and chloroform. The *platinochloride*, $(C_{13}NH_{17})_2 \cdot H_2PtCl_6 + 2H_2O$, forms bright-yellow, lustrous scales, melts at 178°, and on warming becomes black, owing to the separation of platinum. The *acetyl* derivative, $C_{13}NH_{16} \cdot Ac$, crystallises in scales or flat, silvery-white prisms, melts at 68.5–69°, and dissolves readily in most solvents, but only sparingly in water. The *nitroso*-derivative, $C_{13}NH_{16} \cdot NO$ [$NO = 1''$], crystallises by very slow evaporation of its alcoholic solution in short, thick, glassy, monoclinic prisms, $a : b : c = 2.4245 : 1 : 2.75495$; $\beta = 85^\circ$, observed forms $0P$, $\infty P\infty$, $-P$, $+P$, and $+2P\infty$. It melts at 106°.

W. P. W.

Octohydro-derivatives of β -Naphthaquinaldine. By E. BAMBERGER and L. STRASSER (*Ber.*, 24, 2662—2669).— β -Naphthaquinaldine (12 grams), on reduction with sodium (32 grams) and boiling amyl alcohol (350 grams), yields a mixture of an "aromatic" octohydro- β -naphthaquinaldine with a very small quantity of "alicyclic" octohydro- β -naphthaquinaldine. These bases can be separated by the method described in the preceding abstract.

ar.-Octohydro- β -naphthaquinaldine, $C_{14}NH_{18}$, crystallises from light petroleum in colourless, glassy prisms, from dilute alcohol in glistening scales, melts at 75° , volatilises slowly with steam, and dissolves readily in alcohol, benzene, chloroform, &c., but only sparingly in water. It exhibits reducing properties, and on the addition of silver nitrate to its alcoholic solution, gives first a blue colour and then a separation of metallic silver. Ferric chloride added to the warm aqueous solution of its hydrochloride produces a yellow colour which eventually changes to reddish-brown, with the separation of reddish-brown flocks. The *hydrochloride*, $C_{14}NH_{18} \cdot HCl$, crystallises in white, lustrous, feathery crystals, melts at 210° , and dissolves readily in alcohol, but only sparingly in hydrochloric acid. On the addition of platinum chloride to its aqueous solution, yellow needles of a platinum-chloride are obtained, which become black on heating the solution, owing to a separation of platinum. The *nitrate*, $C_{14}NH_{18} \cdot HNO_3$, crystallises in lustrous, white needles, melts at 170° , and is easily soluble in water and dilute nitric acid on boiling, but only sparingly in the cold. The *acetyl* derivative, $C_{14}NH_{18} \cdot Ac$ [$Ac = 1''$], crystallises from light petroleum in aggregates of lustrous needles, melts at 92° , and dissolves readily in most solvents, but only sparingly in water. The *nitroso*-derivative, $C_{14}NH_{18} \cdot NO$, forms straw-yellow, lustrous needles, melts at 86° , and is easily soluble in ether, benzene, chloroform, and boiling alcohol.

1''-Benzeneazo-*ar.*-octohydro- β -naphthaquinaldine, $C_{14}NH_{18} \cdot N_2Ph$ [$N_2Ph = 1''$], is obtained when a solution of octohydro- β -naphthaquinaldine and sodium acetate in aqueous alcohol is treated with the calculated quantity of diazobenzene chloride. By slow evaporation of its solution in light petroleum, it crystallises in pale-yellow, glassy, thick, rhombic prisms, $a : b : c = 0.8037 : 1 : 0.5600$, forms observed $2P_\infty$ and P , melts at 97.5 — 98° , and is extremely soluble in ether, chloroform, and benzene. When boiled with mineral acids, it decomposes in the normal way into octohydro- β -naphthaquinoline, phenol, and nitrogen; as anticipated, however, it does not undergo intramolecular change into the azo-compound on treatment of its alcoholic solution with hydrochloric acid, since the *para*-position is not open in the central ring, which by hydrogenation of the lateral rings has acquired properties identical with those of benzene.

2''-Benzeneazo-*ar.*-octohydro- β -naphthaquinaldine, $C_{14}NH_{18} \cdot N_2Ph$ [$N_2Ph = 2''$], is formed when a cooled dilute alcoholic solution of the hydrochloride of the base is treated with diazobenzene nitrate. It crystallises from alcohol in dark, ruby-red prisms of greenish, bronze-like lustre, and dissolves readily in alcohol, ether, chloroform, &c., but only sparingly in water. The alcoholic solution is raspberry-red in colour, but, on the addition of a drop of concentrated hydrochloric

acid, becomes emerald-green. Concentrated sulphuric acid dissolves it, forming a raspberry-red solution, which, on adding a little water, becomes emerald-green, and on further dilution, becomes rose-coloured and seemingly fluorescent, owing to the precipitation of the colouring matter. *Sulphobenzeneazo-ar.-octohydro-β-naphthaquinoline* is a greenish-black, crystalline powder which dissolves in alcohol and water with a deep-red colour, and in alkalis forming dark claret solutions.

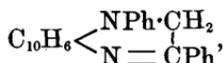
Orthamido-ar.-octohydro-β-naphthaquinaldine [$\text{NH}_2 = 2'$] is prepared by boiling the alkaline solution of the sulphobenzeneazo-derivative with zinc dust until the colour becomes bright-yellow, and subsequently extracting with ether. It exhibits the reactions of an orthodiamido-derivative of benzene on treatment with dilute solutions of ferric chloride or potassium dichromate, and on boiling with acetic acid is converted into *α-methyl-ar.-octohydro-β-naphthaquinaldimidazole*. The imidazole hydrochloride crystallises from alcohol or ether-alcohol in glassy prisms, melts at 262° with decomposition, dissolves readily in acids, and gives no colour reactions with ferric chloride or potassium dichromate.

ac.-Octohydro-β-naphthaquinaldine, $\text{C}_{14}\text{NH}_{19}$, crystallises in long, silky needles, dissolves easily in the ordinary organic solvents, but only sparingly in water, has a strongly alkaline reaction, and volatilises readily with steam. It is destitute of reducing powers, and exhibits the properties of an "alicyclic" base. The *hydrochloride* crystallises in silvery scales, and dissolves readily in water, but only sparingly in hydrochloric acid; the *platinochloride* forms orange-red, flat needles.

W. P. W.

A New Class of Fluorescent Colouring Matters of the Quinoxaline Series. By O. FISCHER and M. BUSCH (*Ber.*, 24, 2679—2683).—An azonium base identical with the compound (m. p. 167°) obtained by oxidising triphenyletho- $\alpha\beta$ -hydronaphthaquinoxaline (this vol., p. 1109) is formed when benzile is treated with phenylorthonaphthylenediamine as described by Witt (*Abstr.*, 1887, 729).

1:3-Diphenyletho- $\alpha\beta$ -dihydronaphthaquinoxaline,



is formed, together with a very small quantity of a dark-red substance described below, when benzoylcarbinol, prepared by hydrolysing acetylacetophenone with barium carbonate, is heated with phenylorthonaphthylenediamine at 150 — 160° in sealed tubes for 4—5 hours. The crude product is dissolved in a mixture of benzene (1 part) and alcohol (3 parts), from which, on keeping for a long time, the quinoxaline is deposited in compact, orange-red needles. It melts at 164 — 165° , and is readily soluble in benzene, but more sparingly in ether and glacial acetic acid, very sparingly in alcohol, and almost insoluble in light petroleum; its solutions show an intense yellowish-green fluorescence. It dissolves in concentrated sulphuric acid and in concentrated hydrochloric acid, yielding a dark brownish-red solution, from which it is reprecipitated in a yellow, flocculent condition on the addition of water. On oxidation with

ferric chloride, it is converted almost quantitatively into diphenyletho-naphthazonium hydroxide, identical with the compound previously described (*loc. cit.*).

The dark-red bye-product mentioned above is obtained in crystals when the alcoholic benzene mother liquors from the quinoxaline base are mixed with ether and then slowly evaporated; it is soluble in benzene and ether, but only sparingly in alcohol and light petroleum, its solutions showing a beautiful purple-red fluorescence; it melts at about 194—196°, and forms a stable salt with sulphuric acid.

n-Methyldiphenyldihydroquinoxaline, $C_6H_4 \left\langle \begin{array}{l} NMe \cdot NHPH \\ N = CPh \end{array} \right.$, is

formed when benzoïn is heated with methylorthophenylenediamine at 160—170° for 5—6 hours; it crystallises from alcohol in concentrically-grouped, yellow needles, melts at 133°, and is readily soluble in benzene and ether, but only moderately easily in alcohol, and very sparingly in light petroleum; its solutions show a greenish-yellow fluorescence. It is a feeble base, its salts being partially decomposed by water; it dissolves in concentrated sulphuric acid, yielding a yellow solution, which first changes to red and then becomes yellow again on the addition of water. When the quinoxaline is heated with ferric chloride and hydrochloric acid in alcoholic solution, it is converted into an ammonium base, the ferrichloride of which crystallises in long, yellow prisms.

F. S. K.

Nitroso-derivatives of the Thiazoles. By E. NÄF (*Annalen*, 265, 108—128).—Diazothiazole hydrate, $\begin{array}{l} CH \cdot S \\ | \\ CH \cdot N \end{array} \rangle C:N \cdot N \cdot OH$, or μ -

nitrosoimidothiazoline, $\begin{array}{l} CH - S \\ | \\ CH \cdot NH \end{array} \rangle C:N \cdot NO$, can be obtained in a slightly impure condition, by gradually adding a well-cooled, concentrated solution of sodium nitrite to a concentrated aqueous solution of amidothiazole nitrate cooled to -10° ; the amorphous, orange-red, flocculent precipitate is quickly separated by filtration at a low temperature and dried in a desiccator. It is very unstable when moist, and even in the dry state it gradually turns black; when quickly heated, it decomposes at about 140° with explosion. It is soluble in alcohol and ether, but insoluble in water; its conversion into chloro- and bromo-thiazole has been previously described by Schatzmann (this vol., p. 744).

μ -Imido-*n*-methylthiazoline, $\begin{array}{l} CH - S \\ | \\ CH \cdot NMe \end{array} \rangle C:NH$, is formed when amidothiazole is heated with methyl iodide in methyl alcoholic solution at 130° for several hours, and the hydriodide obtained in this way decomposed with potash; it is a yellowish-brown, very hygroscopic, strongly alkaline liquid. The *hydriodide*, $C_4H_6N_2S, HI$, crystallises in colourless plates, and melts at 175° . The *hydrochloride* crystallises from water, in which it is very readily soluble, in large plates, and melts at 97° ; the *platinochloride* is sparingly soluble.

n-Methylimidothiazoline, $\begin{array}{l} CH - S \\ | \\ CH \cdot NH \end{array} \rangle C:NMe$, is produced when an

aqueous solution of methylthiocarbamide is warmed with dichloro-ether; it is a yellowish-brown oil, which, on keeping, gradually solidifies to a mass of very hygroscopic crystals. The *hydrochloride*, $C_4H_6N_2S, HCl$, is a semi-crystalline, hygroscopic compound melting at $79-80^\circ$. The *platinochloride* crystallises in long needles.

Dimethylimidothiazoline, $\begin{array}{c} CH-S \\ || \\ CH \cdot NMe \end{array} > C:NMe$, can be obtained by methylating either of the bases just described, but more conveniently by warming an aqueous solution of dimethylthiocarbamide with dichloroether; it is a hygroscopic liquid.

The *hydrochloride*, $C_5H_8N_2S, HCl$, crystallises well, and melts at 222° .

μ -*Nitroso-n-methylimidothiazoline*, $\begin{array}{c} CH-S \\ || \\ CH \cdot NMe \end{array} > C:N \cdot NO$, is precipitated in yellow, lustrous plates when a concentrated solution of sodium nitrite is added to a solution of μ -imidomethylthiazoline hydrochloride in well-cooled, very dilute hydrochloric acid; it melts at 161° with a slight explosion, and is soluble in alcohol and ether, but only sparingly in water. The dry compound is stable, and dissolves unchanged in alkalis, but when treated with concentrated mineral acids, or with powerful reducing agents, it is reconverted into μ -imidomethylthiazoline.

n-Methylthiazolinehydrazine, $\begin{array}{c} CH-S \\ || \\ CH \cdot NMe \end{array} > C:N \cdot NH_2$, is formed in small quantities when an alcoholic solution of the preceding compound is mixed with excess of zinc-dust, and acetic acid gradually added to the well-cooled mixture; it is a yellow, disagreeably smelling oil. The *hydrochloride*, $C_4H_7N_3S, HCl$, and the sparingly soluble *picrate* crystallise in yellow needles.

n-Nitroso- μ -methylimidothiazoline, $\begin{array}{c} CH-S \\ || \\ CH \cdot N(NO) \end{array} > C:NMe$, can be obtained by treating μ -methylimidothiazoline with nitrous acid under the conditions given above; it forms small, yellowish crystals, has a characteristic odour recalling that of acetamide, and is much more unstable than the isomeride described above, being converted into resinous products on keeping in a dry condition, or on boiling with water or alcohol. It turns black when slowly heated, and melts at about 140° , but when heated quickly it explodes at about $110-120^\circ$; it is freely soluble in alkalis and in ammonia, by which it is completely decomposed. The corresponding hydrazine could not be obtained.

The hydrochloride of a base which the author names *thiazoletriazole*, $CH \left\langle \begin{array}{c} S-C:N \\ | \\ CH \cdot N \cdot N \end{array} \right\rangle CH$, is formed when freshly prepared *n*-nitroso- μ -methylimidothiazoline is dissolved in well-cooled 10 per cent. hydrochloric acid, and the solution warmed until no further evolution of gas takes place; on keeping for some time, the *hydrochloride*,



is deposited in needles, which turn brown and lose their water at 130—140°. and melt at 210—220°. The *hydrobromide*,



forms long, prismatic crystals, turns brown on keeping, loses its water at 130—140°, and decomposes completely at a higher temperature, but without melting. The free *base* is a brown oil, which gradually solidifies to a vitreous mass; it is very readily soluble in water, has an alkaline reaction, and reduces Fehling's solution; when its hydrochloride is treated with sodium nitrite in aqueous solution, a large quantity of *n*-nitroso- μ -methylimidothiazoline is formed.

μ -*Phenylimidothiazoline*, $C_9H_8N_2S$, prepared by treating dichlorether with phenylthiocarbamide and decomposing with potash the salt produced, crystallises from alcohol, ether, and benzene in small, colourless needles, and melts at 124°; its salts are not easily obtained in crystals.

Diphenylimidothiazoline, $C_{15}H_{12}N_2S$, obtained from diphenylcarbamide in like manner, is a granular, crystalline substance melting at 105°.

μ -*Phenyl-n-nitrosoimidothiazoline*, $C_9H_7N_3SO$, is precipitated in the form of a microscopic, crystalline powder on treating μ -phenylimidothiazoline with sodium nitrite in well-cooled, dilute hydrochloric acid solution; it forms yellow crystals, melts at 58°, and decomposes on keeping. It is insoluble in alkalis, and, when treated with acids, it is reconverted into μ -phenylimidothiazoline.

F. S. K.

Action of Hydriodic Acid on Quinine and Cinchonine. By E. LIPPMANN and F. FLEISSNER (*Ber.*, **24**, 2827—2829).—The action of hydriodic acid on quinine is similar to that of hydrochloric or hydrobromic acid on the base (*Monatsh.*, **12**), and leads to the formation of hydriodoquinine hydriodide, $C_{20}H_{24}N_2O_2, 3HI$, which, on treatment with ammonia, yielded hydriodoquinine, $C_{20}H_{21}N_2O_2.HI$, with the elimination of 2 mols. of hydrogen iodide. When boiled with alcoholic potash, hydriodoquinine is converted into isoquinine. A better yield of this base is obtained by heating hydriodoquinine hydriodide with water at 150—160° for about six hours, adding the pale-yellow solution to aqueous ammonia, extracting with ether, and drying the ethereal solution over caustic potash. After a short time, the sparingly soluble isoquinine crystallises from the solution, and a further quantity can be obtained by evaporation, the ethereal mother liquor containing quinine.

Hydriodocinchonine hydriodide, $C_{19}H_{22}N_2O, 3HI$, is formed when cinchonine, free from sulphuric acid, is slowly stirred into warm hydriodic acid (sp. gr. 1.7—1.8), and can be freed from cinchonine hydriodide by washing the crystalline precipitate with alcohol. It crystallises in small, bright-yellow, lustrous prisms, decomposes when heated at 215°, and dissolves sparingly in alcohol and cold water, but easily in hot water. On digestion with warm, dilute aqueous ammonia, it is converted into *hydriodocinchonine*, $C_{19}H_{22}N_2O.HI$, which crystallises in slender, silky needles, melts at 158—160°, dissolves very sparingly in ether, but more easily in alcohol, and yields a

platinochloride of the composition $C_{19}H_{22}N_2OHI + H_2PtCl_6$. Cinchonine is regenerated when hydriodicinchonine hydriodide is heated with water under pressure. W. P. W.

Quinethyline. By E. GRIMAUX and A. ARNAUD (*Compt. rend.*, **112**, 1364—1367).—It has been shown in a former communication that quinine is a methyl ether of cupreïne; quinethyline is the corresponding ethyl ether. It is prepared from specially purified cupreïne as follows:—A molecular proportion of dry cupreïne is dissolved in alcohol, to which has been added $1\frac{1}{2}$ mols. of sodium, and heated in sealed tubes, at $95-100^\circ$ with $1\frac{1}{2}$ mols. of ethyl nitrate for from 12 to 15 hours. The alcohol is distilled off, the residue taken up with acidified water, an excess of soda added, and the new base extracted with ether. The ethereal solution is then shaken with dilute sulphuric acid, the aqueous solution separated from the ether, heated on the water-bath, and carefully neutralised by ammonia. When the concentrated liquor is cooled, strongly coloured basic sulphate of the base separates. The crude product is converted into the normal sulphate, which is purified by heating with animal charcoal and subsequently recrystallising it from boiling water. The base is precipitated from a cold, concentrated solution of the normal sulphate by the addition of a slight excess of ammonia. The precipitate is white and amorphous, much resembling quinine; it consists of hydrates melting at 60° .

The dry, pulverulent base may be obtained by desiccating in dry air, and afterwards heating at $100-120^\circ$; it melts at 160° . It is very soluble in all the ordinary solvents for alkaloids, and yields very fluorescent solutions with excess of sulphuric acid. It does not crystallise from alcohol, behaving in exactly the same way as quinine. Large, colourless, transparent crystals of a hydrate may easily be obtained. The base is lævorotatory; its solution in absolute alcohol gives $[\alpha]_D = -169.4^\circ$.

The *normal sulphate*, $C_{21}H_{26}N_2O_2 \cdot SO_4H_2 + 8H_2O$, crystallises in large, colourless, eight-sided prisms, efflorescing rapidly in the air. It dissolves in 51.1 parts of water at 19° , and is very soluble in boiling water. When heated with the calculated quantities of hydriodic acid and iodine in alcoholic solution, it yields small, garnet-red needles differing from the plates of herapathite given by quinine.

The *basic sulphate*, $(C_{21}H_{26}N_2O_2)_2 \cdot SO_4H_2 + H_2O$, is readily prepared from the normal sulphate by dissolving the latter in boiling water and neutralising exactly with dilute ammonia, using litmus as indicator. It forms crystalline plates of a silky lustre, requiring 397 parts of water for solution at 15° . Its solution in dilute hydrochloric acid gives $[\alpha]_D = -233.1^\circ$. The yield of pure basic sulphate was about 35 parts per 100 of cupreïne taken. W. T.

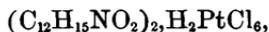
Hydrastine. By M. FREUND and C. DORMEYER (*Ber.*, **24**, 2730—

2741).—Hydrohydrastinine, $CH_2 \begin{matrix} \overset{6}{O} \\ \diagup \quad \diagdown \\ \underset{5}{O} \end{matrix} C_6H_2 \begin{matrix} \overset{2}{CH_2 \cdot NMe} \\ \diagdown \quad \diagup \\ \underset{3}{CH_2 \cdot CH_2} \end{matrix}$ (compare

Freund and Will, Abstr., 1887, 383), is best prepared by reducing hydrastinine with 8 per cent. sodium amalgam in dilute sulphuric acid solution; the yield of crystalline product is 90 per cent. of the base employed.

Hydrohydrastinine methiodide, $C_{11}H_{13}NO_2, MeI$, is deposited in colourless crystals when a slight excess of the theoretical quantity of methyl iodide is added to a methyl alcoholic solution of hydrohydrastinine, and the mixture kept for some time; it crystallises from hot water in needles, and from dilute alcohol in iridescent plates, melts at $227-228^\circ$, and is not acted on by boiling, concentrated potash, or when melted with potash. The *platinochloride*, $(C_{12}H_{16}NO_2Cl)_2, PtCl_4$, is formed when an aqueous solution of the methiodide is digested with silver chloride, and the filtrate treated with platinic chloride; it crystallises from hot water in well-defined needles, and melts at 230° .

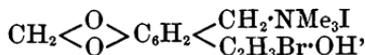
Methylhydrohydrastinine, $CH_2 \left\langle \begin{array}{c} O \\ \diagup \quad \diagdown \\ O \end{array} \right\rangle C_6H_2 \left\langle \begin{array}{c} CH_2 \cdot NMe_2 \\ \diagup \quad \diagdown \\ CH:CH_2 \end{array} \right\rangle$, can be obtained by digesting an aqueous solution of the methiodide just described with silver chloride, and decomposing the product with boiling, concentrated potash; it is an almost colourless, moderately mobile oil, having an amine-like odour, and strong basic properties; it is soluble in ether, alcohol, and carbon bisulphide, and cannot be distilled. The *hydriodide*, $C_{12}H_{15}NO_2, HI$, is easily obtained by dissolving the base in dilute hydrochloric acid, and adding potassium iodide to the solution; it crystallises from hot water in colourless, lustrous, hexagonal prisms, melts at $220-221^\circ$, and is decomposed by potash. On adding potassium dichromate to a dilute solution of the hydriodide, a golden-yellow substance is precipitated in needles which melt at 150° with decomposition. The *platinochloride*,



separates from hot alcohol and water in ill-defined crystals, and melts at 171° . The *methiodide*, $C_{12}H_{15}NO_2, MeI$, is formed by the direct combination of the base with methyl iodide in alcoholic solution; it crystallises from hot water in transparent, hexagonal prisms, melts at $216-217^\circ$, and is not decomposed by boiling concentrated alkalis. The *methochloride*, $C_{12}H_{15}NO_2, MeCl$, is obtained in the form of microscopic, hexagonal prisms when an aqueous solution of the methiodide is digested with silver chloride, and the filtrate evaporated; it crystallises from alcohol in lustrous plates melting at 211° . Its *platinochloride*, $(C_{13}H_{18}NO_2Cl)_2, PtCl_4$, is an indistinctly crystalline compound which melts at 221° , and is almost insoluble in water; the corresponding *aurochloride*, $C_{13}H_{18}NO_2Cl, AuCl_3$, is a yellow, crystalline, sparingly soluble substance melting at 153° . The *ammonium base*, $C_{12}H_{15}NO_2, MeOH$, is a strongly alkaline syrup, readily soluble in water.

Bromomethylhydrohydrastinine, $C_{12}H_{14}NO_2, Br$, is obtained when methylhydrohydrastinine is treated with bromine in carbon bisulphide solution until a permanent coloration is produced, and the brown, semi-solid product agitated with dilute soda. It crystallises from hot water in octahedra, melts at 187° , and is soluble in alcohol.

Bromohydroxymethylhydrohydrastinine methiodide,



is formed when an aqueous solution of methylhydrodrastinine methochloride is treated with bromine-water until a permanent coloration is produced, and the concentrated solution of the product mixed with potassium iodide; it crystallises from water in colourless prisms melting at 177°.

F. S. K.

Pseudotropine. By C. LIEBERMANN (*Ber.*, 24, 2587).—The author has examined the products of oxidation of pseudotropine. The method employed is the same as that employed for the oxidation of ecgonine and tropine (*Abstr.*, 1890, 1449; this vol., p. 749). The main product is tropic acid. It shows all the properties formerly assigned to this compound, has the same solubility in water and alcohol, has a strongly acid reaction, melts at 251°, and dissolves copper oxide and silver oxide. The silver solution deposits a metallic mirror on warming. The solution of the acid reduces potassium permanganate. The *copper* salt, dried at 125°, has the composition $\text{C}_8\text{H}_{12}\text{NO}_4 \cdot \text{CuOH}$. Together with the above acid, ecgonic acid is also obtained.

E. C. R.

Alkaloids of the Areca Nut. By E. JAHNS (*Ber.*, 24, 2615—2617; compare this vol., p. 94).—Further investigation has shown that both arecoline and arecaidine exist ready formed in the areca nut, and that the latter is not derived from the former in the process of extraction. Arecaidine and arecaine are most easily separated by treatment with hydrochloric acid and methyl alcohol, since the former is thereby converted into its methyl derivative, arecoline, whilst the latter remains as hydrochloride.

The examination of larger quantities of material has led to the discovery of a fifth alkaloid in areca nut. This has been termed *guvacine*, from *guvaca*, the Indian name for the areca palm. *Guvacine*, $\text{C}_6\text{H}_9\text{NO}_2$, forms small, lustrous, anhydrous crystals, melts at 271—272° with decomposition, and has a neutral reaction. It does not dissolve in ether, chloroform, benzene, or strong alcohol, but is tolerably soluble in water and dilute alcohol, although to a less degree than the other two crystalline alkaloids. The salts crystallise well, have an acid reaction, and resemble the base in their behaviour with the ordinary solvents. The *hydrochloride*, $\text{C}_6\text{H}_9\text{NO}_2 \cdot \text{HCl}$, crystallises in broad, flat, anhydrous prisms, and is tolerably soluble in water, but only very sparingly in dilute hydrochloric acid; the *sulphate* forms silvery scales; the *nitrate* crystallises in lustrous prisms. The *platinochloride*, $(\text{C}_6\text{H}_9\text{NO}_2)_2 \cdot \text{H}_2\text{PtCl}_6 + 4\text{H}_2\text{O}$, crystallises from water in hexagonal prisms resembling those of the choline derivative, and melts at 211° with frothing and decomposition, whilst the *aurochloride*, $\text{C}_6\text{H}_9\text{NO}_2 \cdot \text{HAuCl}_4$, forms broad, flat prisms which melt at about 194—195°. Search is being made for other alkaloids in the areca nut.

W. P. W.

Lupinidine from White Lupines (*Lupinus albus*, Lin.). By G. CAMPANI and S. GRIMALDI (*L'Orosi*, **14**, 19—24, and *Gazzetta*, **21**, 432—437).—After an historical review of the subject, the authors describe their method of preparing considerable quantities of the extract of lupines, and of separating the alkaloid as platinochloride. This salt has the composition $(C_8H_{15}N)_2 \cdot H_2PtCl_6 + 2H_2O$, as stated by Baumert (*Annalen*, **224**, 325). The free alkaloid, *lupinidine*, $C_8H_{15}N$, when freshly prepared, is a pale-yellow, heavy, oily, alkaline liquid, with an extremely bitter and pungent taste; it is freely soluble in water and alcohol, but only sparingly in ether. It hardens on exposure to air, acquiring a yellowish-brown colour. If it is kept for a few days in a sealed tube, groups of white, acicular crystals separate, and gradually increase until the presence of liquid is almost concealed. This is probably due to the presence of a crystallisable hydrated lupinidine, $C_8H_{15}N \cdot H_2O$, side by side with the anhydrous alkaloid. According to Bufalini, 0.5 c.c. of the solution of the hydrochloride causes death in frogs in a couple of hours, symptoms of general paralysis being previously induced.

S. B. A. A.

Formation of Carbamide by the Decomposition of Arginine. By E. SCHULZE and A. LIKIERNIK (*Ber.*, **24**, 2701—2704).—When arginine (compare Schulze, this vol., p. 857) is boiled with a saturated solution of barium hydroxide, it is decomposed with formation of carbamide; it shows, therefore, a behaviour similar to that of lysatine (compare Drechsel, this vol., p. 95).

F. S. K.

Heat-coagulation of Proteïds. By J. CORIN and Q. AUSIAUX (*Bullet. de l'Acad. roy. de Belgique*, **21**, 345—361).—In a number of experiments made with ox-serum, the statement made by Halliburton (*J. Physiol.*, **5**), that two serum-albumins, separable by fractional heat-coagulation, are present, is confirmed. The temperatures of coagulation found were 73—74° and 79—80° respectively. These temperatures are rather lower than those given by Halliburton, as the true temperature of coagulation is taken as the point when opalescence first occurs. In this last point they agree with Haycraft and Duggan, but differ from them in finding that the concentration of a solution of proteïd has very little influence on the temperature of coagulation; the acidity, however, must be kept constant.

W. D. H.

Toxalbumin Secreted by the Microbe of Blennorrhagic Pus. By HUGOUNENQ and ERAUD (*Compt. rend.*, **113**, 145—147).—Peptonised beef tea that has served for the cultivation of the micrococcus of blennorrhagic pus, when filtered through porcelain and mixed with excess of alcohol, yields a solid substance, which, when redissolved in water, again filtered through porcelain, and again precipitated by alcohol, yields an amorphous, yellowish-white solid, very soluble in water, and resembling the albuminoïds in its chemical and physical properties. It is not coagulated by heat, or by nitric acid, is slowly precipitated by potassium ferrocyanide and acetic acid, but not by magnesium sulphate. It has no diastatic action on starch, sugar, or fibrin, and, when exposed to air in a moist condition, it putrefies

rapidly, with development of a very peculiar odour. It leaves no appreciable residue on incineration, contains phosphorus and 11.45 per cent. of nitrogen, but is free from sulphur. A solution of the toxalbumin sterilised by filtration has no injurious effect when injected under the skin of the dog, and placed on the eye, or in the urethra, but if injected into the testicle it causes suppuration and complete atrophy. No similar effects are produced by the sterilised beef tea or the peptone.

If a solution of asparagine containing meat ashes is used as the cultivation fluid, the microbe develops more slowly, and no toxalbumin is formed. It follows, therefore, that the latter is not simply a secretion of the microbe, but results from its action on the peptone.

C. H. B.

Conversion of Carboxy-hæmoglobin into Methæmoglobin, and Detection of Carbonic Oxide in Blood. By H. BERTIN-SANS and J. MOITESSIER (*Compt. rend.*, 113, 210—211).—The authors find that, contrary to the statements of Weil and of von Anrep, when carboxy-hæmoglobin is mixed with potassium ferricyanide, no compound of carbonic oxide and methæmoglobin is formed, but the product is simply a solution of carbonic oxide in a solution of methæmoglobin, from which it is expelled by the passage of hydrogen or carbonic anhydride, or by being placed in a vacuum, as easily as it is from its solution in water.

In order to detect carbonic oxide in blood, the latter is diluted with twice its volume of water, and mixed with sufficient powdered potassium ferricyanide to ensure complete conversion into methæmoglobin. The flask is then made vacuous, and the gas pumped out is passed into a solution of oxyhæmoglobin contained in a suitable absorption tube. With 400 c.c. of blood, a quantity of carbonic oxide amounting to only one-fifteenth of its volume, can be recognised.

C. H. B.
