

## Organic Chemistry.

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**Chemical Effects of the Silent Electric Discharge.** By MARCELLIN E. BERTHELOT (*Compt. rend.*, 1898, **126**, 561—567, 567—575, 609—616, 616—627).—The author has made a new series of experiments on the chemical effects of the silent electrical discharge, with particular reference to the combination of nitrogen with various carbon compounds. The compound or mixture under examination was enclosed in a narrow space (about 1 mm. across), through which passed the discharge from a coil fitted with a Marcel-Deprez contact-breaker, and connected with a Leyden jar. The spark from the coil under these conditions was 12 to 15 mm. in length; the discharges were alternating. As a rule, the discharge was allowed to act for 24 hours. Liquids with a high vapour tension behaved very much like gases, whereas in the case of liquids such as oil, with a very low vapour tension, it was almost impossible to reach the limit of the reaction. In many cases, the intermediate products were examined, and were usually found to differ materially from the final products. The relative velocities of the primary and secondary reactions play an important part in determining the final result. The velocity and nature of the reactions seem to be functions of the intensity of the discharge. Under all circumstances, it is important to avoid any actual sparking. As a rule, the final equilibrium is dependent on the formation of solid or resinous products which have a low vapour tension and a low electric conductivity.

When absorption of nitrogen takes place, the product is of the nature of an amine or an amido-derivative, and frequently seems to be a poly-amine; azo-, nitroso-, and nitro-derivatives, hydrazines, hydrogen cyanide, or ammonium cyanide are not formed.

Several hydrocarbons were examined, both alone and when mixed with an equal volume of nitrogen. Methane loses about half its hydrogen, and yields a solid product,  $C_{10}H_{18}$ ; a small quantity of acetylene is formed in the early stages of the decomposition, but afterwards disappears. In presence of nitrogen, the methane loses about half its hydrogen, and the nitrogen absorbed is rather less than one-fourth of the volume of hydrogen liberated; the solid product, which has the empirical composition  $C_2H_3N$ , and is probably a tetramine of the nature of a polymerised acetylenamine, is alkaline to litmus.

Ethane loses about one-third of its hydrogen, and the condensation product,  $C_{10}H_{18}$ , has practically the same composition as the product from methane, but is not identical with it. In presence of nitrogen, the solid product,  $C_{16}H_{32}N_4$ , is similar to that obtained from methane, except that the ratio of carbon to nitrogen in the product from ethane is twice as high as in the product from methane. Ethylene is rapidly condensed to a liquid under the influence of the discharge, whilst small quantities of acetylene and ethane are formed; the latter eventually disappear, and the solid product has the composition  $C_8H_{14}$ . In presence of nitrogen, the product is an alkaline solid of

the composition  $C_{16}H_{32}N_4$ , the volume of nitrogen absorbed being practically equal to the volume of hydrogen liberated.

Acetylene yields first a liquid, and afterwards a solid, which decomposes explosively when heated, and is rapidly oxidised when exposed to air. In presence of nitrogen, the phenomena are at first the same as with acetylene alone, but after a time the nitrogen is absorbed, with formation of a solid product,  $C_{16}H_{16}N_2$ . No hydrogen is liberated.

Propylene at first condenses rapidly to a liquid, and afterwards a solid is formed of the composition  $C_{15}H_{26}$ , some hydrogen being liberated. With nitrogen, the phenomena are similar, but gradually nitrogen is absorbed and hydrogen is liberated, the product,  $C_{15}H_{28}N_4$ , being a whitish resin with an alkaline reaction, the volume of nitrogen absorbed being practically double that of the hydrogen liberated.

Trimethylene, when alone, behaves in the same way as propylene, and yields practically the same product; but in presence of nitrogen, the product, although similar to that from propylene, contains less hydrogen, the volume of hydrogen liberated being practically equal to the volume of nitrogen absorbed.

Allylene rapidly condenses to a solid with a pungent empyreumatic odour, a small quantity of hydrogen being liberated in presence of nitrogen. No hydrogen is liberated, but the nitrogen is absorbed, and the product has the composition  $C_{15}H_{20}N_2$ .

Carbonic oxide is converted by the discharge into carbonic anhydride and the suboxide,  $C_4O_3$ , as the author and Brodie showed many years ago; the suboxide is a brown solid which dissolves in water, and forms an acid solution. In presence of nitrogen, the results are the same as with carbonic oxide alone. In presence of excess of hydrogen, the two gases condense in practically equal volumes, without formation of either carbonic anhydride or acetylene. The product  $(CH_2O)_n$  is a mixture of polymerides of formaldehyde, some being soluble and others insoluble in water; they have no reducing action on Fehling's solution. When the carbonic oxide is in excess and not the hydrogen, the product has the empirical composition  $C_3H_4O_3$ , and its aqueous solution has some reducing power. With carbonic oxide, nitrogen, and hydrogen, the product  $(CH_3NO)_n$  may be regarded as a condensed formamide. When the hydrogen in the gaseous mixture is not in excess, the product is a mixture of substances which dissolve in water and yield ammonia when boiled with an alkali, and substances which are insoluble in water and seem to be related to the quinolines. The complex nitrogen derivatives may be regarded as formed by the substitution of nitrogen in the carbohydrate formed by the action of the discharge on the carbonic oxide and nitrogen.

Carbonic anhydride alone yields percarbonic anhydride and the suboxide previously described. With a mixture of carbonic anhydride with twice its volume of hydrogen, the product is a carbohydrate identical with that formed by carbonic oxide under similar conditions. If the anhydride is mixed with an equal volume of nitrogen and three times its volume of hydrogen, the residual gas contains no carbon, but consists of equal volumes of nitrogen and hydrogen; the solid product, when heated with water, yields an effervescent solution containing ammonium nitrite. It may be regarded as a mixture of ammonium

nitrite with the amido-compound formed by carbonic oxide; possibly it may be a true azo-compound dissociable by water. With 4 vols. of hydrogen instead of 6, more of the nitrogen is left.

The action of the silent discharge on carbonic oxide or carbonic anhydride in presence of hydrogen and nitrogen may be compared with the interactions of water and carbonic anhydride in plants, or with the action of heat on salts of formic acid. The general results confirm the author's earlier views as to the great importance of the  $\text{CH}_2\text{O}$  group and its reactions.

In the experiments with alcohols, the reaction was, as a rule, carried to its limit wherever possible.

With methylic alcohol and nitrogen, the latter is absorbed and an equal volume of hydrogen is liberated, together with a small quantity of carbonic oxide; the solid product contains  $\text{C}_4\text{H}_{12}\text{N}_2\text{O}_4$ , and is probably one of the complex amidines or their hydrates. At the beginning of the reaction, some hydrogen, methane, carbonic oxide, and carbonic anhydride are formed, and at a later stage the proportion of methane is still higher, but eventually it disappears, together with the carbonic anhydride.

Ethylic alcohol in presence of nitrogen yields hydrogen, traces of carbonic anhydride, and a solid product,  $\text{C}_{10}\text{H}_{20}\text{N}_4\text{O}_5$ ; the hydrogen liberated per molecule of ethylic alcohol is double that liberated per molecule of methylic alcohol, and the same ratio holds good for the quantity of nitrogen absorbed. In the early stages of the reaction, ethane and carbonic oxide are formed, but subsequently disappear.

Propylic and isopropylic alcohols behave in much the same way as ethylic alcohol. Nitrogen is absorbed, and twice as much hydrogen is liberated; the solid product is  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2$ .

Allylic alcohol yields a strongly alkaline solid product, the empirical formula of which is  $\text{C}_9\text{H}_{16}\text{N}_2\text{O}_3$ . The quantity of hydrogen liberated is very small, and is equal to about one-third of the volume of nitrogen absorbed.

Phenol, under similar conditions, absorbs nitrogen, but no other gas is liberated, and the solid remains neutral. In the case of dihydric phenols, very little nitrogen is absorbed by the meta- and para-derivatives, but the ortho-derivative absorbs a considerable quantity, and yields a neutral product. Pyrogallol absorbs a small quantity of nitrogen, and gives off small quantities of hydrogen and carbonic oxide.

Glycollic ether, with an equal volume of nitrogen, yields small quantities of ethane and hydrogen, but no carbon oxides. A volume of nitrogen equal to the volume of the glycollic ether is absorbed, and the solid product contains  $(\text{C}_2\text{H}_4\text{N}_2\text{O})_n$ . It is an isomeride of cyanamide hydrate.

Methylic ether, with excess of nitrogen, yields the substance  $\text{C}_2\text{H}_{4\cdot3}\text{ON}_{1\cdot25}$ , the ratios approximating closely to those of the compound obtained from ethylic alcohol; hydrogen is liberated in quantity larger than the nitrogen absorbed, but neither carbon oxides nor acetylene is formed.

Ether, with excess of nitrogen, yields a substance,  $\text{C}_4\text{H}_{6\cdot4}\text{N}_2\text{O}$ , the hydrogen liberated having about double the volume of the nitrogen

absorbed, whilst the latter is practically equal to the volume of the ether in the form of gas.

Most of the products formed in presence of nitrogen are probably closed chain compounds belonging to the pyridine and quinoline groups.

C. H. B.

**Formation of Mixed Hydrates of Acetylene and of other Gases.** By ROBERT DE FORCRAND and SULLY THOMAS (*Compt. rend.*, 1897, 125, 109—111).—A crystalline mixed hydrate is obtained when pure acetylene gas saturated with carbon tetrachloride vapour is passed into a flask containing small pieces of ice, and kept at 0°. The pressure in the flask is kept at about 1½ atmospheres by making the outlet tube dip under mercury. The crystals are stable at the atmospheric pressure at temperatures below +5°; at higher temperatures they decompose, evolving a considerable quantity of acetylene. The compound is a mixed hydrate of acetylene and carbon tetrachloride, and is more stable than the simple hydrate of acetylene. Similar compounds have been obtained by using chloroform, ethylenic chloride, methylic iodide, bromoform, tribromomethane, methylenic chloride, or iodide and methylchloroform. Similar compounds may also be obtained by using ethylene, carbonic anhydride, or sulphurous anhydride in place of acetylene.

J. J. S.

**Interaction of Cyanides with Thiosulphates.** By LEONARD DOBBIN (*Chem. News*, 1898, 77, 131).—By grinding together potassium cyanide and potassium thiosulphate and leaving them in contact, the change represented by the equation  $K_2S_2O_3 + KCN = K_2SO_3 + KCNS$  gradually but completely ensues.

D. A. L.

**Dichlorhydrin and Epichlorhydrin.** By HUGO FLEMMING (*Chem. Zeit.*, 1897, 21, 97. Compare *Abstr.*, 1896, i, 333).—Dichlorhydrin, and especially epichlorhydrin, are good solvents for different nitrated celluloses, and also for such substances as celluloid. Gun cotton is readily soluble in epichlorhydrin, but even a 20 per cent. solution is so thick that it requires diluting with alcohol before being used as a varnish. It is suggested that these solvents possess several advantages over the usual solvents employed in the nitrated cellulose industries.

J. J. S.

**Melibiose.** By A. BAU (*Chem. Zeit.*, 1897, 21, 185—188).—The author's determinations of the specific rotatory power of melibiose differ somewhat from those made by Scheibler and Mittelmeier (*Abstr.*, 1890, 1085), but in no case has a crystalline material been obtained, so that even these numbers may not be absolutely correct. The melibiose was obtained from melitriose both by acid inversion and by fermentation. As the result of some 24 determinations  $[a]_D = +134\cdot25$ , or calculated for the ash-free compound  $[a]_D = +136\cdot17$ . The strength of the different solutions was calculated in most cases from Brix's table of the specific gravities at 17·5°. Scheibler's number is +126·7—+126·9°, and the fact that it is low is probably due to the formation of decomposition products during the boiling with alcohol.

It has been found that moderately concentrated solutions of melibiose have a higher reduction factor than very concentrated solutions, when the boiling is continued for 4 minutes; when boiled for a longer time, a further quantity of cuprous oxide is precipitated. The factor for 4 minutes is about 90—93 per cent. of that for maltose.

Compounds with calcium, barium, strontium, potassium, and sodium have been prepared; these resemble the corresponding derivatives of milk-sugar. It also resembles milk-sugar in its hydrolysis, it is inverted by hydrochloric, sulphuric, or oxalic acid, but not by lactic, tartaric, or citric acid. For inversion by melibiase, compare Abstr., 1896, i, 453. Melibiase is not fermented by *Saccharomyces cerevisiae*, OF, UF, OS, US; *S. ellipsoideus*, II, Hansen; *S. apiculatus*; *S. Logos* (Van Laer); *Monilia candida*; nor by *Schizosaccharomyces Pombe* (Lindner). Melitriose is not fermented by *Saccharomyces apiculatus*. Melibiase is used technically for determining whether a top yeast is adulterated with a bottom yeast.

J. J. S.

**Arabinose and Semicarbazide.** By WILHELM HERZFELD (*Chem. Centr.*, 1897, ii, 894; from *Zeit. Ver. Rübenzuck.-Ind.*, 1897, 604—605).—When hot solutions of arabinose (1 mol.) and semicarbazide (1 mol.) in 95 per cent. alcohol are mixed, boiled for an hour, and the mixture then evaporated, crystals of *arabinosesemicarbazide*,  $C_6H_{13}N_3O_5$ , are obtained; this melts and decomposes at 163—164°, is easily soluble in cold water, insoluble in ether, benzene, and chloroform, and dissolves in methylic or ethylic alcohol only on boiling for some time. The rotatory power of an alcoholic solution containing 0·5 gram in 100 c.c. is  $-0\cdot35^\circ$ , and of an aqueous solution containing 0·1 gram in 50 c.c.  $-0\cdot15^\circ$ . Benzylidenesemicarbazide is obtained by boiling an aqueous solution of arabinosesemicarbazide with benzaldehyde; after filtering, the solution is dextrorotatory. E. W. W.

**Effect of Pressure and Temperature on the Conversion of Starch into Sugar.** By FRIEDRICH LIPPmann (*Chem. Centr.*, 1897, ii, 557; from *Österr. Zeit. Zucker-Ind.*, 26, 657—668).—The author describes processes of saccharification carried out under pressures obtained by the use of compressed gases, but at temperatures only slightly above 100°. A number of experiments are described in which pure potato-starch was treated with 3 per cent. of its weight of concentrated sulphuric acid diluted with 10 times its volume of water. Heating was effected by blowing in steam, and the various pressures were obtained by using compressed air, carbonic anhydride, or sulphurous anhydride. The results of 8 experiments showed that as the pressure is increased, the diminution in the time required to effect the conversion becomes relatively less and less, and that the most rapid conversion is obtained when the temperature corresponds to the boiling point of the solution at the given pressure. Rise of temperature has much more effect than increase of pressure, but at temperatures above 120—130° the processes of decomposition and recombination about balance. The best results showed on the average a content of about 96 per cent. of dextrose. Other conditions being similar, pressure has little effect on the purity of the product.

E. W. W.

**Action of Diastase on Ungelatinised Starch.** By ELEK VON SIGMOND (*Chem. Centr.*, 1897, ii, 614; from *Woch. Brauerei*, 14, 412).—According to the author, the results obtained by Lintner's method (*Woch. Brauerei*, 1890, 22) are uncertain if the mixture is not stirred. From experiments in which a mixture of 2 grams of starch with 50 grams of water and 50 c.c. of malt extract were kept stirred, the author finds that the temperatures of gelatinisation and of solution of potato-starch are identical, namely, 65°; for maize-starch these temperatures are 68° and 70° respectively; for rice-starch, 72° and 83°; for wheat-starch, 62° and 60—65°, and for rye-starch, 55° and 55—60° respectively. When potato-starch is heated with diastase at 65°, 93·06 per cent. is inverted; under similar conditions, 63·5 of maize-starch, 25·3 of rice-starch, 94·26 of wheat-starch, and 91·28 per cent. of rye-starch undergo this change. The author is unable to confirm Lintner's statement with reference to the similarity of the behaviour of maize- and rice-starch, and finds, moreover, that wheat-starch is more readily attacked at 60° than rye-starch.

E. W. W.

**A New Carbohydrate. Caroubin.** By JEAN EFFRONT (*Compt. rend.*, 1897, 125, 38—40).—The grain of *Ceratonia siliqua* has the following composition:—Water, 11·40; nitrogenous matter, 18·92; carbohydrates, 62·00, and fatty matter, 2·3 per cent. The nitrogenous matter is very unequally distributed in the grain. The carbohydrates of the albumen are completely absorbed during germination, whilst those of the spermoderm are not. The carbohydrate of the albumen, for which the author suggests the name *caroubin*, resembles to a certain extent *d*-galactan, but differs from it in its products of hydrolysis; its method of extraction is given in detail. It is a white, spongy, friable substance having the same percentage composition as cellulose. Placed in contact with water, or with normal sodium hydroxide, it forms a jelly or transparent viscid mass, the addition of 3—4 grams of the substance to a litre of water giving the liquid the consistency of a thin syrup. Cold hydrochloric acid dissolves it, but the liquid does not reduce Fehling's solution. With hot nitric acid, it yields levulinic acid. Dilute warm mineral acids hydrolyse the carbohydrate, yielding a dextrogyrate solution which has strong reducing properties.

J. J. S.

**Theory of the Sulphite Process and the Constitution of Lignin.** By PETER KLASON (*Bied. Centr.*, 1898, 27, 138; from *Svensk kem. tidskr.*, 1897, 9, 135—138).—When coniferin is heated at 108° with calcium hydrogen sulphite, the coniferylic alcohol combines with the sulphite, forming a salt of the dibasic coniferylsulphonic acid. This can only be explained on the assumption that the alcohol of the coniferin contains the group  $-\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$ , and the ring being necessarily broken when the sugar is eliminated, an unsaturated compound, or else polymerisation, results.

The behaviour of the lignin of pine wood (lignylglycide) indicates that it is also a glucoside containing an aromatic group. It contains, besides methoxyl, hydroxyl, and active carbonyl groups. The number

of carbon atoms it contains is between 18 and 22. When wood containing lignin is boiled with calcium hydrogen sulphite, the lignylglycide is converted into readily soluble sulphonate, but when the wood is treated with dilute mineral acids, the lignylglycide is converted into a dark-coloured resin containing about 40 carbon atoms.

N. H. J. M.

**Methylhydroxyethylamine and Methyldihydroxydiethylamine.** By LUDWIG KNORR and HERMANN MATTHES (*Ber.*, 1898, 31, 1069—1072. Compare *Abstr.*, 1889, 1218).—Methylhydroxyethylamine and methyldihydroxydiethylamine have now been prepared pure by the method previously described (*Abstr.*, 1897, 313). Methylhydroxyethylamine boils at 159°, is a colourless, strongly basic oil, with a characteristic odour, fumes in the air, has a sp. gr. = 0·9370 at 20°/4°, and an index of refraction  $n_D = 1\cdot4385$  at 20°, and is miscible with water, alcohol, and ether. It yields precipitates with mercuric chloride, phosphomolybdic acid, and potassium bismuthiodide. The *picrate* forms slender, matted needles melting at 148—150°; the *aurochloride* crystallises in anhydrous prisms melting at 145—146°, and the *platinochloride* in compact tablets decomposing at 125—130°.

Methyldihydroxydiethylamine is a thick, colourless, strongly basic oil which fumes in the air, boils at 246—248° (corr.) under a pressure of 747 mm., and is miscible with water and alcohol, but is only sparingly soluble in ether. It has a sp. gr. = 1·0377 at 20°/4°, and an index of refraction  $n_D = 1\cdot4678$  at 20°. It yields precipitates with mercuric chloride phosphomolybdic acid, tannin, and potassium bismuthiodide. The *picrate* melts at 94—95°, and the *aurochloride* at 101—102°, whilst the *platinochloride* decomposes at 148—150°.

A. H.

**Alcohol Bases from Ethylamine.** By LUDWIG KNORR and WERNER SCHMIDT (*Ber.*, 1898, 31, 1072—1077).—Ethylene oxide reacts vigorously with ethylamine, forming a mixture of hydroxydiethylamine and dihydroxytriethylamine, which can be separated by fractional distillation. *Hydroxydiethylamine*,  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHET}$ , is a colourless, strongly basic oil, which has a faint odour, and boils at 167—169° (corr.) under a pressure of 751 mm., its vapour fuming strongly in the air. It is easily soluble in water, alcohol, and ether, and readily attacks copper and brass, as well as organic tissues. It has a sp. gr. = 0·9140 at 20°/4°, and a molecular refraction = 25·66, the index of refraction,  $n_D$ , being 1·4440 at 20°. It yields characteristic precipitates with mercuric chloride, phosphomolybdic acid, potassium cadmio-iodide, tannin, and potassium bismuthiodide.

The *hydrochloride* forms lustrous, deliquescent needles, whilst the *aurochloride* crystallises in light yellow needles melting at 127°, and the *platinochloride* forms deliquescent crystals which decompose at about 146°. The *picrate* crystallises in pale yellow, monosymmetric prisms melting at 125—127°.

*Dihydroxytriethylamine*,  $\text{N}(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH})_2$ , is a yellowish oil which has a slight ammoniacal odour, and boils at 251—252° (corr.) under a pressure of 750 mm. It is only sparingly soluble

in ether, is very hygroscopic, and readily attacks copper and the epidermis, but has little action on cork ; the sp. gr. = 1·0135 at 20°/4°, and the molecular refraction = 36·37, the index of refraction,  $n_D$ , being 1·4663 at 20°. The base yields characteristic precipitates with mercuric chloride, phosphomolybdic acid, potassium cadmioiodide, tannin, and potassium bismuthiodide. The *picrate* crystallises in yellow fascicular groups of needles melting at 100—101°. The *hydrochloride* forms deliquescent plates, whilst the *aurochloride* crystallises in light orange-yellow prisms melting at 81°, and the *platinochloride*,  $(C_6H_{15}NO_2)_2H_2PtCl_6 + H_2O$ , forms flat, orange-yellow hygroscopic prisms which melt at 49—50°, whereas the anhydrous salt melts at 108—110°. The *ethiodide*,  $C_6H_{15}NO_2EtI$ , forms lustrous, thin plates melting at 212—214°.

A. H.

**Relation of Tervalent to Quinquivalent Nitrogen.** By ARTHUR LACHMAN (*Amer. Chem. J.*, 1898, 20, 283—288).—Dimethylnitrosamine and diethylnitrosamine form hydrochlorides which are very unstable salts, readily decomposing at a slightly elevated temperature into nitrosyl chloride and the amine. Diphenylnitrosamine takes up dry hydrogen chloride at ordinary temperatures, with immediate elimination of nitrosyl chloride.

Diethylnitrosamine reacts rapidly with zinc ethyl when heated to 100°, basic gases being given off and tarry matter remaining ; but diphenylnitrosamine reacts violently with zinc ethyl to form an amorphous, yellow additive product of unknown composition, melting at about 135°. Water converts it into zinc hydroxide, diphenylamine, and an unstable base which reduces Fehling's solution.

When hydroxylamine acts on diphenylnitrosamine, an additive product is formed which at once decomposes into nitrous oxide and diphenylamine.

It appears that, in all these cases, the quinquivalent nitrogen compound readily splits up into simpler substances containing tervalent nitrogen. A diversity among the attached groups is necessary for the existence of quinquivalent nitrogen, for no compound is known in which all five radicles are alike in chemical character, and all attempts to prepare such a compound have proved abortive.

A. W. C.

**Diacetonehydroxylamine, and Stereoisomeric Aliphatic Ketoximes.** By CARL D. HARRIES and LUDWIG JABLONSKI (*Ber.*, 1898, 31, 1371—1384. Compare this vol., i, 121).—The absence of stereoisomerism among the oximes of unsymmetrical aliphatic ketones has been already the subject of remark (compare Meyer and Scharvin, *Abstr.*, 1897, i, 612), but no satisfactory explanation of the circumstance has been put forward. The authors have found that the oxime of mesitylic oxide is an exception to this rule, being capable of existence in two forms, which probably owe their isomerism to steric influences.

Another ketone having an ethylenic linking in the  $\alpha\beta$ -position has been shown to yield isomeric oximes ; methylcyclohexenoneoxime, prepared by Hagemann, melts at 88—89° (*Abstr.*, 1893, i, 393), whilst the substance described by Knoevenagel (*Abstr.*, 1895, i, 48) melts at 50—60°. The authors have heated the hydrochloride of the latter

form at 80°, obtaining in this manner the salt of the other modification; they therefore regard the oxime having the higher melting point as the analogue of stable mesityloxime, the more readily fusible derivative corresponding to labile mesityloxime.

*Diacetonehydroxylamine*, OH·NH·CMe<sub>2</sub>·CH<sub>2</sub>·COMe, is prepared by the action of hydroxylamine on mesitylic oxide in presence of sodium methoxide, and is purified by conversion into the oxalate; it crystallises from light petroleum, melts at 52°, and boils at 94—95° under a pressure of 9—10 mm. The substance is very hygroscopic, dissolving in water and organic solvents; it reduces Fehling's solution immediately when gently heated. The *oxalate*, which crystallises from a mixture of alcohol and ether, and melts at 145—147°, is extremely soluble in absolute alcohol; the *picrate* melts at 107—108°, the *hydrochloride* is hygroscopic, and the *platinochloride* and *aurochloride* crystallise slowly in six-sided prisms. The *benzoyl* derivative crystallises in lustrous leaflets, and melts at 165°; it dissolves in dilute caustic soda, and does not reduce Fehling's solution. The *phenylthiocarbamide* crystallises from light petroleum, and melts at 110—112°; when gently heated, it reduces Fehling's solution, and when boiled with caustic soda yields mesitylic oxide. Reduction with sodium amalgam converts diacetonehydroxylamine into diacetonealkamine.

*β-Nitrosoisopropylacetone*, NO·CMe<sub>2</sub>·CH<sub>2</sub>·COMe, obtained by boiling a solution of diacetonehydroxylamine in chloroform with mercuric oxide in a reflux apparatus, crystallises in stout, white prisms, and melts to a blue liquid at 75—76°; it is highly volatile, and has a pungent, irritating odour.

*Dinitrosodi-isopropylacetone*, CO(CH<sub>2</sub>·CMe<sub>2</sub>·NO)<sub>2</sub>, is prepared by oxidising triacetonedihydroxylamine under the same conditions; it crystallises from benzene or from toluene, and melts at 132—133° to a deep blue liquid.

*3 : 5 : 5-Trimethyldihydroisoxazole*,  $\text{CMe}_2-\overset{\text{O}}{\underset{\text{CH} \cdot \text{CMe}_2}{\text{N}}}-\text{NH}$ , is another product of the action of hydroxylamine on mesitylic oxide in presence of sodium methoxide; it is a mobile, highly refractive liquid which boils at 52° and 162—164° under pressures of 9 mm. and 760 mm. respectively.

*α-Mesityloxime*, CMe<sub>2</sub>·CH·CMe<sub>2</sub>·NOH, boils at 85° under a pressure of 10 mm.; it dissolves readily in dilute acids and alkalis, and resists the action of Fehling's solution. The *hydrochloride* is prepared by passing dry hydrogen chloride into an ethereal solution of the fraction of the oxime which boils at 92—94°, under a pressure of 15 mm., this fraction having been obtained by the action of free hydroxylamine on the ketone; on adding dry ether to the solution in absolute alcohol, it crystallises in regular, four-sided plates. The salt has no definite melting point, but sinters below 55° and melts at about 62°, although solid fragments remain suspended in the liquid at about 70°; at 80°, it suddenly becomes solid, being converted into the hydrochloride of the stable form.

*β-Mesityloxime* melts at 48—49°, resembling the labile modification in chemical properties; it boils at 92° and 102° under pressures of 9 mm. and 13 mm. respectively. The *hydrochloride*, prepared in the

manner already described, and also by the action of hydroxylamine hydrochloride on mesitylic oxide, crystallises in long needles, and melts and decomposes at  $123^{\circ}$ . The salt is produced when a solution of the labile salt in absolute alcohol is allowed to remain during two days.

The stable modification of methylcyclohexenoneoxime is obtained when hydroxylamine hydrochloride (1 mol.) acts on methylcyclohexenone. When two molecular proportions are employed, the compound,  $C_7H_{14}N_2O_2H_2O$ , is produced; this crystallises from hot water in four-sided prisms, and melts at  $83-84^{\circ}$ . Its behaviour towards mercuric oxide, which converts it into a deep blue nitroso-derivative, shows the substance to be a hydroxylamino-oxime.

M. O. F.

**Alkylic Isocyanates [Carbimides] and Heat of Formation of Liquid Cyanic Acid.** By PAUL LEMOULT (*Compt. rend.*, 1898, 126, 43-45).—In the preparation of alkylcarbimides (alkylic isocyanates) by Wurtz's method, it is necessary to use potassium cyanate which has been recently prepared, and to take care that all the compounds used are free from water. 100 grams of potassium cyanate and 200 grams of sodium ethyl sulphate give about 12 grams of pure ethylic isocyanate; a quantity of the polymeride is formed at the same time.

Methylcarbimide,  $CO:NMe$ , is a colourless liquid boiling at  $40^{\circ}$ , and polymerising with the greatest readiness. The molecular heat of combustion at constant volume is 268.9 Cal., and at constant pressure 269.3 Cal.; the molecular heat of formation at constant pressure is +22.8 Cal. Ethylcarbimide boils at  $60^{\circ}$ . Its molecular heat of combustion at constant volume is 424.2 Cal., and at constant pressure 424.4; its molecular heat of formation is +31 Cal. It follows from these numbers that the two compounds are true homologues. The heat evolved during polymerisation of methylcarbimide is 34.7 Cal., and for ethylcarbimide 34.9 Cal.; taking the mean of these two numbers, and subtracting it from the heat of formation of cyanuric acid (55.45 Cal.) it gives 20.65 Cal., which should be the heat of formation of liquid cyanic acid.

J. J. S.

**Bromacraldehyde and Tribromopropaldehyde.** By OSCAR PILOTY and ALFRED STOCK (*Ber.*, 1898, 31, 1385-1388).—*Bromacraldehyde*,  $CH_2:CBrCHO$ , prepared by the action of a boiling, aqueous solution of sodium acetate on dibromopropaldehyde, is a colourless, mobile liquid having an intensely irritating smell, and gradually undergoes decomposition with development of a yellow coloration. The substance boils at  $28.5^{\circ}$ ,  $37^{\circ}$ ,  $49^{\circ}$ , and  $111^{\circ}$  (corr.), under pressures of 11 mm., 14 mm., 27 mm., and 420 mm. respectively, slowly undergoing decomposition when distilled under atmospheric pressure; it has the sp. gr. = 1.68°. The aldehyde is neutral to litmus, and dissolves somewhat readily in warm water, more sparingly, however, in cold; it reduces Fehling's solution vigorously when heated.

*Tribromopropaldehyde*,  $CH_2BrCBr_2CHO$ , is the product of the action of bromine on the foregoing substance; it has the sp. gr. = 2.51, and remains unchanged when protected from light, which turns it yellow. It boils at  $85.5^{\circ}$  (corr.) under a pressure of 11 mm., but under atmospheric pressure it decomposes above  $155^{\circ}$ , yielding

hydrogen bromide. The aldehyde dissolves with difficulty in cold water, but is miscible with ether, benzene, methylic alcohol, and ethylic alcohol, generating heat with the latter. When exposed to air, it absorbs moisture, yielding the *hydrate* which contains  $2\text{H}_2\text{O}$  and crystallises from water in large rhombic plates; it melts at  $55-57^\circ$ , and reduces Fehling's solution when heated.

M. O. F.

**A New Cyclic Ketone.  $\Delta^6$ -Methylcyclohexenone-3.** By AUGUSTE BÉHAL (*Compt. rend.*, 1898, 126, 46-49).—The benzoyl derivative, melting at  $167^\circ$ , from the ketone isolated from wood oil, when treated with alkalis, gives an oxime melting at  $121.5^\circ$ , and this, on hydrolysis with hydrochloric acid, yields a *ketone*,  $\text{C}_7\text{H}_{10}\text{O}$ , boiling at  $192^\circ$  and melting at  $12^\circ$ . It does not combine with sodium hydrogen sulphite, or yield iodoform on treatment with iodine and alkalis. In carbon bisulphide solution, it readily combines with bromine, yielding a *dibromide* which is easily soluble in warm alcohol or light petroleum. The ketone reacts with phosphorus pentachloride, yielding a deep greenish-blue liquid, which, when distilled in steam, yields a small quantity of a heavy oil with an odour resembling that of terebenthene, a small quantity of a crystalline product and the regenerated ketone. When oxidised with permanganate, the ketone yields acetic and levulinic acids only. The author considers these reactions best agree with the formula for the ketone,



J. J. S.

**Alkylic Salts of Chlor- and Brom-acetic Acid.** By RUDOLF L. STEINLEN (*Chem. Centr.*, 1897, ii, 659; from *Bul. Acad. roy. Belg.*, [iii], 34, 101-108).—*Propylic chloracetate* is an oil of an ethereal odour, of sp. gr. =  $1.0944$  at  $15^\circ/4^\circ$ , and boils at  $149^\circ$ . *Butylic chloracetate* is a colourless liquid of sp. gr. =  $1.0675$  at  $15^\circ/4^\circ$ , boils at  $170^\circ$ , and has an odour similar to the preceding salt. *Propylic bromacetate* is a colourless liquid which soon becomes dark, has a sp. gr. =  $1.4166$  at  $15^\circ/4^\circ$ , and  $1.4099$  at  $20^\circ/4^\circ$ , and boils at  $178^\circ$  under  $765$  mm. pressure; its vapour, like that of the following salts, has a very irritating action on the eyes. *Isopropyllic bromacetate* is a yellowish oil, of sp. gr. =  $1.399$  at  $15^\circ/4^\circ$ , and boils at  $165.5^\circ$  under  $769$  mm. pressure. *Iso-butyllic bromacetate* is a yellowish oil which rapidly becomes dark, boils at  $188^\circ$  under  $752$  mm. pressure, and has sp. gr. =  $1.3327$  at  $15^\circ/4^\circ$ , =  $1.3269$  at  $20^\circ/4^\circ$ . All these substances are insoluble in water and soluble in alcohol and ether.

A table is given showing how the substitution of chlorine by bromine in the analogous alkylic salts of chloracetic or bromacetic acid raises the boiling point regularly by  $16-18^\circ$ .

E. W. W.

**Effect of Temperature on the Acidity of Acids.** By PAUL DEGENER (*Chem. Centr.*, 1897, ii, 936; from *Festschrift Techn. Hochschule Braunschweig*, 1897, 451-464).—When asparagine is titrated with normal alkali in the cold, using unneutralised phenolphthalein as indicator, only  $0.264$  equivalent of alkali is required for each molecule of acid, and if the solution is then heated to  $100^\circ$ , a further quantity of  $0.540$  equivalent of alkali is necessary to neutralise the solution. If the solution is heated to  $100^\circ$  before titrating,  $0.96$  equi-

valent of alkali is required, and, on cooling, the solution becomes alkaline, and, when cold, 0·69 equivalent of sulphuric acid must be added to destroy the red coloration. Ammonia is not liberated when the solutions are heated, and the author attributes this change in acidity to the decomposition of more complex molecules, and not to the hydrolysis of the asparagine. Aspartic acid requires 0·94 equivalent of alkali at 0°, and 1·208 at 100°; the hot neutralised solution becomes alkaline on cooling, and, "after neutralising the excess required 1·024—1·058 equivalents of alkali." (?) To neutralise sulphurous acid in the cold, 15·6 per cent. more alkali than is necessary to form  $K_2SO_3$  must be added, and, when heated, the solution becomes alkaline. According to the author, orthosulphurous acid,  $S(OH)_4$ , is present in the cold solution, and this, when the solution is warmed, decomposes into sulphurous acid and water.

Butyric acid at 0° takes up 97·9, and at 100°, 98·55 per cent. of the calculated amount of alkali; the change of colour is sharp, as is generally the case with acids which contain no hydroxyl groups. Acetic and oxalic acids combine with the theoretical quantity of alkali, both in the cold and when heated. Glutaric acid requires 77—77·5 c.c., and succinic acid, both at 0° and at 100°, 101·7 c.c., instead of 100 c.c. Lactic acid at 0° takes up only sufficient alkali to combine with the carboxyl groups, but, at 100°, 9—12 per cent. more is used. Malic acid requires 93·4 c.c. in the cold, and 95·0 c.c. at 100°, instead of 92·0 c.c., and tartaric acid, when warmed, requires 101 c.c. instead of 100 c.c. In the case of these hydroxy-acids, and also of citric acid, probably some alkali is used to combine with the hydroxyl groups. When tartaric acid is dried at 100°, and a solution of it then at once titrated, only 60 c.c. of alkali are required in the cold, and 89·5 c.c. when heated. According to the author, this is due to the formation, without loss of weight, of an internal anhydride, which is only slowly hydrolysed. Citric acid dried at 100° behaves in a similar way. Phosphoric acid in the cold combines with 63 per cent. of the alkali necessary to form the tribasic phosphate. E. W. W.

**δ-Amidovaleric Acid.** By HEINRICH SALKOWSKI (*Ber.*, 1898, 31, 776—783).—A sample of δ-amidovaleric acid obtained in the putrefaction of glue was compared with a sample prepared synthetically by oxidising benzoylpiperidine with potassium permanganate, and hydrolysing the product with hydrochloric acid (Schotten, *Abstr.*, 1888, 1104), and with another obtained years before (*Abstr.*, 1883, 925) in the putrefaction of fibrin and flesh. The aurochlorides had the same melting point and crystalline form [monoclinic;  $a:b:c = 1\cdot1756:1:1\cdot0043$ ;  $\beta = 48^\circ 23' 40''$ ]; the benzoyl derivatives melt at the same temperature, which is 105·1°, as determined by a thermometer immersed in the solidifying substance.

When the orange aurochloride,  $C_5H_{11}NO_2HAuCl_4 + H_2O$ , is recrystallised from water, a yellow salt, with the unusual composition  $C_5H_{11}NO_2AuCl_3$ , is obtained; this can also be obtained, although with difficulty, by the direct combination of  $AuCl_3$  with amidovaleric acid. Recrystallisation from dilute hydrochloric acid reconverts it into the original aurochloride. C. F. B.

**Use of Zinc Oxide in the Preparation of Fermentation Lactic Acid.** By JOHANNES GADAMER (*Chem. Centr.*, 1897, ii, 937; from *Apoth.-Zeit.*, 12, 642—643).—The author attributes Kassner's failure to obtain lactic acid by fermenting a solution of sugar in presence of zinc oxide (this vol., i, 296) to his using a large quantity of old cheese, which does not induce energetic fermentation, instead of sour milk, which contains abundant lactic acid bacteria. When the latter is employed, zinc dextrolactate is obtained. Calcium carbonate, which Kassner used instead of zinc oxide, is probably a favourable material for the growth of lactic acid bacteria. Commercial lactic acid is either inactive or dextrorotatory.

E. W. W.

**Autoracemisation.** By PAUL WALDEN (*Ber.*, 1898, 31, 1416—1422. Compare this vol., i, 178).—The author has repeatedly shown that, under the influence of heat, the specific rotatory power of halogen substituted ethereal salts readily undergoes change. Data are collected in the present paper showing that compounds of a certain class exhibit diminution of rotatory power after lapse of time, without being submitted to external influences. Of the compounds which have been examined, methylic *d*-bromosuccinate, ethylic *d*-bromosuccinate, isopropylidene *d*-bromosuccinate, isobutylic *d*-bromosuccinate, methylic *d*-phenylbromacetate, isobutylic *d*-phenylbromacetate, and *d*-phenylbromacetic acid exhibit this phenomenon, which, however, is not shown by propylic *d*-bromosuccinate, methylic *d*-chlorosuccinate, isopropylidene *d*-chlorosuccinate, methylic acetylmalic acid, ethylic isobutyrylmalic acid, methylic *d*-chloropropionate, ethylic *d*-phenylchloracetate, ethylic *l*-mandelate, and ethylic isovaleryl-*l*-mandelate.

The author recognises the following points.

1. There exist active compounds, particularly bromine substituted compounds of succinic, propionic, and phenylacetic acids, which exhibit a decrease of rotational activity if kept for a considerable period; in some cases, the rotatory power is completely lost, and the change in question is associated with both liquid and solid states.

2. The diminution or loss of activity is spontaneous, and proceeds without decomposition on the part of the active substance, the composition, and such physical constants as boiling point, density, and refractive index, undergoing no change.

3. The alteration is permanent, and neither fractionation nor crystallisation of the product is capable of restoring the original rotation.

4. The phenomenon depends on the structure of groups which enter compounds of the same type, shown by the difference in behaviour of propylic and isopropylidene *d*-bromosuccinates; it is also associated with the nature of the four groups attached to the asymmetric carbon atom, being non-existent in the case of hydroxy-compounds, hardly recognisable among chloro-derivatives, although well defined in the case of bromo-compounds.

M. O. F.

**Partial Racemism.** By ALBERT LADENBURG and W. HERZ (*Ber.*, 1898, 31, 937—938).—The solubility of the quinine salt of *l*-pyrotartaric acid in alcohol has now been determined, and it has been found that 100 parts of alcohol dissolve 15 parts of this compound, 4·2 parts of the salt of the dextro-acid, and 3·2 parts of the salt of the inactive

acid. From this it follows that the salt of the inactive acid is not a mixture of the salts of the dextro- and laevo-acids, but is an individual salt derived from the racemic acid.

A. H.

**A Method of Preparing Ethylic Alkylideneacetoacetates.** By EMIL KNOEVENAGEL (*Ber.*, 1898, 31, 730—737).—It has been shown that benzaldehyde (1 mol.) will react at a low temperature with ethylic acetoacetate (1 mol.), under the influence of a little piperidine, forming ethylic benzylideneacetoacetate,  $\text{CHPh:CAC}\cdot\text{COOEt}$  (*Abstr.*, 1896, i, 232). This will react with a second molecule of ethylic acetoacetate, yielding ethylic benzylidenediacetoacetate,  $\text{CHPh}(\text{CHAc}\cdot\text{COOEt})_2$  (*Hantzsch, Abstr.*, 1886, 77; *Knoevenagel, Abstr.*, 1896, i, 210). More examples of these reactions have been investigated, both aromatic and aliphatic aldehydes being used. The aldehyde and ethylic acetoacetate were usually mixed at  $-10^\circ$  to  $-15^\circ$ , a small quantity of piperidine was added, one drop at a time and at intervals of several minutes, and the mixture was then allowed to remain at the same temperature, sometimes for a day or two. In some cases the product crystallised out; if it did not, the mixture was washed with dilute sulphuric acid (to remove piperidine) and then with water, dried over dehydrated sodium sulphate, and distilled under diminished pressure. The aldehydes experimented with were cuminaldehyde, orthonitrobenzaldehyde, salicylaldehyde, furfuraldehyde, cinnamaldehyde, acetaldehyde, isobutyraldehyde, isovaleraldehyde, and oenanthaldehyde. Most of the acetoacetates had been obtained before by the use of other condensing agents, such as acetic anhydride or hydrochloric acid; the diacetoacetates obtained were also known previously.

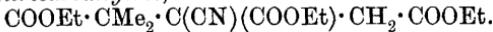
The following compounds, or boiling points, are new, however. *Ethylic cumylideneacetoacetate*, boiling at  $198^\circ$  under 10 mm. pressure. *Ethylic cinnamylideneacetoacetate*, boiling at  $213$ — $214^\circ$  under 17 mm. pressure. *Ethylic oenanthylideneacetoacetate*, boiling at  $145^\circ$  under 10 mm. pressure, and with sp. gr. =  $0.9647$  at  $21^\circ$ . Acetylcoumarin is the product when salicylaldehyde is used; it, as well as its phenylhydrazone (the hygroscopic sodium salt of which melts at  $160^\circ$ ) and oxime were described (Arnot, *Inaug.-Diss.*, Heidelberg, 1896) before the publication of Rap's results (*Gazzetta*, 1897, 27, ii., 498; this vol., i, 317). Ethylic ethylideneacetoacetate boils at  $107^\circ$ ,  $101^\circ$ ,  $96^\circ$ , and  $94^\circ$  under pressures of 20, 15, 11 and 9 mm. respectively. Ethylic isobutylideneacetoacetate boils at  $118$ — $124^\circ$  under 12 mm., ethylic isoamylideneacetoacetate at  $136$ — $138^\circ$  under 9 mm. pressure, and has a sp. gr. =  $0.9623$  at  $21.5^\circ$ .

C. F. B.

**Syntheses by the Aid of Ethylic Cyanosuccinate.** By LÉONCE BARTHE (*Compt. rend.*, 1897, 125, 182—183).—A mixture of sodium (3.45 grams), alcohol (150 c.c.), and ethylic cyanosuccinate (30 grams) is added to trimethylenic bromide, and the mixture heated in a reflux apparatus for 5 hours on the water bath. After distilling off the alcohol, the residue is well washed with water and purified by distillation under diminished pressure, or by crystallising from alcohol. The product, *ethylic  $\beta\beta_1$ -dicyanoheptane-aa, $\beta\beta_1$ -tetracarboxylate* ( $3:7$ -*dicyanononanedioate-3:7-dimethyloate),  $\text{CH}_2[\text{CH}_2\cdot\text{C}(\text{CN})(\text{COOEt})\cdot\text{CH}_2\cdot\text{COOEt}]_2$ ,*

crystallises in white, silky crystals melting at 69° and boiling at 215° under 75 mm. pressure.

When a solution of sodium (2·9 grams) in absolute alcohol is mixed with ethylic cyanosuccinate (25 grams), then added to ethylic *a*-bromoisobutyrate (24 grams), and the reaction completed by heating for 3 hours on the water bath; the product isolated as described above is a colourless oil boiling at 233—235° under 25 mm. pressure, and is *ethylic cyanodimethyltricarballylate*,



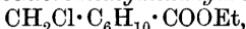
J. J. S.

**The Naphthenes of Russian Petroleum.** By OSSIAN ASCHAN (*Chem. Zeit.*, 1897, 21, 242, and 287—288).—A résumé of work previously published by the author and others. Compare *Abstr.*, 1883, 564; 1884, 1276; 1887, 648, 922; 1891, 1053, 1481; 1892, 847, 1182, 1310, 1311; 1895, i, 339, 411, and 1896, i, 210, 286, 350.

The conclusion arrived at is that these naphthenes are probably mixtures, and they are not, as was previously supposed, reduction products of benzene hydrocarbons but probably contain pentamethylene derivatives.

J. J. S.

**Reduction of Benzylaminecarboxylic Acids.** By ALFRED EINHORN [and JOSEF BRANTL] (*Annalen*, 1898, 300, 156—179. Compare *Abstr.*, 1896, i, 551).—*Orthomethylolhexahydrobenzoic acid* (*exo-hydroxyhexahydro-orthotoluic acid*),  $\text{OH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_{10} \cdot \text{COOH}$ , is the chief non-nitrogenous product of reducing *orthodiethylbenzylaminecarboxylic acid* with amylic alcohol and sodium, and is also obtained by the reduction of phthalide; it crystallises from benzene in aggregates of small, prismatic needles, and melts at 112°. The *sodium* and *barium* salts crystallise in needles, the *methyl*c salt boils at 155° under a pressure of 18 mm., and the *ethylic* salt at 160—162° under a pressure of 32 mm. *Ethylic orthochloromethylhexahydrobenzoic acid*,



boils at 145—147° under a pressure of 15 mm. When oxidised with potassium permanganate, *orthomethylolhexahydrobenzoic acid* is converted into *trans-hexahydrophthalic acid*.

In addition to *exo-hydroxyhexahydro-orthotoluic acid*, reduction of phthalide gives rise to *hexahydrophthalide*,  $\text{C}_6\text{H}_{10} \begin{array}{c} \text{CH}_2 \\ < \end{array} \text{CO} \text{--} \text{O}$ ; it is a colourless liquid having an agreeable odour, and it boils at 160—165° under a pressure of 60 mm.

*Hexahydro-orthotoluic acid* is another product of the reduction of phthalide and *exo-hydroxyhexahydro-orthotoluic acid*, and when distilled with zinc chloride, it yields hexahydrotoluene.

M. O. F.

**Compound of Phosphoric Anhydride with Benzene.** By H. GIRAN (*Compt. rend.*, 1898, 126, 592—593).—When a mixture of two parts of phosphoric anhydride and three parts of benzene is heated in a sealed tube at 110—120° for several hours, a very unstable, brick-red solid product is obtained which decomposes when exposed to air, but can be kept in an atmosphere of benzene. It is also decomposed

by water, but dissolves without change in alcohol, and when this solution is treated with barium carbonate, a gelatinous mass is formed which, after washing with absolute alcohol and drying at 110—120°, has the composition  $C_6H_2P_8O_{20}Ba_2$ , and is the barium salt of *benzenetetradi-metaphosphoric acid*,  $C_6H_2(PO:O_2:PO\cdot OH)_4$ , formed by the union of 1 molecule of benzene with 4 mols. of phosphoric anhydride.

The alcoholic solution of the crude acid may be neutralised with barium ethoxide instead of with the carbonate. C. H. B.

**The Benzene Ring.** By NICOLAI A. MENSCHUTKIN (*Ber.*, 1898, 31, 1423—1429. Compare this vol., i, 186).—A study of the formation of the benzene ring involves the consideration of two questions, namely, the production of a hexatomic ring from an open chain, and the influence on the decomposition velocity of the anilines exerted by the carbon linkings of the ring.

In order to throw light on the first of these questions, the author has compared the velocity constants of the action of allylic bromide on  $\alpha$ -pentylamine (1189), hexamethyleneamine (1309),  $\alpha\beta$ -pentylamine (586), and  $\beta$ -methylhexamethyleneamine (884), and points out that the conversion of an open chain into a hexatomic ring having the same simple linkings between the carbon atoms is not attended with diminution of the velocity constant.

Assuming that the influence exerted by the nature of the union between carbon atoms is the same in a closed ring as in an open chain, it is possible to study the second of the above questions by considering the velocity constants of the anilines. By comparing the velocity constants of propylamine (3783) and allylamine (1903), it will be seen that if Kekulé's formula for benzene is accepted, the constant for aniline should be considerably lower than that of hexamethyleneamine; the same effect would be anticipated if Claus' view of the structure of the benzene ring is accepted, because the velocity constant of  $\alpha\alpha$ -pentylamine is 270. As a matter of fact, the constants proper to hexamethyleneamine and aniline are 1309 and 68 respectively. Another point of difference which is due to this cause lies in the lower values obtained when anilines are acted on by methylic bromide as compared with allylic bromide, whereas in the aliphatic series the converse generalisation holds good; this is illustrated by the following table (compare also Abstr., 1895, ii, 385).

	$C_3H_5Br.$	MeBr.
Aniline .....	68	24
Methylaniline .....	504	179
Orthotoluidine .....	54	13
Metatoluidine .....	445	86
Paratoluidine.....	96	52
<i>v</i> -Ortho-xylidine .....	400	51
<i>as</i> -Meta-xylidine .....	235	30
<i>psi</i> -Cumidine .....	174	46

The aromatic amines, such as benzylamine, differ from the anilines,

displaying the characteristics of aliphatic amines to the exclusion of those features which are associated with the benzene ring. Thus the velocity constants of benzylamine,  $\alpha$ -phenylethylamine, and  $\omega$ -mesitylamine, with allylic bromide, are 997, 750, and 1718; with methylic bromide, the constants of benzylamine and  $\omega$ -mesitylamine are 2722 and 4565 respectively.

Corresponding differences are revealed on comparing the etherification constants of alcohols with those of phenols, and of aliphatic acids with those of aromatic acids.

M. O. F.

**Carbonates of the Dihydroxybenzenes.** By ALFRED EINHORN [and EUGEN LINDENBERG] (*Annalen*, 1898, 300, 135—155).—When catechol carbonate,  $C_6H_4\begin{array}{c} O \\ \diagdown \\ O-CO \end{array}$ , is recrystallised from absolute alcohol, it becomes in part converted into ethylic catechol carbonate,  $OH \cdot C_6H_4 \cdot O \cdot COOEt$ . It is also decomposed by primary and secondary bases, yielding compounds of the type  $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NRR'$ . Whilst ethylenediamine gives rise to dicatecholdicarbethylenediamide,  $C_2H_4(NH \cdot CO \cdot O \cdot C_6H_4 \cdot OH)_2$ , hydrazine forms the two compounds dicatecholcarbohydrazide,  $N_2H_2(CO \cdot O \cdot C_6H_4 \cdot OH)_2$ , and catecholcarbohydrazide,  $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot NH_2$ . The latter is of value in detecting aldehydes, with which it forms derivatives of the type  $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot NCHR$ , and possesses the advantage of solubility in alkalis, from which it is separated unchanged by acids; hitherto, however, it has not been induced to combine with ketones, and therefore affords a means of distinguishing between this class of compounds and aldehydes.

Although the conversion of catechol carbonate into ethylic catechol carbonate under the influence of absolute alcohol is complete at 100°, the carbonates of resorcinol and quinol are scarcely changed under these conditions, first undergoing complete conversion when heated at 130° and 160° respectively; the products, however, have not been isolated. With piperidine, resorcinol carbonate yields two compounds, resorcinolcarbopiperide,  $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NC_5H_{10}$ , which dissolves in alkalies, and resorcinoldicarbodipiperide,  $C_6H_4(O \cdot CO \cdot NC_5H_{10})_2$ , which is insoluble in alkalies. Quinol carbonate behaves in a similar manner.

It is probable that the carbonates of resorcinol and quinol are not monomolecular, and the authors therefore represent them by the general formula  $(C_6H_4O_2CO)_x$ .

*Ethylic catecholcarbonate*,  $OH \cdot C_6H_4 \cdot O \cdot COOEt$ , crystallises from a mixture of alcohol and ether in colourless needles and melts at 58°; it has an aromatic odour and a burning taste, and does not develop colour with ferric chloride. Distillation regenerates catechol carbonate with elimination of alcohol.

*Amylic catechol carbonate*,  $OH \cdot C_6H_4 \cdot O \cdot COO \cdot C_5H_{11}$ , crystallises from petroleum in leaflets and melts at 53°; it has an aromatic odour.

*Catecholcarbanilide*,  $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NHPh$ , crystallises from alcohol in small, white scales, and melts at 146°. *Catecholcarboparaphenetidide*,  $OH \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot C_6H_4 \cdot OEt$ , crystallises in lustrous leaflets and also melts at 146°.

*Catecholcarbophenylhydrazide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPH}$ , slowly reduces a cold solution of silver nitrate, and is oxidised by Fehling's solution when gently heated ; it crystallises from methylic alcohol in leaflets and melts at  $157^\circ$ .

*Dicatecholcarbylethylenediamide*,  $\text{C}_2\text{H}_4(\text{NH} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$ , is prepared by the action of ethylenediamine on catechol carbonate (2 mols.) ; it crystallises from absolute alcohol in highly lustrous leaflets and melts at  $165 \cdot 5^\circ$ .

*Catecholcarbodiethylamide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NET}_2$ , which crystallises in beautiful prisms from a mixture of ether and petroleum, melts at  $78^\circ$ , and dissolves without decomposition in dilute caustic soda. It belongs to the monoclinic system. [ $a:b:c = 1 \cdot 2261 : 1 : 0 \cdot 95498$  ;  $\beta = 114^\circ 26'$ .]

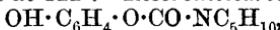
*Catecholcarbopiperidide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10}$ , crystallises from absolute alcohol in white prisms and melts at  $121^\circ$ . When boiled with alcohol during half an hour, it is resolved into its components, but dissolves without change in cold, dilute, caustic alkali.

*Dicatecholcarbohydrazide*,  $\text{N}_2\text{H}_2(\text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_2$ , is prepared by adding hydrazine (2.8 grams) to finely powdered catechol carbonate (15 grams), and cooling the clear solution which is produced ; on dissolving the crystals in dilute caustic soda, and treating the filtered liquid with hydrochloric acid, the dihydrazide is precipitated, whilst the hydrochloride of the monohydrazide remains in solution. The dihydrazide crystallises from absolute alcohol in colourless plates and melts at  $207^\circ$ .

*Catecholcarbohydrazide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , crystallises from very dilute spirit in white needles, and melts at  $154^\circ$ , becoming solid above this temperature, and finally decomposing at  $240^\circ$ ; it is insoluble in benzene and ether, but dissolves in hot alcohol and water. The substance slowly reduces a cold solution of silver nitrate and Fehling's solution when warmed with it ; ferric chloride develops a dark coloration. The *acetyl* derivative melts at  $180^\circ$ . The *benzylidene* derivative crystallises from alcohol in colourless needles and melts at  $175^\circ$ ; the *ortho*-hydroxybenzylidene and *para*-hydroxybenzylidene derivatives melt at  $162^\circ$  and  $175^\circ$  respectively, the *paramethoxybenzylidene* derivative at  $192^\circ$ . The *ethylidene* derivative melts at  $125^\circ$ ; unlike the foregoing products of condensation, this compound undergoes decomposition when dissolved in alkalis.

*Resorcinol carbonate*,  $(\text{C}_6\text{H}_4\text{O}_2 \cdot \text{CO})_2$ , is prepared by passing carbonyl dichloride into a continuously agitated solution of resorcinol in pyridine, cooled with ice ; after half an hour the gelatinous precipitate is transferred to water, when the carbonate separates as a white, amorphous powder. It melts and evolves gas at  $190^\circ$ .

*Resorcinoldicarbodipiperidide*,  $\text{C}_6\text{H}_4(\text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10})_2$ , separates in large, transparent plates on adding a few drops of alcohol to the solution in ether ; it melts at  $122^\circ$ . *Resorcinolcarbopiperidide*,



is soluble in alkalis, and crystallises from a mixture of ether and petroleum in colourless prisms. It melts at  $107^\circ$ .

*Quinol carbonate*,  $(\text{C}_6\text{H}_4\text{O}_2 \cdot \text{CO})_2$ , is insoluble in common solvents and does not melt below  $280^\circ$ .

*Quinolcarbopiperidide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NC}_5\text{H}_{10}$ , which separates on adding ethylic acetate to the alcoholic or ethereal solution, melts at  $270^\circ$ .

*Quinolcarbohydrazide*,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , is a white, crystalline powder and melts at  $168^\circ$ . M. O. F.

**Action of Cyanamide on Bromanil in Presence of Potassium Hydroxide.** By H. IMBERT (*Compt. rend.*, 1898, 126, 529—530).—A solution of cyanamide (8·4 grams), in water (100 grams), is added to finely divided tetrabromoquinone (24·6 grams), the mixture is boiled, and small pieces of potassium hydroxide are added, care being taken that the bromanil remains in excess; the liquid is filtered hot, and as the filtrate cools crystals separate which can be obtained pure after two or three crystallisations from boiling water. The crystals have the form of long needles, some have a green and others a brown appearance, probably the effect of polychroism. Its aqueous solution has a green colour, which changes to violet on the addition of hydrochloric acid; if the acidified solution is shaken with ethylic acetate, the latter assumes a ruby-red colour. Both the green and violet solutions are decolorised by sulphurous anhydride. Analyses point to the compound being *dipotassium dicyanimidodibromdihydroxyquinone*,  $\text{CN}_2 \cdot \text{C}_6\text{Br}_2(\text{OK})_2 \cdot \text{CN}_2 + 2\text{H}_2\text{O}$ . The corresponding *silver* and *barium* compounds have been obtained by double decomposition. Chloranil reacts in a similar manner, and benzoquinone itself gives *dicyanimidobenzoquinone*. J. J. S.

**Veratrylenediamine.** By CHARLES MOUREU (*Compt. rend.*, 1897, 125, 31—34).—Veratrole, when treated at  $0—5^\circ$  with concentrated nitric acid (sp. gr. = 1·48), yields a *dinitro*-derivative crystallising in lemon-yellow needles and melting at  $129—130^\circ$ . The two nitro-groups appear to be in the *ortho*-position relatively to one another, since on reduction with tin and hydrochloric acid an *orthodiamine*, *veratrylenediamine*,  $\text{C}_6\text{H}_2(\text{OMe})_2(\text{NH}_2)_2$ , is obtained; this crystallises in small, colourless prisms melting at  $131—132^\circ$ , and dissolves readily in water, alcohol, or chloroform, but is only sparingly soluble in ether. All its solutions rapidly become dark coloured on exposure to the air, and even the solid base after exposure for several hours assumes a violet colour.

**Veratrylphenanthrazine**,  $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{matrix} \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ \text{N} : \text{C} \cdot \text{C}_6\text{H}_4 \end{matrix} >$ , obtained when a warm alcoholic solution of the base (0·84 gram) is added to a boiling acetic acid solution of phenanthraquinone (1·04 grams), crystallises from toluene in small, yellow needles melting at  $255^\circ$ , and gives a violet coloration with sulphuric acid.

**Veratrylene-ethenylamidine**,  $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{matrix} \text{NH} \\ \text{N} \end{matrix} > \text{CMe}$ , formed when the base is heated for some time with acetic acid, is readily soluble in water, sparingly in ether, and melts at about  $170^\circ$ ; its aqueous solution yields precipitates with both platinum chloride and picric acid.

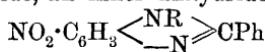
**Veratrylbenzaldehyde**,  $\text{C}_6\text{H}_2(\text{OMe})_2 < \begin{matrix} \text{CPh} \cdot \text{N} \cdot \text{CH}_2\text{Ph} \\ \text{N} — \text{C}_6\text{H}_2(\text{OMe})_2 \end{matrix} >$ , is obtained in the form of its hydrochloride when an aqueous solution of veratrylenediamine hydrochloride reacts with benzaldehyde; the *hydrochloride* crystallises

from dilute alcohol in small, colourless needles melting at 134—135°. All these reactions indicate that the base is an ortho-diamine. J. J. S.

**Action of Benzoic Chloride on Monosubstituted Orthodiamines.** By FERNAND MUTTELET (*Compt. rend.*, 1897, 125, 107—109).—Substituted ortho-diamines of the type  $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NH}_2)(\text{NHR})$  [ $\text{NHR} : \text{NH}_2 = 1 : 2 : 4$ ], where R = phenyl, ortho- or para-tolyl, methyl,  $\alpha$ - or  $\beta$ -naphthyl radicles, react with benzoic chloride in two different ways. (1) At a low temperature and in the presence of a solvent such as benzene a benzoyl derivative of the type



is formed. (2). At a high temperature (200°), and in the presence of an excess of the chloride, an inner anhydride of the type



is produced.

*Orthobenzamidoparannitrophenylaniline*,  $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NHBz})\cdot\text{NPh}$ , crystallises from alcohol in yellowish brown needles melting at 201—202°. *Orthobenzamidoparanitroparatolylaniline* forms yellow needles melting at 210—211°; *orthobenzamidoparanitroorthotolylaniline* melts at 164—165°, and *orthobenzamidoparanitro-β-naphthylaniline* melts at 217—218°.

The anhydride,  $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{array}{c} \text{NPh} \\ \swarrow \\ \text{---} \\ \searrow \end{array}\text{N}\geqslant\text{CPh}$ , is obtained when paranitro-orthamidophenylaniline (1 part) is heated with benzoic chloride (2 parts), first gently and then at about 210—215°, in an oil bath until hydrogen chloride ceases to be evolved; when cold, the mass is treated with sodium carbonate, and, after boiling, the insoluble portion is washed with hot water and recrystallised from boiling alcohol; it crystallises in needles melting at 181°.

The following is a list of the anhydrides which have been obtained in a similar manner.

R = Paratolyl, colourless needles melting at 177—178°.

R = Orthotolyl, yellowish needles melting at 172—173°.

R =  $\alpha$ -Naphthyl, small yellow crystals melting at 171—173°.

R =  $\beta$ -Naphthyl, yellow needles melting at 177—178°.

R = Methyl, yellow crystals melting and decomposing at 140°.

J. J. S.

**A New Group of Amidines.** By FERNAND MUTTELET (*Compt. rend.*, 1897, 125, 243—245).—When the anhydrides obtained by the action of benzoic chloride on monosubstituted orthodiamines (see preceding abstract) are reduced with tin and hydrochloric acid, amidines of the type  $\text{NH}_2\cdot\text{C}_6\text{H}_3\begin{array}{c} \text{NR} \\ \swarrow \\ \text{---} \\ \searrow \end{array}\text{N}\geqslant\text{CPh}$  are formed.

R.	Melting point of product.
Phenyl .....	191°
Paratolyl .....	193°
Orthotolyl.....	145—146°
$\beta$ -Naphthyl .....	195°

A hydrate of the phenyl derivative containing  $1\text{H}_2\text{O}$  has been obtained, it melts at 172—173°; the corresponding hydrate of the

$\beta$ -naphthyl derivative melts at 165—166° losing its water and then melting again at 195°.  
J. J. S.

**Behaviour of Diazomethane towards Nitramines and Aromatic Nitro-compounds.** By JOHN LEATHART HEINKE (*Ber.*, 1898, 31, 1395—1400). Compare Degner and von Pechmann, *Abstr.*, 1897, i, 264).—Diazomethane converts nitrourethane into nitromethylurethane. It has a similar action on nitramine, yielding principally dimethylnitramine, along with the isomeride described by Franchimont and Umbgrove (*Abstr.*, 1897, i, 8); there is also formed the compound,  $C_5H_{11}NO_4$ , which boils at 110—112°, and yields potassium carbonate when treated with alcoholic potash.

The nitro-compounds which have shown themselves to be indifferent towards diazomethane are nitromethane, nitrobenzene, nitrotoluene, parabromonitrobenzene, bromodinitrobenzene, and trinitromesitylene.

Symmetrical trinitrobenzene reacts with diazomethane (4 mols.) liberating nitrogen, and yielding the compound,  $C_{10}H_{11}N_5O_6$ , which crystallises from dilute acetic acid in colourless, rhombic plates, and melts at 194—195°, when it decomposes; it is indifferent towards cold caustic soda, yielding a red solution when the liquid is boiled. The substance gives Liebermann's reaction, and under the influence of acids and alkalis is resolved into nitrous acid and the base,  $C_{10}H_{10}N_4O_4$ , which crystallises from dilute alcohol in white, lustrous plates and melts at 164—165°.

Symmetrical trinitrotoluene yields the compound,  $C_{10}H_{11}N_5O_6$ , which crystallises from dilute acetic acid in yellowish needles, and melts at 177°.

Picric chloride gives rise to the compound,  $C_9H_8N_5O_6Cl$ , which crystallises from dilute acetic acid in bright yellow needles, and melts at 176—177°. Alcoholic hydrogen chloride eliminates nitrous acid, yielding the base,  $C_9H_7N_4O_4Cl$ , which crystallises from dilute alcohol in yellowish needles and melts at 179—180°; the acetyl derivative forms colourless needles and melts at 156—157°.

Symmetrical trinitrophenyl acetate acts readily with diazomethane, yielding the compound,  $C_{11}H_{11}N_5O_7$ , which separates from dilute acetic acid in yellowish, hexagonal prisms; it melts at 144°. M. O. F.

**Compounds of Phenylhydrazine with Metallic Nitrates.** By JOSEPH MOITESSIER (*Compt. rend.*, 1897, 125, 183—185).—The nitrates of metals of the manganese series combine directly with phenylhydrazine in much the same manner as the corresponding haloids (*Abstr.*, 1897, i, 561, 562; this vol., i, 133). These salts, which give the reactions of phenylhydrazine, and also those of the metal they contain, deflagrate when heated, leaving a residue of the metallic oxide.

*Cobalt nitrate phenylhydrazine*,  $Co(NO_3)_2 \cdot 2N_2H_3Ph + H_2O$ , obtained when an excess of phenylhydrazine is quickly added to a 10 per cent. aqueous solution of cobalt nitrate previously diluted with twice its volume of 95 per cent. alcohol, crystallises in microscopic needles, is sparingly soluble in cold water or alcohol, more readily in hot water, and insoluble in ether or chloroform. When heated, it turns blue, then brown, and does not melt below 260°.

*Zinc nitrate phenylhydrazine*,  $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{N}_2\text{H}_3\text{Ph}$ , is obtained when a 10 per cent. alcoholic solution of phenylhydrazine is gradually added to a 10 per cent. alcoholic solution of zinc nitrate; the precipitate formed contains zinc oxide, from which it may be freed by boiling with alcohol and allowing it to crystallise. In appearance it resembles boric acid, is soluble in hot water or alcohol, but insoluble in ether or chloroform, and melts and decomposes at  $170^\circ$ .

The *cadmium salt*,  $\text{Cd}(\text{NO}_3)_2 \cdot 3\text{N}_2\text{H}_3\text{Ph}$ , may be obtained in a similar manner by using a 5 per cent. alcoholic solution of cadmium nitrate. It melts at  $185^\circ$  and decomposes at about  $190^\circ$ . The *nickel derivative*,  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{N}_2\text{H}_3\text{Ph}$ , obtained by quickly adding phenylhydrazine to a 20 per cent. alcoholic solution of nickel nitrate, forms a clear blue precipitate, which is sparingly soluble in chloroform, but insoluble in ether, and deflagrates at  $141^\circ$ .

J. J. S.

**Action of Halogen-substituted Derivatives of Aliphatic Compounds on Phenylhydrazine.** By HEINRICH BRUNNER and KARL EIERMANN (*Ber.*, 1898, 31, 1406—1416. Compare this vol., i, 158).—The action of chloroform on phenylhydrazine gives rise to phenylhydrazine hydrochloride, phenylic isocyanide, benzene, ammonium chloride, hydrogen chloride, and nitrogen; the same products, substituting aniline for benzene, are obtained when a solution of carbon hexachloride in ether is mixed with phenylhydrazine. Carbon tetrachloride yields phenylhydrazine hydrochloride, phenylic isocyanide, hydrogen chloride, aniline, and nitrogen; whilst ethylenic dichloride also gives rise to phenylhydrazine hydrochloride when mixed with the base. Bromoform and phenylhydrazine give the hydrobromide, along with phenylic isocyanide, benzene, hydrogen bromide, ammonium bromide, and nitrogen, the analogous change taking place under the influence of iodoform; ethylenic dibromide produces phenylhydrazine hydrobromide when mixed with the base. When chloral, diluted with 25 volumes of ether, is mixed with phenylhydrazine, nitrogen is liberated, and the hydrochloride of the base produced; the other products of the action are benzoic chloride, phenylic isocyanide, aniline, ammonia, and ammonium chloride (compare also Causse, *Abstr.*, 1897, i, 543).

The compound,  $\text{C}_{28}\text{H}_{26}\text{N}_7\text{O}_2\text{Cl}$ , obtained on mixing aqueous solutions of phenylhydrazine hydrochloride and chloral hydrate, is a reddish-brown, amorphous substance, readily soluble in alcohol, chloroform, and glacial acetic acid, but dissolving with difficulty in benzene and petroleum; it is insoluble in water and ether. The latter agent precipitates it from the solution in chloroform as a yellowish-red substance, and when separated from alcohol or glacial acetic acid by addition of feebly acidified water it is orange-coloured. It becomes brown at  $140^\circ$ , and chars at  $145^\circ$ . Nitric acid converts it into picric acid, whilst alcoholic potash eliminates ammonia, the odour of isocyanide becoming afterwards perceptible; when heated with zinc dust, it yields ammonia, aniline, and an isocyanide. The *acetyl*, *benzoyl* (two), *silver*, *ethyl*, and *propyl* derivatives are amorphous; an amorphous compound,  $\text{C}_{28}\text{H}_{24}\text{N}_7\text{Cl}_3$ , is obtained by the action of phosphorus pentachloride.

The compound,  $C_{28}H_{26}N_2O_2Br$ , prepared from phenylhydrazine hydrochloride and bromal hydrate, is a yellow, amorphous powder, resembling the foregoing compound in chemical behaviour. The *acetyl*, *benzoyl*, *silver*, *ethyl*, and *propyl* derivatives, and the compound obtained by the action of phosphorus pentachloride, are amorphous.

The compound,  $C_{16}H_{16}N_3ClO$ , is produced when aqueous solutions of phenylhydrazine hydrochloride and butylechloral hydrate are gently heated ; the substance itself, the *acetyl*, *benzoyl*, *silver*, *ethyl*, and *propyl* derivatives, and the compound obtained by the action of phosphorus pentachloride, are all amorphous.

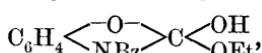
The authors discuss the possible constitution of the above-mentioned compounds. M. O. F.

**Hydrocinnamide.** By MARCEL DELÉPINE (*Compt. rend.*, 1898, 126, 648—651).—Hydrocinnamide, obtained by the action of ammonia on cinnamaldehyde and melting at 106—108°, is really a hydrate,  $2C_{27}H_{24}N_2 + H_2O$ , which explains the formation of the hydrochloride and the regeneration of the base from it by the action of ammonia. Hydrocinnamide is therefore analogous in this respect to amarine and anisine. Direct estimation of the water was found to be impracticable owing to the rapid alteration of the compound when heated.

The heat of combustion of hydrocinnamide is 8962·8 cals. ; molecular heat of combustion at constant volume, 3450·68 cal. ; at constant pressure, 3453·5 cal. ; heat of formation —81·2 Cal. ; heat of formation of the hydrate (liquid water) —79·4 Cal. It follows that  $3C_9H_8O$  liquid +  $2NH_3$  diss. =  $C_{27}H_{24}N_2$  solid +  $3H_2O$  liquid develops +48·4 Cal. These results show that hydrocinnamide is one of the glyoxalidines, a conclusion which is confirmed by the formation of salts, its basic function being more active than that of amarine; it may therefore be termed cinnamine. It also forms a compound with silver nitrate, and resembles amarine in its behaviour with methylic iodide and benzyl chloride.

C. H. B.

**The Reduction of Ethylic Orthonitrophenylic Carbonate : Ethylic Orthohydroxyphenylcarbamate.** By JAMES H. RANSOM (*Ber.*, 1898, 31, 1055—1066).—Bender's ethylic amidophenylic carbonate,  $NH_2 \cdot C_6H_4 \cdot O \cdot COOEt$ , melting at 95° (*Abstr.*, 1887, 38), was prepared by reducing ethylic orthonitrophenylic carbonate by shaking it with tin and strong hydrochloric acid and cooling meanwhile. It is identical with Groenvik's ethylic hydroxyphenylcarbamate,  $OH \cdot C_6H_4 \cdot NH \cdot COOEt$ , melting at 85° (*this Journal*, 1877, i, 472), prepared from orthamidophenol and ethylic chloroformate. The true melting point of the substance is 85°; its constitution is probably  $C_6H_4 < O > C < OH > OEt$ . It yields a *benzoyl* derivative,



which melts at 75·5°; this can also be obtained from ethylic chloroformate and benzoylorthamidophenol,  $OH \cdot C_6H_4 \cdot NHBz$ , which is itself best obtained by the action of benzoic chloride (1 mol.) on orthamidophenol (2 mols.) in ethereal solution. When this benzoyl derivative is heated in a bath at 240—245°, alcohol comes over first, then a

small quantity of ethylic benzoate, and, lastly, a fraction which contains *benzoylcarbonylamidophenol*,  $C_6H_4\begin{array}{c} O \\ \swarrow \quad \searrow \\ N \quad C_6H_5 \end{array}CO$ , melting at 173—174°, together with a little carbonylamidophenol (from which the former can be prepared by benzoylation), and a little *benzenylamido-phenol*,  $C_6H_4\begin{array}{c} O \\ \swarrow \quad \searrow \\ N \quad C_6H_5 \end{array}CPh$ , which melts at 101—102°, and can also be prepared by distilling benzoylcarbonylamidophenol.

*Orthanisidine*, when heated with ethylic chloroformate in alkaline aqueous solution, yields *ethylic orthomethoxyphenylcarbamate*,  $OMe \cdot C_6H_4 \cdot NH \cdot COOEt$ , boiling at 180—182° under 26 mm. pressure. A product identical with this ought to be obtained by methylating the original substance mentioned above, if Groenvik's formula for it were correct; this substance could not be made to yield a methylic derivative, however. Ethylic orthomethoxyphenylcarbamate, when treated with bromine in carbon bisulphide solution, yields a *monobromo-substitution derivative* which melts at 101·5—102·5°.

*Ethylic paranitrophenyl carbonate* can be prepared from paranitrophenol in alkaline solution by the action of ethylic chloroformate, and also by dissolving ethylic phenyl carbonate in fuming nitric acid at 0°; it melts at 67—68°. Unlike the ortho-isomeride, it is reduced by tin and alcoholic hydrochloric acid, in the normal manner, to *ethylic paramidophenyl carbonate*,  $NH_2 \cdot C_6H_4 \cdot O \cdot COOEt$ , which melts at 35—36°; the *hydrochloride* of this melts and decomposes at 197°, the yellow *platinochloride* melts at 237°, and the *carbamide* (from the hydrochloride and potassium cyanate) at 149—150°. C. F. B.

**Some-N-Phosphines and N-Phosphonium Compounds.** By C. A. AUGUST MICHAELIS (*Ber.*, 1898, 31, 1037—1047).—Compounds analogous to those prepared from phosphorus trichloride and piperidine (*Abstr.*, 1895, i, 682) have been prepared with phosphenyl chloride,  $PPhCl_2$ , and similarly constituted chlorides, instead of phosphorus chloride. These trichlorides react with tetrahydroquinoline also, but the reaction is less energetic, and there is no need to cool with ice, or even to dilute with ether; the products, too, form phosphonium compounds less readily than the analogous piperidine derivatives, and that only with methylic iodide, as a rule. No aliphatic N-phosphines have been obtained as yet.

[With GEORG SCHLÜTER].—*Phenyldipiperidine-N-phosphine*,  $(C_5H_{10}N)_2PPh$ , from piperidine (4 mols.) and phosphenyl chloride (1 mol.) in ethereal solution, melts at 78°. With chlorine gas in light petroleum solution, it yields deliquescent *phenyldipiperidine-N-phosphine chloride*,  $(C_5H_{10}N)_2PPhCl_2$ ; this is converted by water into the *phosphine oxide*,  $(C_5H_{10}N)_2PPhO$ , which is better prepared, however, by the action of phosphenyl oxychloride,  $PPhOCl_2$ , on piperidine; it is hygroscopic and melts at 68°. The *phosphine sulphide*, obtained by prolonged heating of the phosphine with excess of sulphur at 130°, melts at 92° and is very stable. With carbon bisulphide, the phosphine first forms a yellowish-white compound, probably  $(C_5H_{10}N \cdot CS \cdot S)_2PPh$ , which melts at 144°; when

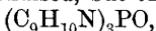
crystallised repeatedly from a mixture of benzene with ether, this loses half its carbon bisulphide, yielding a yellow substance, presumably  $C_5H_{10}N \cdot CS \cdot S \cdot PPh \cdot NC_5H_{10}$ , which melts at  $137^\circ$ . *Phenyl dipiperidinemethylphosphonium iodide* (from the phosphine and methylic iodide at the ordinary temperature), *chloride*, and yellowish-red *platinochloride*,  $(C_5H_{10}N)_2PPhMeI$ , &c., melt at  $167^\circ$ ,  $130^\circ$ , and  $178^\circ$  respectively; the *ethylphosphonium iodide* at  $174^\circ$ , and the yellow, deliquescent *benzylphosphonium chloride* at  $204^\circ$ . The methylphosphonium hydroxide is a syrup; when heated, it loses piperidine and forms methylphenylphosphinic acid,  $O:PPhMe \cdot OH$ .

[With FREUNDLICH.]—*Paratolyldipiperidine-N-phosphine*,  $(C_5H_{10}N)_2P \cdot C_6H_4Me$ ,

melts at  $80^\circ$ ; the hygroscopic *phosphine oxide*,  $(C_5H_{10}N)_2PO \cdot C_6H_4Me$ , at  $60^\circ$ ; the *phosphine sulphide* at  $88^\circ$ , and the pale yellow compound with carbon bisulphide (2 mols., a compound with  $1CS_2$  could not be obtained) at  $139^\circ$ . The *methyl-, ethyl-, propyl- and isobutyl-phosphonium iodides*,  $(C_5H_{10}N)_2P \cdot C_6H_4Me \cdot MeI$ , &c., melt at  $186^\circ$ ,  $191^\circ$ ,  $197^\circ$ , and  $204^\circ$  respectively; the *benzylphosphonium chloride* at  $125^\circ$ . By heating the methylphosphonium hydroxide at  $150$ — $180^\circ$ , *paratolylmethylphosphinic acid*,  $C_6H_4Me \cdot PMeO \cdot OH$ , was obtained; it melts at  $120^\circ$ ; its *silver salt* was analysed.

[With CURT ROEBER.]—*Chlorophenyl-, anisyl-, and phenetyl-dipiperidine-N-phosphines*,  $(C_5H_{10}N)_2P \cdot C_6H_4R$  [R = Cl; OMe; OEt], melt at  $95^\circ$ ,  $69^\circ$  and  $84^\circ$  respectively. They were prepared in the same way as *phenyldipiperidine-n-phosphine*, and resemble that substance in their reactions.

[With J. GROSSHEIM.]—*Tetrahydroquinoline-N-phosphine*,  $(C_9H_{10}N)_3P$ , from tetrahydroquinoline and phosphorous chloride, melts at  $202$ — $204^\circ$ , and is decomposed by acids into tetrahydroquinoline and phosphorous acid; it cannot readily be oxidised, but the *phosphine oxide*,



is obtained by the action of tetrahydroquinoline on phosphorus oxychloride; it melts at  $90$ — $91^\circ$ . The N-phosphine (1 mol.) will unite with sulphur (1 mol.), however, at  $170^\circ$ , but not very readily; the resulting *phosphine sulphide*,  $(C_9H_{10}N)_3PS$ , crystallises in the regular system and melts at  $192^\circ$ . *Tetrahydroquinolinemethylphosphonium iodide, chloride*, and reddish-yellow *platinochloride*,  $(C_9H_{10}N)_3PMel$ , &c., melt at  $188^\circ$ ,  $148$ — $150^\circ$ , and  $230^\circ$  respectively.

*Phenylditetrahydroquinoline-N-phosphine*,  $(C_9H_{10}N)_2PPh$ , from tetrahydroquinoline and phenyl chloride, melts at  $150^\circ$ ; the *phosphine oxide*,  $(C_9H_{10}N)_2PPhO$ , at  $216^\circ$ , and the *methylphosphonium iodide*,  $(C_9H_{10}N)_2PPhMeI$ , at  $136^\circ$ .

*Paratolylditetrahydroquinoline-N-phosphine*,  $(C_9H_{10}N)_2P \cdot C_6H_4Me$ , melts at  $140^\circ$ , the *phosphine oxide*,  $(C_9H_{10}N)_2PO \cdot C_6H_4Me$ , at  $181^\circ$ .

C. F. B.

**Behaviour of Alkylic Iodides with Alkylic Phosphites, or O-Phosphines.** By C. A. AUGUST MICHAELIS and R. KAEHNE (*Ber.*, 1898, 31, 1048—1055).—The phenyllic, parachlorophenyllic, para- and meta-tolylic, and pseudocumenylic salts of phosphorous acid,  $(OR_3)_3P$

(1 mol.), react with methylic iodide (1 mol.) at suitable temperatures, and also with benzylic chloride, yielding compounds,  $(OR)_3PMeI$  or  $(OR)_3PCl \cdot CH_2Ph$ ; with ethylic iodide, they would not combine in the same way; the products were often oils, but these sometimes solidified on cooling, or on washing with ether. They are decomposed by alkalis, and even by water, hydriodic acid, phenol, and an alkylic methyl- or benzyl-phosphinate being formed,  $(OR)_3PMeI + H \cdot OH = HI + R \cdot OH + (OR)_2PMeO$ . Ethylic phosphite will not combine with methylic iodide; instead of a normal compound, its decomposition products are obtained; one of these is *methylphosphinic acid*, for the preparation of which this reaction is convenient (see later.).

*Triphenolmethyl-O-phosphonium iodide*,  $(OPh)_3PMeI$ , prepared as indicated at  $100^\circ$ , melts at  $70-75^\circ$ , and is very deliquescent; *phenylic methylphosphinate*,  $(OPh)_2PMeO$ , melts at  $36-37^\circ$ . *Triphenolbenzyl-O-phosphonium chloride*,  $(OPh)_3PCl \cdot CH_2Ph$ , prepared at  $175^\circ$ , was not obtained pure; *phenylic benzylphosphinate*,  $(OPh)_2PO \cdot CH_2Ph$ , melts at  $60^\circ$ .

*Parachlorophenylic phosphite (parachlorophenol-O-phosphine)*,  
 $(C_6H_4Cl \cdot O)_3P$ , boils at  $290-297^\circ$  under 15 mm. pressure. *Triparachlorophenolmethyl-phosphonium iodide*,  $(C_6H_4Cl \cdot O)_3PMeI$ , melts at  $71^\circ$ . *Parachlorophenylic methylphosphinate*,  $(C_6H_4Cl \cdot O)_2PMeO$ , boils at about  $245^\circ$  under 20 mm. pressure.

*Paratolylic phosphite (triparacresol-O-phosphine)*,  $(C_6H_4Me \cdot O)_3P$ , from paracresol (3 mols.) and phosphorous chloride (1 mol.), boils at  $250-255^\circ$  under 10 mm. pressure. *Triparacresolmethyl-O-phosphonium iodide*,  $(C_6H_4Me \cdot O)_3PMeI$ , prepared at  $100^\circ$ , could not be obtained quite pure; *paratolylic methylphosphinate*,  $(C_6H_4Me \cdot O)_2PMeO$ , boils at  $220-225^\circ$  under 12 mm. pressure.

*Metatolylic phosphite (trimetacresol-O-phosphine)* boils at  $235-238^\circ$  under 7 mm. pressure, at  $240-243$  under 10 mm. *Trimetacresol-methyl-O-phosphonium iodide*, prepared at  $100^\circ$ , is very hygroscopic, and was not obtained pure; *metatoluic methylphosphinate* boils at  $200-205^\circ$  under 7 mm. pressure.

*Pseudocumenylic phosphite (pseudocumenol-O-phosphine)*,  
 $(C_6H_2Me_3 \cdot O)_3P$ , boils at  $270-274^\circ$  under 16 mm. pressure, and has a sp. gr. =  $1.097$  at  $17^\circ$ . The methylphosphonium iodide was not obtained solid. *Pseudocumenylic methylphosphinate*,  $(C_6H_2Me_3 \cdot O)_2PMeO$ , melts at  $79-90^\circ$ .

When ethylic phosphite is heated with methylic iodide for 12 hours at  $220^\circ$ , an inflammable gas, presumably ethylene, is formed, and also ethylic iodide, and a solid product from which methylphosphinic acid,  $PMeO(OH)_2$ , can be isolated. This solid is dissolved in nitric acid, fuming nitric acid added, and the whole evaporated to dryness; the residue is then dissolved in water, and treated with excess of lead oxide made into a thin paste with water. From the mixture of lead salts formed, lead oxide and lead methylphosphinate are extracted with excess of acetic acid, lead phosphate remaining undissolved, the lead

in the filtrate is precipitated with hydrogen sulphide, and the filtrate freed from acetic acid by repeated evaporation with water, when the methylphosphinic acid is left as a white, crystalline mass, resembling spermaceti in appearance.

C. F. B.

**Action of Phosphorus Thiochloride on Solutions of Phenols in Aqueous Alkalies.** By WILHELM AUTENRIETH and OTTO HILDEBRAND (*Ber.*, 1898, 31, 1094—1111. Compare this vol., i, 14).—When a solution of phenol in 15—20 per cent. aqueous soda is heated on the water bath with phosphoryl thiochloride, *triphenylic thiophosphate*,  $\text{PS}(\text{OPh})_3$ , is formed and crystallises from alcohol in slender prisms melting at  $53^\circ$ . It is scarcely attacked by aqueous alkalies, but is readily hydrolysed by alcoholic soda, *diphenoxythiophosphoric acid*,  $\text{PS}(\text{OPh})_2\text{OH}$ , being produced. This substance is, moreover, always formed by the action of the thiochloride on an alkaline solution of phenol, both in the cold and on heating, and is also produced by the hydrolysis of diphenoxythiophosphoryl chloride with alcoholic soda; it is a yellowish oil which cannot be distilled, and readily dissolves in alkalies. The sodium salt crystallises in lustrous plates and is soluble in alcohol.

When phosphoryl thiochloride is added to a well cooled alkaline solution of phenol, two compounds are produced, which are the mono- and di-phenoxo-derivatives. *Diphenoxythiophosphoryl chloride*,  $\text{PS}(\text{OPh})_2\text{Cl}$ , crystallises in forms resembling those of gypsum, and melts at  $66$ — $67^\circ$ ; it is stable towards water, hydrochloric acid, and aqueous alkalies, but is converted by alcoholic soda into diphenylthiophosphoric acid. The chloride is converted by aqueous ammonia into *diphenoxythiophosphamide*,  $\text{PS}(\text{OPh})_2\text{NH}_2$ , which crystallises in white, nacreous plates melting at  $115^\circ$ , and is sparingly soluble in hot water. *Diphenoxythiophosphanilide*,  $\text{PS}(\text{OPh})_2\text{NHPH}$ , formed by the action of aniline on the amide, crystallises in slender prisms melting at  $92^\circ$ . *Diphenoxythiophosphodiethylamide*,  $\text{PS}(\text{OPh})_2\text{NEt}_2$ , crystallises in lustrous prisms melting at  $58^\circ$ .

*Phenoxythiophosphoryl dichloride*,  $\text{OPh}\cdot\text{PSCl}_2$ , is a colourless liquid which can be distilled under diminished pressure. *Phenoxythiophosphodiamide*,  $\text{PS}(\text{OPh})(\text{NH}_2)_2$ , crystallises in lustrous plates melting at  $119^\circ$ ; *Phenoxythiophosphodianilide*,  $\text{OPh}\cdot\text{PS}(\text{NHPH})_2$ , forms lustrous crystals melting at  $126^\circ$ , whilst the corresponding *phenylhydrazide*,  $(\text{OPh})\cdot\text{PS}(\text{NH}\cdot\text{NHPH})_2$ , crystallises in lustrous, slender needles melting at  $136^\circ$ .

*Phenoxythiophosphamic acid*,  $\text{OPh}\cdot\text{PS}(\text{NH}_2)\cdot\text{OH}$ , is prepared by heating the dichloride with aqueous ammonia, and crystallises in slender needles melting at  $127$ — $128^\circ$ ; when boiled with water, it yields ammonium phosphate, phenol and hydrogen sulphide. Alcoholic soda converts the dichloride into *phenoxythiophosphoric acid*,  $\text{OPh}\cdot\text{PS}(\text{OH})_2$ , which has only been obtained as a syrup.

Paracresol readily reacts with phosphorus thiochloride, but the sole product of the reaction appears to be *diparatolyloxythiophosphoryl chloride*,  $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_2\text{Cl}$ , which melts at  $53^\circ$ , and closely resembles the corresponding phenyl derivative in its properties. *Diparatolyloxy-*

*thiophosphamide*,  $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_2\cdot\text{NH}_2$ , crystallises in lustrous plates melting at  $131^\circ$ , whilst the *anilide* crystallises in slender needles and melts at  $106^\circ$ .

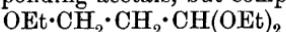
*Triparachlorophenyllic thiophosphate*,  $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Cl})_3$ , crystallises in tablets and melts at  $113$ — $114^\circ$ . *Diparachlorophenoxythiophosphoryl chloride*,  $\text{PS}(\text{O}\cdot\text{C}_6\text{H}_4\text{Cl})_2\text{Cl}$ , melts at  $92^\circ$ , and when treated with ammonia yields the corresponding *amide*, which crystallises in lustrous plates melting at  $96^\circ$ .

$\beta$ -Naphthol reacts very vigorously with the thiochloride, forming a mixture of the mono- and di-chlorides, which cannot be directly separated, but when treated with ammonia yields the corresponding amides, which can readily be obtained pure.  $\beta$ -*Naphthoxythiophosphodiamide*,  $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{PS}(\text{NH}_2)_2$ , crystallises in lustrous plates melting at  $176^\circ$ , whilst  $\beta$ -*naphthoxythiophosphamide*,  $\text{PS}(\text{OC}_{10}\text{H}_7)_2\cdot\text{NH}_2$ , separates from dilute alcohol in slender needles melting at  $215^\circ$ . A. H.

**Iodinium Compounds Prepared by the Action of the Iodo-chlorides on Mercury Organic Compounds.** By CONRAD WILIGERODT (*Ber.*, 1898, 31, 915—922).—The iodochlorides react with mercurydiphenyl and phenylmercuric chloride to form double salts of the iodinium chlorides with mercuric chloride. *Diphenyliodinium mercurichloride*,  $(\text{Ph}_2\text{ICl})_2\text{HgCl}_2$ , which decomposes at  $203^\circ$ , is formed by the action of phenyliodochloride both on mercurydiphenyl and phenylmercuric chloride, and is also produced when solutions of diphenyliodinium chloride and mercuric chloride are mixed. Phenylmercuric chloride does not appear to form any similar double salt, and the author was unable to obtain the salt,  $\text{Ph}_2\text{ICl}_2\text{HgCl}_2$ , described by Hartmann and Meyer (*Abstr.*, 1894, i, 461). *Phenylorthotolyliodinium chloride*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{IPhCl}$ , crystallises in short prisms melting at  $213$ — $214^\circ$ ; the *platinochloride* in yellow needles, decomposing at about  $191^\circ$ ; the *mercurichloride* in long, white needles melting at  $135$ — $137^\circ$ , whilst the *dichromate* decomposes at  $141$ — $143^\circ$ ; the *iodide* crystallises in short, colourless prisms decomposing at  $165^\circ$ ; the *nitrate* decomposes at  $183$ — $185^\circ$ , and the *sulphate* at  $171^\circ$ . The corresponding *hydroxide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{IPh}\cdot\text{OH}$ , has hitherto only been obtained in aqueous solution. *Phenylparatolyliodinium chloride* forms large, white prisms, melts at  $208^\circ$ , and is more readily soluble in water than the *ortho*-compound. The *platinochloride* decomposes at  $195$ — $198^\circ$ ; the *dichromate* explodes at  $155$ — $157^\circ$  and the *iodide* decomposes at  $170^\circ$ , whilst the *mercurichloride* crystallises in matted plates, melting at  $157^\circ$ , and the *nitrate* in large plates melting at  $138$ — $140^\circ$ . The hydroxide has only been obtained in the form of an amorphous, varnish-like mass. *Phenyl- $\beta$ -naphthyl iodinium chloride*,  $\text{C}_{10}\text{H}_7\cdot\text{IPhCl}$ , crystallises in short, acicular plates melting at  $197^\circ$ , and forms a *platinochloride* which decomposes at  $171$ — $173^\circ$ , and an *iodide* which decomposes at  $156$ — $160^\circ$ . The *hydroxide* forms a crystalline mass which has a strongly alkaline reaction. It was found impossible to obtain a phenylethyliodinium chloride by the action of an iodochloride on either mercury ethide or ethylmercurichloride, the products being ethylic chloride, iodobenzene, and ethylmercurichloride or mercuric chloride. A. H.

**Acetals of Aldehydes and Ketones.** By LUDWIG CLAISEN (*Ber.*, 1898, **31**, 1010—1019. Compare E. Fischer and Giebe, this vol., i, 168).—Pursuing his discoveries regarding the formation of acetals of aldehydes, ketones, and ketonic acids by the agency of orthoformates (*Abstr.*, 1896, i, 464; 1897, i, 188), the author has been led to replace the orthoformates by the hydrochlorides of imidoformates; these are known to yield orthoformates with alcohol at the ordinary temperature (Pinner, *Abstr.*, 1883, 731), and they are now found to react with ketones, &c., in alcoholic solution, yielding acetals in accordance with the equation  $\text{CR}_2\text{O} + 2\text{EtOH} + \text{OEt}\cdot\text{CH}\cdot\text{NH}\cdot\text{HCl} = \text{CR}_2(\text{OEt})_2 + \text{H}\cdot\text{COOEt} + \text{NH}_4\text{Cl}$ . The ketone (1 mol.) is mixed with alcohol (5 mols.), the mixture well cooled, and the imidoformate hydrochloride ( $\frac{1}{4}$  mols.) is gradually added, after which the whole is allowed to remain for several days, first in a refrigerator, then at the ordinary temperature. Plenty of ether is then added, the liquid is filtered from ammonium chloride, treated with ice and water containing a few drops of ammonia, and the ethereal layer removed and dried with potassium carbonate. The ether is next evaporated, and the residue fractionated under diminished pressure if the acetal have a high boiling point, otherwise under atmospheric pressure, in which case it is advisable first to let the liquid remain for some time with plenty of calcium chloride, in order that the alcohol may be removed as completely as possible. In some cases, no reaction occurs; for example, with benzophenone, although acetophenone does react, ethylic benzoylformate yields no acetal, although the pyruvate (acetylformate) does. Nor does camphor or carvole yield an acetal; the latter, in fact, gives + limonene. The yield is about the same as by E. Fischer's method in the case of aliphatic and of nitro- and chloro-aromatic aldehydes; those aldehydes which correspond with stronger acids seem to give a larger yield. In the case of other aromatic aldehydes, the new method is to be preferred, and it also yields acetals in the case of ketones, unlike the other method. By using methylic alcohol and methylic imidoformate, dimethylacetals can be obtained. The acetals obtained are enumerated below, together with such of their constants (boiling points and specific gravities at  $15^\circ$ ) as have not been published before; when the name of the aldehyde, &c., is alone given, the *ethyl*-acetal only is described in the paper.

Acetaldehyde, oenanthaldehyde, acraldehyde, and crotonaldehyde do not yield the corresponding acetals, but compounds



and  $\text{OEt}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ , the latter of which boils at  $73$ — $74^\circ$  under 14 mm. pressure. [The author prefers these formulae to those,  $\text{OEt}\cdot\text{CHMe}\cdot\text{CH}(\text{OEt})_2$  and  $\text{OEt}\cdot\text{CHEt}\cdot\text{CH}(\text{OEt})_2$ , proposed by Newbury (*Abstr.*, 1891, 285)].  *$\alpha\beta$ -Dibromopropionaldehyde*: *dimethylacetal*,  $108^\circ$ , under 15 mm.; *diethylacetal*,  $127$ — $129^\circ$ , under 22 mm.; the latter of these is converted by alcoholic potash into the *diethylacetals* of *monobromacraldehyde*,  $181$ — $183^\circ$ , and *propiolaldehyde*,  $140^\circ$ . *Furfuraldehyde*: *diethylacetal*,  $189$ — $191^\circ$ , sp. gr. =  $1\cdot0075$ . *Benzaldehyde*. *Cinnamaldehyde*: *dimethylacetal*,  $244$ — $245^\circ$ , sp. gr. =  $1\cdot0633$ ; *diethylacetal*,  $257$ — $259^\circ$ , sp. gr. =  $0\cdot9254$ . *Metanitrobenzaldehyde*: *dimethylacetal*,  $162$ — $164^\circ$  under 19 mm., sp. gr. =  $1\cdot209$ ; *diethylacetal*,  $178^\circ$ , under 21 mm., sp. gr. =  $1\cdot131$ . *Anisaldehyde*: *dimethylacetal*; *diethylacetal*,  $261$ — $263^\circ$ ; sp.

gr. = 0·9908. *Piperonaldehyde*: dimethylacetal, sp. gr. = 1·206; *diethylacetal*, 279—281° (153—154°, under 11 mm.), sp. gr. 1·129. *Cinnamaldehyde*; *dimethylacetal*, 125—127°, under 11 mm., sp. gr. = 1·023; *diethylacetal*, 264—266° (140—142°, under 12 mm.), sp. gr. = 0·981. *Monobromocinnamaldehyde*: *dimethylacetal*, 161—162°, under 15 mm., sp. gr. = 1·358; *diethylacetal*, 170—171°, under 15 mm., sp. gr. = 1·266; both of these yield *acetals* of *phenylpropiolaldehyde* when heated with alcoholic potash.

*Acetone*. *Acetophenone*: *dimethyl*, *diethyl* (212—216°, with some decomposition; compare following abstract), and *dipropyl-acetals*. *Ethylic pyruvate*: *diethylacetal*, 190—191°. [A fuller account of the acetals of ketones and ketonic acids is to be given in a later paper.]

*Acetaldehyde diethylacetal* (1 mol.), when heated with acetic anhydride (1 mol.) at 150° in a sealed tube, yields a compound,  $\text{OAc}\cdot\text{CHMe}\cdot\text{OEt}$ , boiling at 125—130°; sp. gr. = 0·941. In a similar way (except that further heating at 200° is necessary), *benzaldehyde diethylacetal* yields a compound  $\text{OAc}\cdot\text{CHPh}\cdot\text{OEt}$ , boiling at 243—245°. C. F. B.

**Action of Agents which can remove the elements of Alcohol on some Acetals.** By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1019—1021).—In the case of ethylic acetoacetate diethylacetal (*Abstr.*, 1896, 464), it has been shown that distillation under atmospheric pressure can remove the elements of alcohol from an acetal,  $\text{CH}_3\cdot\text{CR}(\text{OEt})_2$ , forming a compound  $\text{CH}_2\cdot\text{CR}(\text{OEt})$ . In general, however, this is not the case; some agent is necessary in order to remove the alcohol. Phosphoric anhydride may be used (as with ethylic pyruvate acetal), but it cannot be used alone in the case of acetals of aldehydes and ketones, for these, especially the latter, are very easily decomposed by acids. A mixture of phosphoric acid with a tertiary amine, such as pyridine or quinoline (ordinary acetal), may be used however; the base serves to neutralise the ethylphosphoric acid which is formed. In the case of acetals that more readily lose alcohol, the phosphoric anhydride may be replaced by an acid chloride; if the expected product have a low boiling point, quinoline and benzoic chloride should be used; if a high one, pyridine and acetic chloride (acetophenone acetal). A few compounds prepared by this method from acetals are enumerated below, with their boiling points; a more detailed account is to be published later.

*Ethylic a-ethoxyacrylate*,  $\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{COOEt}$ , 180°; hydrolysis converts it into *a-ethoxyacrylic acid*, which melts at 62°. [Merz and Otto's acid, melting at 110° (*Abstr.*, 1890, 957), is possibly the  $\beta$ -ethoxy acid].  $\text{CH}_2\cdot\text{CPh}\cdot\text{OEt}$ , 209—211°.  $\text{CH}_2\cdot\text{CMe}\cdot\text{OEt}$ , 59—62°;

$\text{CH}_2\cdot\text{CMe}\cdot\text{OMe}$ , 38°.

*Ethylic vinylic ether*,  $\text{CH}_2\cdot\text{CH}\cdot\text{OEt}$ .

C. F. B.

**Propargylaldehyde [Propiolaldehyde] and Phenylpropargylaldehyde [Phenylpropiolaldehyde].** By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1021—1023).—The acetals of these aldehydes are prepared by heating the acetals of  $\alpha\beta$ -dibromopropaldehyde and  $\alpha$ -bromocinnamaldehyde respectively with alcoholic potash; when heated with dilute sulphuric acid, they yield the aldehydes. These aldehydes are decomposed by aqueous soda in the cold, acetylene or phenylacetylene

being evolved and a formate formed; the action is in some respects analogous to that of alkalis on chloral.

*Propiolaldehyde*,  $\text{CH}:\text{C}\cdot\text{CHO}$ , boils at  $59-61^\circ$ , and affects the nose and eyes even more than acraldehyde does. A crystalline anilide and hydrazone were prepared. The *dimethylacetal* boils at  $110^\circ$ , the *diethylacetal* at  $139-141^\circ$ ; the latter forms a feebly explosive silver derivative,  $\text{CAG}:\text{C}\cdot\text{CH}(\text{OEt})_2$ .

*Phenylpropiolaldehyde*,  $\text{CPh}:\text{C}\cdot\text{CHO}$ , which boils at  $118^\circ$  under 17 mm. pressure, decomposes and gives off carbonic oxide when distilled under atmospheric pressure. The anilide, hydrazone, phenylhydrazone, semicarbazone, and hydrocyanide were prepared, and also condensation products with acetone, acetophenone, and malonic acid. The *diethylacetal* boils at  $148^\circ$  under 14 mm. pressure.

C. F. B.

**Normal Octyl Compounds.** By PAUL LIPINSKI (*Ber.*, 1898, 31, 938—942).—*Octylphenyl methyl ketone*,  $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ , formed by the action of acetic chloride on octylbenzene in the presence of aluminium chloride, is a yellowish oil with a faint aromatic odour. The *oxime* crystallises in white plates melting at  $42-43^\circ$ . *Octylphenyl phenyl ketone*,  $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ , is a yellowish-brown oil which boils at  $104-110^\circ$  under a pressure of 85 mm., and yields an *oxime* melting at  $106-107^\circ$ . *Octylphenylazo-a-naphthol*,  $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_8\cdot\text{OH}$ , crystallises from alcohol in red plates, which are prepared by nitrating octylbenzene, reducing, and treating the solution of the product of reduction with nitrous acid and *a-naphthol*. *Paramethyloctylbenzene* (para-octyltoluene) melts at  $11-12^\circ$ , boils at  $281-283^\circ$ , and is converted by oxidation into terephthalic acid. *Para-octyltoluenesulphonic [para-methyloctylsulphonic] acid*, obtained by shaking paramethyloctylbenzene with fuming sulphuric acid, forms white, deliquescent crystals. The salts of *barium* and *lead* are soluble in water and crystallise well. *Mononitroparamethyloctylbenzene*,  $\text{C}_8\text{H}_{17}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$ , which is produced, along with the dinitro-compound, by the action of fuming nitric acid on paramethyloctylbenzene, melts at  $19-20^\circ$ , forming a yellowish oil which cannot be distilled. The *dinitro*-compound is also an oil which cannot be distilled. *Paramethyloctylphenyl methyl ketone*,  $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ , is a yellowish liquid which has not been further examined.

A. H.

**A New Method of Preparing Acid Cyanides.** By LUDWIG CLAISEN (*Ber.*, 1898, 31, 1023—1024).—When pyridine is added slowly to an ethereal solution of benzoic chloride and anhydrous hydrogen cyanide, benzoic cyanide is obtained, together with some dibenzoic di-cyanide :  $\text{C}_6\text{H}_5\cdot\text{COCl} + \text{HCN} + \text{C}_5\text{NH}_5 = \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CN} + \text{C}_5\text{NH}_5\cdot\text{HCl}$ . The reaction is probably a general one, and affords a convenient means of preparing acid cyanides. If the acid chloride be added to a mixture of hydrogen cyanide with pyridine, the polymeric cyanide is almost the only product.

C. F. B.

**Paraxylylacetic Acid.** By GUERBET (*Compt. rend.*, 1897, 125, 34—37).—A good yield of Claus' paraxylyl methyl ketone can only be obtained under the following conditions. Aluminium chloride (20 grams), placed in a reflux apparatus, is covered with dry

carbon bisulphide, the flask is heated to 50°, and a mixture of acetic chloride (75 grams) and paraxylene (100 grams) gradually added from a dropping funnel, a further quantity of aluminium chloride (40 grams) being finally added. The operation takes about half an hour, and the mixture is then poured on to ice.

*Paraxylylacetamide*, obtained when the ketone (5 grams), 95 per cent. alcohol (4 grams), ammonium hydrosulphide (15 grams), and sulphur (2 grams) are heated for 48 hours at 200°, crystallises from alcohol in large, colourless needles melting at 154°. When hydrolysed by boiling with alcoholic potash (33 per cent.) for 8 days, it yields *paraxylylactic acid*,  $C_6H_3Me_2 \cdot CH_2 \cdot COOH$ , which crystallises from 60 per cent. alcohol in colourless, prismatic needles melting at 128°. The *potassium* salt is extremely deliquescent; the *sodium* salt crystallises with  $1H_2O$ , the *calcium* salt with  $3H_2O$ ; the *barium* salt is anhydrous and much more soluble than the calcium salt. The *methylic* salt boils at 253—254°, and the *ethylic* salt at 261.5°.

When oxidised with potassium permanganate, the acid yields unsymmetrical trimesic acid.

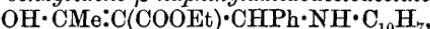
J. J. S.

**Tautomerides.** By ROBERT SCHIFF (*Ber.*, 1898, **31**, 1388—1395. Compare this vol., i, 237).—The author has shown that sodium ethoxide converts the ketonic modification of ethylic benzylidenediacetoacetate into the enolic form, which develops an intense coloration with ferric chloride, whilst piperidine exerts the converse influence.

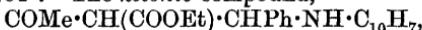
When ethylic ethylidenediacetoacetate (Knoevenagel, *Abstr.*, 1895, i, 51), is prepared from ethylic acetoacetate (2 mols.) and acetaldehyde (1 mol.) in presence of piperidine, the ketonic form crystallises from the liquid, and develops no coloration with ferric chloride; when the alcoholic solution is boiled, however, the enolic isomeride is generated. In order to prepare the latter, the ketonic salt is mixed with cold alcoholic sodium ethoxide (2 mols.), and, in presence of ice, treated with the corresponding amount of dilute hydrochloric acid; lustrous needles separate, developing a deep violet coloration with ferric chloride, but this property is gradually lost when the crystals are exposed to air, until, when quite dry, the substance is indifferent towards the agent, and melts at 78—79°.

Benzylideneaniline is a convenient agent for fixing tautomeric forms; in fact, all analogous condensation products of aromatic bases and aldehydes, excepting salicylaldehyde, appear suitable for this purpose.

*Enolic ethylic benzylidene- $\beta$ -naphthylamidoacetoacetate,*



is prepared by adding finely divided benzylidene- $\beta$ -naphthylamine to the enolic modification of ethylic acetoacetate (Kahlbaum); it dissolves in a small proportion of warm benzene, and separates as a white, crystalline precipitate on adding petroleum to the cold solution. It melts at 100—101°. The *ketonic* compound,



is obtained from common specimens of ethylic acetoacetate by adding benzylidene- $\beta$ -naphthylamine, and a small quantity of piperidine; it

melts at 74—75°, and yields ethylic phenylcarbinolacetooacetate (*loc. cit.*) under the influence of sodium ethoxide.

*Ketonic ethylic dianilidobenzylideneacetonedicarboxylate,*  
 $\text{CO}[\text{CH}(\text{COOEt})\cdot\text{C}\text{HPh}\cdot\text{NHPH}]_2$ ,

is obtained on adding a few drops of piperidine to mixed solutions of ethylic acetonedicarboxylate and benzylideneaniline (2 mols.) in benzene; it melts at 117—118°, and gives no coloration with ferric chloride. When piperidine is not employed, a mixture of the ethereal salt and benzylideneaniline (2 mols.) yields, after some hours, a white, insoluble compound which melts at 134°, and is isomeric with the foregoing substance; the authors regard it as a mixture form of the tautomeric modifications. The *enolic* compound,

$\text{NHPH}\cdot\text{CHPh}\cdot\text{CH}(\text{COOEt})\cdot\text{C}(\text{OH})\cdot\text{C}(\text{COOEt})\cdot\text{CHPh}\cdot\text{NHPH}$ ,  
 is produced on mixing benzene solutions of ethylic acetonedicarboxylate and benzylideneaniline in molecular proportion; the white, micro-crystalline substance is washed with light petroleum and benzene, and melts at 139°.

*Ethylic benzylidenediacetonedicarboxylate,*

$\text{CHPh}[\text{CH}(\text{COOEt})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt}]_2$ ,

prepared by adding 2 vols. of alcohol and a small quantity of piperidine to a mixture of benzaldehyde and ethylic acetonedicarboxylate (2 mols.), melts at 130°, and is in part resolved into its components under the influence of boiling alcohol.

*Ketonic anilidobenzylideneacetylacetone,*

$\text{COMe}\cdot\text{CH}(\text{COMe})\cdot\text{CHPh}\cdot\text{NHPH}$ ,

is obtained on adding a small quantity of piperidine to a mixture of benzylideneaniline and acetylacetone in molecular proportion; it separates when petroleum is added to its benzene solution, and melts at 83—84°. The substance develops a feeble red coloration with ethereal ferric chloride. The *compound* obtained without the influence of piperidine is the isomeric mixture form, and melts at 103°; it develops an intense red coloration with ferric chloride. The *enolic* compound,  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{COMe})\cdot\text{CHPh}\cdot\text{NHPH}$ , is formed in presence of a small quantity of dry sodium ethoxide; it crystallises from benzene on the addition of petroleum, in lustrous, white needles and melts at 109°. A deep red coloration with ferric chloride reveals the hydroxyl character of this modification.

Benzylidenediacetylacetone (Knoevenagel, *loc. cit.*), resembles ethylic benzylidenediacetoacetate and ethylic ethylidenediacetoacetate in chemical behaviour; the ketonic form melts at 167—168°, and is indifferent towards ferric chloride.

*Ketonic anilidobenzylidenebenzoylacetone,*

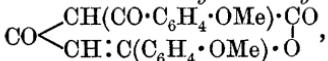
$\text{COMe}\cdot\text{CH}(\text{COPh})\cdot\text{CHPh}\cdot\text{NHPH}$ ,

cannot be crystallised owing to its insoluble character; it melts at 172—173°, and is probably a polymeride. The *enolic* compound,  $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{COPh})\cdot\text{CHPh}\cdot\text{NHPH}$ , crystallises very slowly from petroleum, and melts at 83—84°; it develops an intense dark red coloration with ferric chloride.

M. O. F.

**Ethylic Anisoylacetoacetate and its Derivatives.** By ALBERT SCHOONJANS (*Chem. Centr.*, 1897, ii, 616; from *Bull. Acad. roy. Belg.*, [iii], 33, 810—820).—A yield of 110 per cent. of anisic chloride is

obtained from anisic acid by heating the dry acid (1 mol.) with phosphorus pentachloride (1 mol.), then removing the phosphorus oxychloride by means of a current of dry air, and distilling the residue on a L. Meyer's air bath. *Anisic chloride* is a colourless, highly refractive liquid, boils at 160—164° under a pressure of 35 mm., at 152—153° under 24 mm., and at 145° under 14 mm.; when mixed with cold water and cooled, it forms matted needles which melt at 22°. *Ethylic anisoylacetoacetate*, prepared like the benzoylacetoacetate, forms an oily liquid which decomposes when distilled in a vacuum. With copper acetate, its alcoholic solution forms the compound  $\text{Cu}(\text{C}_{14}\text{H}_{15}\text{O}_5)_2$ , which crystallises from hot alcohol in small tablets, and from chloroform, in which it is very soluble, in small, lustrous needles. When ethylic anisoylacetoacetate is shaken with twice its weight of 10 per cent. ammonia, a yellow precipitate forms which dissolves on warming, and then *ethylic anisoylacetate* separates as a colourless oil of pleasant odour; this oil is insoluble in water, but miscible with alcohol and ether, boils at 140—142° under a pressure of 10 mm., has a sp. gr. = 1·0338 at 19°, gives a deep red coloration with ferric chloride in alcoholic solution, and with copper acetate an olive-green substance,  $\text{Cu}(\text{C}_{12}\text{H}_{13}\text{O}_4)_2$ , which crystallises from alcohol or chloroform in small needles, and decomposes at 180°. By the action of hydroxylamine hydrochloride in glacial acetic acid on ethylic anisoylacetate, a substance, which is probably *anisylisoaxazolone*, is formed; it crystallises from hot alcohol in long, yellow needles, melts and decomposes at 143°, is slightly soluble in light petroleum, easily soluble in hot benzene, and soluble in cold alkalies; with ferric chloride in alcoholic solution, it forms an inky-black liquid, reduces ammoniacal silver solutions, and is easily decomposed by alcoholic potassium hydroxide in the cold. *Dehydroanisoylacetic acid*,



is obtained from the brown mass which remains after rectifying the ethylic anisoylacetate, by washing with ether and crystallising from hot chloroform and alcohol. It crystallises in very light, golden-yellow, iridescent leaflets, is easily soluble in chloroform, slightly so in hot alcohol, but insoluble in the other usual solvents; with concentrated sulphuric acid, it gives a yellowish-red solution, which, on heating, becomes brown with a green fluorescence, and finally colourless; with ferric chloride in alcoholic solution, it gives a purple-red coloration. It dissolves in cold ammonia, and the solution, when evaporated, yields the unchanged substance. When the ammoniacal solution is neutralised with nitric acid and silver nitrate added, a yellow precipitate, which is soluble in ammonia and not affected by light, is obtained.

E. W. W.

**Amides of two substituted Orthoaldehydo-acids.** By AUGUSTIN BISTRZYCKI and ENRIQUE FYNN (*Ber.*, 1898, **31**, 922—929).—The substance obtained by the action of phosphorus pentachloride on bromopionic acid, which was described by Tust (*Abstr.*, 1892, 1209) as a trichloride,  $\text{COCl} \cdot \text{C}_6\text{HBr}(\text{OMe})_2 \cdot \text{CHCl}_2$ , is in reality the monochloride,  $\text{COCl} \cdot \text{C}_6\text{HBr}(\text{OMe})_2 \cdot \text{CHO}$ , and melts at 98—99°. On treatment with ammonia, it yields the amide, which, after crystallisation from chloro-

form, melts at 200°, whilst Tust gives 180° as the melting point after recrystallisation from water. The amide readily reacts with hydroxylamine hydrochloride, two products being formed. The first of these has the composition of the normal oxime, and crystallises in needles which melt and decompose at 267°; when heated with acetic anhydride, however, it simply yields an *acetyl* derivative, melting at 242°, and not bromopiazone,  $C_6HBr(OMe)_2 < \begin{matrix} CO \cdot NH \\ | \\ CH \cdot N \end{matrix} > CH_2$ , as might have been expected;

it seems probable, therefore, that this compound is not, in reality, a simple oxime. The second product,  $C_{10}H_8NBrO_5$ , crystallises in fascicular groups of needles melting at 227°, and is an oxidation product; it yields an *acetyl* derivative, which crystallises in tablets and melts at 159°. *Bromopiazone*, which is readily obtained by the action of hydrazine sulphate on bromopianic acid, crystallises in colourless, matted needles melting at 231—232°; its *acetyl* derivative also forms colourless needles melting at 173°. Bromopianic amide itself does not yield an anhydride when it is treated with acetic anhydride, but is converted into a *diacetyl* derivative,  $C_{10}H_8BrNO_4Ac_2$ , which crystallises in needles melting at 150°.

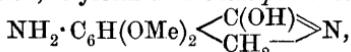
*Nitro-opianic chloride*,  $NO_2 \cdot C_6H(OMe)_2(CHO) \cdot COCl$ , forms faintly yellow, lustrous plates melting at 137—138°. The corresponding *amide* crystallises in yellow, lustrous needles, which melt and decompose at 203°; this compound behaves towards hydroxylamine in a precisely similar manner to the bromopianic amide, and the *compound* produced crystallises in yellow needles which melt and decompose at 265°, whilst the *acetyl* derivative crystallises in tablets, and decomposes at 246°.

A. H.

**Condensation Products from the Amides of two Orthoaldehydo-acids.** By AUGUSTIN BISTRZYCKI and EDWARD FINK (*Ber.*, 1898, 31, 930—936. Compare the foregoing abstract).—Bromopianic amide is converted by phosphorus oxychloride into *bisbromometa-opindolone*,

$C_6HBr(OMe)_2 < \begin{matrix} CO \cdot N \\ | \\ CH \cdot CH \end{matrix} > C_6HBr(OMe)_2$ , which forms a very sparingly soluble, brownish powder, and can be heated to 325° without undergoing any change. By reduction with tin and hydrochloric acid, it is converted into *dihydrobisbromometa-opindolone*,  $C_{20}H_{18}N_2Br_2O_6$ , a white, amorphous mass, and *bromohemipinic isoimidine*,  $C_6HBr(OMe)_2 < \begin{matrix} C(OH) \\ || \\ CH_2 \end{matrix} > N$ , which crystallises in white needles melting at 203°; this compound yields an *acetyl* derivative,  $C_{12}H_{12}NBrO_4$ , which crystallises in small, white needles melting at 177—178°.

*Bisnitrometa-opindolone*,  $(C_{10}H_8N_2O_5)_2$ , is prepared in a similar manner to the bromo-derivative, which it closely resembles in properties. On reduction, it yields *amidohemipinic isoimidine*,



the hydrochloride of which forms small, white needles; the free base crystallises in small prisms melting and decomposing at 223—224°, whilst the *diacetyl* derivative crystallises in white needles and decomposes at 242°. *Amidohemipinic isoimidine* can readily be converted

into the bromo-compound described above by means of the diazo-reaction, and this proves that, in bromopianic acid, the bromine atom occupies the same position in the ring as the nitro-group of nitro-opionic acid, which is known to have the constitution [COOH : CHO : (OMe)<sub>2</sub> : Br = 1 : 2 : 5 : 6 : 3].

A. H.

**Derivatives of Orthosulphobenzoic Anhydride.** By MICHAEL DRUCK SOHON (*Amer. Chem. J.*, 1898, 20, 257—278).—Orthosulphobenzoic anhydride, obtained by the action of phosphorus pentachloride on the acid potassium salt or by distilling the acid with phosphoric anhydride, forms clear, colourless, monoclinic, deliquescent crystals, melts at 129·5°, sublimes at or below its melting point, and can be distilled. Alcohols dissolve it with formation of the acid salts of orthosulphobenzoic acid. The *methyl* and *ethyl* hydrogen salts, and also their *silver* and *potassium* salts, are described.

Phenols act on the anhydride at a temperature of 130—135° with the production of sulphonphthaleins, which decompose on heating to a slightly higher temperature (about 150°) with evolution of hydrogen sulphide and formation of darker and less soluble products, which were not further investigated. No evidence of the formation of benzoylbenzenesulphonic acids could be obtained. The sulphonphthaleins are intensely coloured substances, more soluble in water than the corresponding derivatives of phthalic acid, and soluble in alcohol, from which they can be obtained crystalline by precipitation with ether.

*Phenolsulphonphthalein*,  $\text{SO}_2\left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{O} \end{array} \right\rangle \text{C}(\text{C}_6\text{H}_4\cdot\text{OH})_2$ , is precipitated as a bright red, crystalline powder, but on slow evaporation of a glacial acetic acid solution, it separates in distinct nodules of radiating needles, appearing blue-green by reflected and deep red by transmitted light ; it is about as sensitive to acids and alkalis as phenolphthalein, the colour of the alkaline solution varying from red to purple. When treated with zinc dust in alkaline solution, small, granular crystals of *phenol-sulphonphthalin* are formed, and with bromine in glacial acetic acid solution, it yields *dibromophenolsulphonphthalein* as a granular, purplish, crystalline powder. It gives a yellow solution with acids, and a blue to purple coloration with alkalis ; it is extremely delicate as an indicator, being sensitive to ammonia but not to carbonic anhydride.

*Phenolsulphonphthalein* does not give an acetyl derivative, and when fused with potash is converted into a sulphite, phenol, and para-dihydroxybenzophenone.

*Orthocresolsulphonphthalein*,  $\text{C}_{21}\text{H}_{18}\text{SO}_5$ , separates from water in crystals, appearing bottle-green by reflected and deep carmine by transmitted light ; its neutral or slightly acid solution is yellow, but with alkalis it gives a purple to carmine colour. With bromine, it forms a *dibromo*-derivative, and it can be acetylated.

*Paracresolsulphonphthalein* was not obtained pure ; it has a yellow colour, and is somewhat fluorescent.

*Resorcinolsulphonphthalein*,  $\text{SO}_2\left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{O} \end{array} \right\rangle \text{C} \left\langle \begin{array}{c} \text{C}_6\text{H}_3(\text{OH}) \\ | \\ \text{C}_6\text{H}_3(\text{OH}) \end{array} \right\rangle \text{O}$ , is a

bright reddish-yellow powder, intensely fluorescent in alkaline solution. The bromine derivative is not as intense in colour as eosin.

*Orcinolsulphonphthalein* is easily produced, and has been already described by Gilpin (*Amer. Chem. J.*, 16, 528).

*Quinolsulphonphthalein* was obtained as a dark-brown mass, *pyrogallolsulphonphthalein* (*sulphongallein*) as a bluish-brown powder, *meta-amidophenolsulphonphthalein* as a reddish-brown powder, and the corresponding *para*-compound as a dark-coloured mass. Salicylic acid, when melted with the anhydride, gives a bright red colouring matter.

*Ammonium benzaminesulphonate*, obtained by the action of ammonia on the anhydride, crystallises from alcohol in needles melting at 256—257°. The corresponding *barium* and *potassium* salts are also described.

A similar reaction is given with aniline and the toluidines, with production of a salt of the base with a benzanimido-acid. The free acids are exceedingly soluble, and could not be obtained in a crystalline form, but the salts crystallise slowly from concentrated solutions. They are decomposed by boiling with acids or alkalis, yielding the base and orthosulphobenzoic acid, and with phosphorus pentachloride the corresponding sulphinide derivative is obtained.

*Aniline benzanimidosulphonate* separates from alcohol in white tufts of radiating needles. The *barium*, *ammonium*, *potassium*, *cadmium*, *sodium*, *copper*, *silver*, and *lead* salts are also described, from the last of which the *free acid* was obtained as a syrup by means of hydrogen sulphide.

*Paratoluidine benzoparatoluido-orthosulphonate* forms clusters of short, sharply-pointed needles, and the corresponding *orthotoluidine*-derivative, nodules of radiating needles. The *barium* and *potassium* salts are described.

The anhydride acts on acetamide and benzamide as a dehydrating agent, giving rise to the corresponding nitrile and orthosulphobenzoic acid; and with phosphorus pentachloride produces both chlorides of orthosulphobenzoic acid, excess of the reagent, continued action, and high temperature favouring the formation of the unsymmetrical chloride.

A. W. C.

**Paramethoxyorthosulphobenzoic Acid.** By P. R. MOALE (*Amer. Chem. J.*, 1898, 20, 288—298).—*Paramethoxyorthosulphobenzoic acid*,  $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \cdot \text{SO}_3\text{H} + 2\frac{1}{2}\text{H}_2\text{O}$ , prepared from paratoluidine-orthosulphonic acid according to the directions of Parks (*Abstr.*, 1893, i, 585), crystallises from water in long, transparent, colourless needles melting at 104°. When heated in a test-tube to 145°, it lost water, and fine needles sublimed, but could not be obtained in sufficient amount for analysis. The *potassium*, *calcium*, *magnesium*, and *lead* salts are described.

When heated together with resorcinol, *paramethoxysulphonfluorescein* is obtained as a reddish, granular mass which dissolves in alkalis with a beautiful, reddish-green fluorescence; neither this nor the corresponding *orcinal* compound could be obtained quite pure. With phenol, a dirty-brown mass is formed, with which it was found impossible to deal satisfactorily.

A. W. C.

Decomposition of Paradiazo-orthotoluenesulphonic Acid with Absolute Methylic Alcohol in presence of other Substances. By P. R. MOALE (*Amer. Chem. J.*, 1898, 20, 298—302).—When paradiazo-orthotoluenesulphonic acid is acted on with sodium methoxide in methylic alcohol solution, and the product treated respectively with phosphorus pentachloride and ammonia, orthotoluene-sulphonamide is obtained in small amount, showing that the alkali causes the “hydrogen reaction” to take place to some extent. The residue is a black, tarry mass with which nothing could be done.

No definite results were arrived at when the decomposition was carried out with sodium ethoxide or caustic potash in ethylic alcohol solution, but by the action of dry ammonia gas in absolute methylic alcohol solution, and subsequent treatment of the residue with phosphorus pentachloride and ammonia, the amide of paratoluidine-orthosulphonic acid was obtained.

With aniline and methylic alcohol, three reactions take place according to the proportions of the reacting substances, one common product, and apparently three or four dyes, being formed.] A. W. C.

Silver Paraphenolsulphonate. By FRANCESCO ZANARDI (*Chem. Centr.*, 1897, ii, 547; from *Boll. Chim. Farm.*, 36, 449—452).—Paraphenolsulphonic acid is obtained as a thick syrup by decomposing barium paraphenolsulphonate with the calculated quantity of sulphuric acid. The aqueous solution of the acid, when treated with silver carbonate and evaporated at 20—25°, yields slender, white, prismatic needles of the silver salt; this is odourless, dissolves in 3 parts of water and in 80 parts of alcohol, and is insoluble in ether, chloroform, and carbon bisulphide; it is acted on by light, decomposes at 120°, and might be used as a disinfectant. E. W. W.

Parabenzoyldiphenylsulphone. By LYMAN C. NEWELL (*Amer. Chem. J.*, 1898, 20, 302—318).—Paratolylphenylsulphone prepared from paratoluenesulphonic chloride by Friedel and Craft's reaction, forms hexagonal plates melting at 124—125°. When oxidised with chromic acid in glacial acetic acid solution, it yields *paraphenylsulphonebenzoic acid*, crystallising from alcohol in small, white prisms melting at 273° (uncorr.), and not at above 300° as stated by Michael and Adair (*Abstr.*, 1878, 415). The *calcium*, *barium*, and *sodium* salts are described. The free acid and its salts are readily acted on by phosphorus pentachloride yielding *paraphenylsulphonebenzoic chloride*,  $\text{SO}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , which forms glistening, white plates, or short, white needles melting at 145·2—145·8°, and this substance, when treated with excess of concentrated ammonium hydroxide, is converted into *paraphenylsulphonebenzamide*, separating from alcohol in small transparent, acicular crystals melting at 242—243° (uncorr.); and with aniline it yields *paraphenylsulphonebenzanilide*, crystallising from alcohol in transparent, small prisms melting at 202—203° (uncorr.). *Parabenzoyldiphenylsulphone*,  $\text{SO}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$ , prepared from the chloride by the action of benzene in presence of aluminium chloride, crystallises from alcohol in fine, white, lustrous needles, which, when dry, pack together like felt, and melt at 133° (uncorr.). It may be recovered unchanged from its solution in warm, concentrated nitric acid,

or cold, concentrated sulphuric acid, and is not attacked by boiling alcoholic potash. On fusion with potash, it does not decompose into benzoic acid and diphenylsulphone like the corresponding ortho-compound (compare Remsen and Saunders, Abstr., 1895, i, 474), but the exact nature of the decomposition products could not be determined.

On treatment with phenylhydrazine, the sulphone yields a *phenylhydrazone*,  $\text{NHPh}\cdot\text{N}:\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Ph}$ , separating from alcohol in lustrous, lemon-yellow needles melting at  $184^\circ$ , and also a small amount of a substance, which appears to be acetophenylhydrazide. The formation of this substance can only be explained by supposing that the alcohol used in the experiment may have been oxidised to acetic acid, which may then have united with the excess of phenylhydrazine present. The corresponding *oxime* crystallises from alcohol in irregular leaflets melting at  $201^\circ$ .

The author has confirmed the work of Remsen and Saunders, who failed to obtain either an oxime or a phenylhydrazone from ortho-benzoyldiphenylsulphone.

A. W. C.

**Action of Phenyl- and Tolyl-hydroxylamines on Aromatic Thionylamines.** By AUGUST MICHAELIS and KARL PETOU (*Ber.*, 1898, 31, 984—997).—A benzene solution of thionylaniline reacts with phenylhydroxylamine, yielding azobenzene and aniline phenylsulphonamate. Other thionylamines and  $\beta$ -substituted hydroxylamines react in a similar manner, 2 molecules of the former always reacting with 4 molecules of the latter. The reaction is a little more complex when the thionylamine and hydroxylamine contain different radicles, for example,  $\text{R}\cdot\text{N}: \text{SO}$  and  $\text{R}'\text{NH}\cdot\text{OH}$ . When R and R' are similar, then the azo-compound is formed merely from the hydroxylamine, and has the symmetrical formula  $\text{R}'\cdot\text{N}:\text{N}\cdot\text{R}'$ , a mixed sulphonamate,  $\text{R}'\text{NH}\cdot\text{SO}_3\text{NH}_3\text{R}'$ , being formed at the same time. An exception to this is found in the reaction between parathionyltoluidine and phenylhydroxylamine, when the mixed azo-compound, benzeneazotoluene, is formed.

When the two radicles, R and R', are very different, then a mixed azo-compound is always formed, for example, when xylol-,  $\psi$ -cumyl- or naphthyl-thionylamines react with phenyl- or tolyl-hydroxylamines. These mixed azo-compounds are often red liquids, which can be purified by distillation in steam. In only one case, namely, by the action of paratolylhydroxylamine on metathionyltoluidine, was it found that the azo-compound was formed from the thionylamine, and had the symmetrical structure  $\text{R}\cdot\text{N}:\text{N}\cdot\text{R}$ , whilst a simple sulphonamate (2 mols.),  $\text{R}'\text{NH}\cdot\text{SO}_3\text{NH}_3\text{R}'$ , was formed at the same time.

A solution of phenylhydroxylamine (4 grams) in dry benzene (100 grams) readily reacts with thionylaniline (2·78 grams) also dissolved in benzene; after several hours, a crystalline mass of Wagner's aniline phenylsulphonamate (Abstr., 1886, 708) separates, and azobenzene remains dissolved in the benzene. Similarly, paratolylhydroxylamine (2 mols.) and thionylaniline (1 mol.) yield *paratoluidine phenylsulphonamate*, crystallising in white plates and melting at  $236^\circ$ , and an orange-yellow, crystalline azo-compound melting at  $68$ — $72^\circ$ , probably orthotolueneazoparatoluene. Thionylaniline and orthotolylhydroxylamine

yield azo-orthotoluene and *orthotoluidine phenylsulphonamate*, which melts at 205° giving a bluish-purple liquid.

Thionylaniline and metatolylhydroxylamine yield *metatoluidine phenylsulphonamate*, which carbonises at 250°, and Jacobson's benzene azometatoluene (Abstr., 1896, i, 96).

Phenylhydroxylamine and parathionyltoluidine yield a mixture of sulphonamates melting at 223°, and benzeneazoparatoluene melting at 70—71°. Schultz (Abstr., 1884, 903), has previously described this compound as melting at 63°. Paratolylhydroxylamine and para-thionyltoluidine yield parazotoluene and *paratoluidine paratolylsulphonamate* melting at 210—211°. [In other parts of the paper this is stated to melt at 235—236°]. Orthotolylhydroxylamine and para-thionyltoluidine yield *orthotoluidine paratolylsulphonamate* melting at 228°, and *orthoazoxytoluene*,  $(C_7H_7)_2N_2O$ , which crystallises from alcohol in yellow needles melting at 59°. Metatolylhydroxylamine and para-thionyltoluidine yield *metatoluidine paratolylsulphonamate* melting at 225—226°, and metazotoluene melting at 54—55°. Orthothionyltoluidine and phenylhydroxylamine yield a mixture of sulphonamates melting at 238—239°, and Jacobson's benzeneazo-orthotoluene. Orthothionyltoluidine and paratolylhydroxylamine give *paratoluidine orthotolylsulphonamate*, melting at 241°, and parazotoluene.

The same thionyl compound reacts with orthotolylhydroxylamine, yielding *orthotoluidine orthotolylsulphonamate*, melting at 212°, and *orthoazotoluene*, and with metatolylhydroxylamine yielding *metatoluidine orthotolylsulphonamate*, melting at 208°, and metazotoluene. Metathionyltoluidine and phenylhydroxylamine yield a mixture of sulphonamates and benzeneazometatoluene. The same thionyl compound reacts with paratolylhydroxylamine, yielding *paratoluidine paratolylsulphonamate*, melting at 235—236°, and metazotoluene. This is the only instance in which it has been found that the azo-compound is derived solely from the thionylamine. Metathionyltoluidine and orthotolylhydroxylamine yield a mixture of sulphonamates, melting at 219°, and Schultz's metatoluene-azo-orthotoluene. The same thionylamine and metatolylhydroxylamine yield *metatoluidine metatolylsulphonamate*, melting at 202°, and metazotoluene. Thionylmetaxylidine reacts with phenylhydroxylamine, yielding a mixture of sulphonamates and benzeneazometaxylylene; the latter is a red oil and is identical with the compound obtained by the action of nitrosobenzene on unsymmetrical metaxylylidine.

*Paratolueneazometaxylylene* is obtained by the interaction of asymmetrical metathionylxylylidine and paratolylhydroxylamine; when purified by distillation in steam and recrystallisation from alcohol, it forms yellowish-red, flat needles melting at 62°.

Thionylpseudocumidine reacts with phenylhydroxylamine, yielding a mixture of sulphonamates, melting at 218°, and *benzeneazopseudocumene*, which is a red oil. *Paratolueneazopseudocumene* crystallises in yellow needles melting at 58°. Benzeneazo-*a*-naphthalene, obtained from thionyl-*a*-naphthylamine and phenylhydroxylamine, crystallises from alcohol in small brick-red crystals melting at 70°; Nietzki and Zehntner (Abstr., 1893, i, 275) give the melting point as 63.5°. *Metatoluene-azo-a-naphthalene* melts at 43—44°.

Phenylhydroxylamine and thionyl-paraphenylenediamine react better in chloroform than in benzene solution; a crystalline sulphonamate, consisting probably of a mixture of aniline phenylsulphonamate and aniline paraphenylenedisulphonamate, is deposited, which carbonises between 200° and 300° without melting. The chloroform solution contains the triazo-compound,  $\text{PhN}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ , which, after recrystallisation from alcohol and sublimation, forms orange-red needles; it melts at 166—167°, and, when carefully heated, sublimes. Paratolylhydroxylamine, when treated in a similar manner, yields the triazo-compound,  $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$ , melting at 201—202°. Both these compounds are sparingly soluble in alcohol or ether, somewhat more soluble in benzene, and readily soluble in chloroform. J. J. S.

**Oxidation of Paranitrotoluenesulphonic Acid.** By ARTHUR G. GREEN and ANDRÉ R. WAHL (*Ber.*, 1898, **31**, 1078—1080. Compare this vol., i, 200).—In reply to the criticism of Ris and Simon (this vol., i, 322), the authors point out that the compound described by them as dinitrobenzyldisulphonic acid was in reality the free acid and not the sodium hydrogen salt as maintained by Ris and Simon. When a solution of normal sodium dinitrobenzylsulphonate is acidified, the nature of the product depends on the conditions. Strong solutions yield the monosodium salt, dilute solutions the free acid. Solutions of intermediate strength yield the monosodium salt when slowly cooled, but when the liquid is quickly cooled, the free acid separates in plates which are converted into the monosodium salt by prolonged contact with the mother liquor. The authors also maintain the accuracy of their formula,  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_{10}$ , for the dinitrostilbenesulphonic acid, as against the formula,  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{S}_2\text{O}_9$ , proposed by Ris and Simon, and have further confirmed it by a quantitative reduction experiment, carried out with a weighed amount of zinc dust, the excess of zinc being afterwards estimated by Wahl's method (this vol., ii, 190). A. H.

**Reduction of Aromatic Ketones by Sodium and Alcohol.** By AUGUST KLAGES and PAUL ALLENDORFF (*Ber.*, 1898, **31**, 998—1010).—Purely aromatic ketones,  $\text{CRR}'\text{O}$ , are reduced by sodium in boiling ethyl alcoholic solution to methane derivatives,  $\text{CH}_2\text{RR}'$ . Mixed aliphatic-aromatic ketones,  $\text{CH}_3\cdot\text{CRO}$ , are only reduced to carbinols,  $\text{CH}_3\cdot\text{CHR}\cdot\text{OH}$ ; a little of the melthane derivative,  $\text{CH}_3\cdot\text{CH}_2\text{R}$ , is indeed obtained, but this is doubtless due to a secondary reaction, namely, the reduction of a styrene derivative,  $\text{CH}_2\cdot\text{CHR}$ , which is also present in small amount among the products of the reaction. Two purely aromatic ketones, tetramethyldiamidobenzophenone (Michler's ketone) and its tetrethyl analogue, resemble the mixed ketones in that they yield carbinols. The ketones used were prepared by condensing an acid chloride with an aromatic hydrocarbon in the presence of freshly prepared aluminium chloride (Friedel-Craft's reaction); light petroleum was found to be a suitable medium in which to effect this. In almost all the reactions described in the paper, the product was eventually distilled under diminished pressure. The substances obtained are enumerated below.

Diphenylmethane,  $\text{CH}_2\text{Ph}_2$ . Parabenzyltoluene,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\text{Me}$ . *Parabenzoylecumene*,  $\text{CPhO}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$ , boils at  $334-336^\circ$  under ordinary pressure, at  $203-204^\circ$  under 20 mm., and has a sp. gr. =  $1\cdot0364$  at  $18^\circ/4^\circ$ ; *paraisopropylidiphenylmethane*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$ , boils at  $310^\circ$  under ordinary pressure, at  $176^\circ$  under 13 mm., and has a sp. gr. =  $1\cdot007$  at  $18^\circ/4^\circ$ . Benzoylpseudocumene,  $\text{CPhO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , [ $\text{Me}:\text{CPhO} = 1:2:4:5$ ], boils at  $328^\circ$  under normal and at  $211^\circ$  under 23 mm. pressure, and has a sp. gr. =  $1\cdot0332$  at  $18^\circ/4^\circ$ ; *benzylpseudocumene*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , boils at  $308-312^\circ$  under ordinary pressure, at  $190-191^\circ$  under 20 mm., and has a sp. gr. =  $1\cdot0151$  at  $18^\circ/4^\circ$ . Benzoylmesitylene,  $\text{CPhO}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , [ $\text{Me}_3:\text{CPhO} = 1:3:5:2$ ]; *benzylmesitylene*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_2\text{Me}_3$ . Parethoxybenzophenone,  $\text{CPhO}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , boils at  $242^\circ$  under 40 mm. pressure; *parethoxydiphenylmethane*,

$\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}$ , boils at  $317^\circ$ ,  $217^\circ$ , and  $203^\circ$  under ordinary pressure, 37 mm. and 12 mm. respectively, and could not be hydrolysed.

Tetramethyldiamidobenzhydrol,  $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ . *Tetraethylamidobenzhydrol*,  $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , melts at  $78^\circ$ , and yields, with hydroxylamine and sodium hydrogen carbonate in alcoholic solution, a substance which melts at  $128-129^\circ$ , and contains 11·6 per cent. of nitrogen.

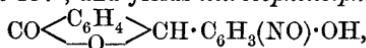
*Phenylmethylcarbinol*,  $\text{CHMePh}\cdot\text{OH}$ , boils at  $203\cdot6^\circ$  (corr.) under  $745\cdot4$  mm., at  $118^\circ$  under 40 mm., and has a sp. gr. =  $1\cdot007$  at  $21^\circ$ ; the *benzoate* boils at  $189^\circ$  under 20 mm. pressure, and under pressures greater than 25 mm. breaks up more or less into styrene and benzoic acid; the *phenylcarbamate* melts at  $94^\circ$ . The ethylbenzene also obtained in the reduction of acetophenone when added to bromine to which a little aluminium has been added previously, yields a *tetrabromo-substitution derivative* melting at  $138-139^\circ$ . Acetylpsuedocumene,  $\text{C}_6\text{H}_2\text{Me}_3\text{Ac}$  [ $\text{Me}_3:\text{Ac} = 1:2:4:5$ ], boils at  $137-138^\circ$  under 20 mm. pressure, and has a sp. gr. =  $1\cdot001$  at  $18^\circ/4^\circ$ ; its *oxine* melts at  $85-86^\circ$ ; *trimethylphenethylol*,  $\text{OH}\cdot\text{CHMe}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , [ $\text{Me}_3:\text{CHMe} = 1:2:4:5$ ], boils at  $252-253^\circ$  with slight decomposition under ordinary pressure, at  $140-141^\circ$  and  $138^\circ$  under 18 and 15 mm.; the *acetate* boils under the ordinary pressure at  $254-257^\circ$  with slight decomposition, and at  $130^\circ$  under 13 mm.; the *phenylcarbamate* melts at  $108^\circ$ ; the *chloride* can be obtained, although only in an impure state, by treating the carbinol with phosphorus pentachloride at the ordinary temperature, or saturating it with gaseous hydrogen chloride at  $0^\circ$ ; it boils at  $125-129^\circ$  under 13 mm. pressure, and loses hydrogen chloride when distilled under higher pressures. *1:2:4-Trimethyl-5-vinylbenzene*,  $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , is obtained when the above mentioned acetate is boiled with methyl alcoholic potash; it distils over at  $97^\circ$  under 22 mm. pressure, and leaves a residue of a *polymeride* (*a*), which, after crystallisation from alcohol and light petroleum, melts at  $118^\circ$ . Moreover, the boiling point of the substance itself under atmospheric pressure, originally  $212-214^\circ$ , rises as the distillation is repeated, partial polymerisation no doubt taking place; and if hydrogen chloride be removed from the above-mentioned chloride by warming it gently with aniline, or if the corresponding carbinol be warmed with syrupy phosphoric acid, a second

*polymeride* ( $\beta$ ), melting at  $163^\circ$ , is obtained. The unpolymerised substance forms a *dibromide*, which melts at  $65-66^\circ$ . Acetylmesitylene has a sp. gr. = 0.985 at  $18^\circ/4^\circ$ . *Trimethylphenethylool*, [ $\text{Me}_3\text{CHMe} = 1:3:5:2$ ], isomeric with the last carbinol, melts at  $71^\circ$ , and boils at  $248^\circ$  under ordinary pressure, at  $141^\circ$  under 24 mm.; the *acetate* boils at  $252^\circ$  under ordinary pressure, at  $134-135^\circ$  under 15 mm.; the *phenyl-carbamate* melts at  $124^\circ$ ; the (impure) *chloride* boils at  $126-127^\circ$  under 16 mm. pressure. *1:3:5-Trimethyl-2-vinylbenzene* is obtained when the last-mentioned carbinol is treated with phosphoric anhydride, but not when the acetate is boiled with methyl alcoholic potash; it boils at  $208-210^\circ$  without polymerising, but is converted by 80 per cent. sulphuric acid into a *polymeride* which melts at  $62^\circ$ , and boils and decomposes slightly at  $178-180^\circ$  under 19 mm. pressure. This polymeride is also obtained when the chloride is warmed with aniline, it remains behind in the flask when the product is distilled with steam, whilst a small quantity of the unpolymerised substance passes over.

C. F. B.

**Dimethylanilinephthaloylic Acid.** By HEINRICH LIMPRICHT [and E. KÖNIG] (*Annalen*, 1898, 300, 228—239).—*Dimethylanilinophthaloylic acid*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , is obtained by adding aluminium chloride in small quantities at a time to a solution of phthalic anhydride and dimethylaniline in carbon bisulphide, and subsequently heating the mixture for 3—4 hours in a reflux apparatus; it melts at  $205^\circ$ , and separates from alcohol in two forms, one of which is anhydrous, the other containing 1 mol. of alcohol. The barium salt dissolves readily in water, and the silver salt melts at about  $180^\circ$  to a black liquid; the *hydrochloride* forms thin leaflets, and melts to a reddish-brown liquid at about  $190^\circ$ . The *nitroso-derivative*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , contains  $1\text{H}_2\text{O}$ , which is removed at  $112-120^\circ$ , the anhydrous substance melting at  $164^\circ$ ; the barium salt forms red, prismatic crystals, which rapidly effloresce and become yellow on exposure to the air. Boiling caustic soda eliminates dimethylamine from the nitroso-derivative, giving rise to *nitrosophenolphthaloylic acid*,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{NO}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , which separates from ethylic acetate in bright yellow, prismatic crystals, and melts at  $178^\circ$ .

*Dimethylanilinophthalide*,  $\text{CO} < \begin{matrix} \text{C}_6\text{H}_4 \\ \diagdown \\ \text{O} \end{matrix} > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , is prepared by heating dimethylanilinophthaloylic acid with ammonia and zinc dust during 2 hours, and melts at  $188^\circ$ ; it dissolves in caustic soda, but is almost insoluble in boiling sodium carbonate. The *nitroso-derivative* melts at  $157^\circ$ , and yields *nitrosophenolphthalide*,



under the influence of hot caustic soda; the latter nitroso-compound melts at  $153^\circ$ , and yields a *barium* salt when dissolved in baryta.

*Dimethylanilinohydrophthaloylic acid*,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$ , produced on heating dimethylanilinophthaloylic acid with zinc dust and ammonia for 12 hours at  $70-80^\circ$ , melts at  $173^\circ$ ; the *barium* salt forms small, white prisms. The *nitroso-derivative* crystallises from alcohol, and melts at  $133^\circ$ .

M. O. F.

**Triphenylethanone (Benzoyldiphenylmethane).** By A. GARDEUR (*Chem. Centr.*, 1897, ii, 660—662; from *Bull. Acad. roy. Belg.*, [iii], 34, 67—100).—From triphenylethanone,  $\text{CHPh}_2\cdot\text{COPh}$ , prepared by Delacre's method (*Compt. rend. Assoc. franç. Congrès de Pau*, 181) the author obtained the benzoyl derivative by heating it with benzoic chloride for 2—3 days at  $240^\circ$ , although attempts to prepare it by Saint Pierre's method (*Bull. Soc. Chim.*, [iii], 5, 292) failed. This compound does not combine with hydrogen bromide, yet its constitution probably corresponds with the enolic form,  $\text{CPh}_2\cdot\text{CPh}\cdot\text{OBz}$ , for when reduced with sodium amalgam in alcohol, it yields triphenylethylic alcohol,  $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{OH}$ . When the benzoyl derivative was treated with alkali, however, either no reaction took place, or triphenylethanone of the ordinary ketonic form was produced. Delacre's sodium compound of triphenylethanone is a derivative of the ketonic type, for when heated with chlorobenzene, it yields triphenylmethane which can only result from the intermediate formation of tetraphenylethanone,  $\text{CPh}_3\cdot\text{COPh}$ . *Triphenylchlorehanone*,  $\text{CPh}_2\text{Cl}\cdot\text{COPh}$ , prepared by passing chlorine into an almost boiling solution of triphenylethanone in light petroleum, is a yellowish oil which, with water, forms triphenylethanone,  $\text{OH}\cdot\text{CPh}_2\cdot\text{COPh}$ . This is best prepared, however, by heating triphenylbromethanone with silver benzoate for 24 hours at about  $200^\circ$ , and then hydrolysing the benzoate thus obtained. The benzoate crystallises from glacial acetic acid and alcohol in needles, and melts at  $169^\circ$ . By heating a solution of triphenylethanone in glacial acetic acid with phenylhydrazine, small, crystalline needles of a substance which melts at  $144^\circ$ , and is probably the corresponding phenylhydrazone, are obtained. *Triphenylethanonephenylhydrazone*, which is prepared in a similar way, crystallises from glacial acetic acid in star-shaped needles, and melts at  $156^\circ$ . When triphenylbromethanone is reduced with zinc dust and glacial acetic acid, triphenylethanone and triphenylethylic alcohol,  $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{OH}$ , are formed. The latter, when heated with benzoic chloride, forms a *benzoate* which crystallises from glacial acetic acid in needles, and melts at  $145^\circ$ . By the action of bromine in glacial acetic acid on triphenylethylic alcohol or its benzoate, *triphenylbromethylene*,  $\text{CPh}_2\cdot\text{CBrPh}$ , is obtained; this crystallises from glacial acetic acid in needles, melts at  $115^\circ$  and with hydrogen bromide forms an unstable additive compound which melts at  $106$ — $110^\circ$ , and with water yields triphenylethanone of the ordinary ketonic form. *Triphenylchlorethylene* obtained by the action of phosphorus pentachloride on triphenylethanone, crystallises from alcohol in short cylinders, and melts at  $117^\circ$ ; when phosphorus pentabromide acts on triphenylethanone, triphenylbromethanone is formed. Triphenylethanediol (*triphenylethylenic glycol*),  $\text{OH}\cdot\text{CPh}_2\cdot\text{CHPh}\cdot\text{OH}$ , obtained in theoretical yield by the action of 10 times the calculated quantity of 7—8 per cent. sodium amalgam on a solution of triphenylethanone in alcohol, crystallises in needles and melts at  $164^\circ$ ; the *diacetyl* derivative crystallises from glacial acetic acid, and melts at  $214^\circ$ . Attempts to obtain triphenylethanone of the enolic form by withdrawing water from the glycol by means of hydrogen chloride, hydrogen bromide, or zinc chloride, yielded only the ordinary triphenylethanone. In one experiment, however, in which the glycol was melted with zinc

chloride, an oil was formed whose alcoholic solution, after remaining for a few days, deposited needles which melted at 100—102°, and appeared to be a mixture of the ordinary triphenylethanone with another substance, although the former alone was obtained on recrystallisation. When triphenylethylenic glycol is reduced with zinc and acetic acid, triphenylethanone is formed. By the action of potassium hydroxide and sodium acetate on the glycol, or by keeping it in a molten condition for some time, benzaldehyde and benzhydrol are obtained ; in addition to these products, *benzhydrol ether*,  $O(CHPh_2)_2$ , which crystallises from alcohol in needles and melts at 118°, is formed when the glycol is submitted to dry distillation.

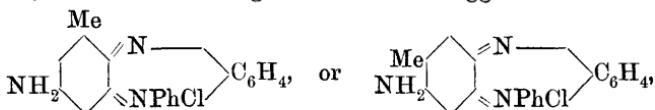
*Triphenylethylenic oxide*,  $O<sup>CPh_2</sup><sub>CHPh</sub>$ , prepared by the action of phosphoric anhydride on a solution of triphenylethylenic glycol in benzene, crystallises from glacial acetic acid in envelope-like crystals, melts at 105°, is stable in alkaline solutions, but in acid solutions or by recrystallisation is converted into the ordinary triphenylethanone.

E. W. W.

**Aposafranines and Azonium Compounds from Toluosafranines.** By FRIEDRICH KEHRENN and ALEXANDER WETTER (*Ber.*, 1898, 31, 966—977).—The amido-group is best removed from Geigy's tolusafranine chloride by the following process. A solution of the chloride (60 grams) in the requisite quantity of boiling water is treated with dilute sulphuric acid so that a crystalline mass is obtained ; this is cooled to 0°, and then treated with a little more than the theoretical quantity of sodium nitrite in concentrated aqueous solution ; the resulting dark blue diazo-solution is gradually added to an equal volume of alcohol, also cooled to 0°, and the alcohol distilled ; sulphuric acid (5 c.c.) is added to the dark red liquid, and the mixture allowed to remain for 12 hours. A crystalline mass, consisting of about equal quantities of methyl- and dimethyl-aposafranine derivatives, separates, and a considerable quantity of the dimethyl derivative remains in the mother liquor. The methylaposafranine is best purified by the aid of its chloride, which is much less soluble in dilute hydrochloric acid than the chloride of the dimethyl derivative. The separation is only completed after repeated solution in water and precipitation with dilute hydrochloric acid. *Methylaposafranine chloride*,  $C_{19}H_{16}N_3Cl$ , crystallises in long, pale yellow needles, is moderately soluble in water and readily in alcohol, yielding blood-red solutions ; its alcoholic solution also exhibits a strong, light red fluorescence. Saturated aqueous solutions are completely precipitated on the addition of a few drops of dilute hydrochloric acid. Alkalies precipitate the base, but carbonates in dilute solution do not do so. Both in physical and chemical properties, the chloride resembles rosinduline chloride. The *nitrate* is also sparingly soluble in water, but practically insoluble in dilute nitric acid ; the *platinochloride*,  $(C_{19}H_{16}N_3)_2PtCl_6$ , crystallises in small, reddish-brown plates, and is practically insoluble in water. The *acetyl* derivative of the chloride crystallises in long, yellowish-brown needles, which are soluble in water or alcohol, yielding yellowish-red solutions ; the acetyl deriva-

tive differs completely from the corresponding derivative of aposafranine chloride (Abstr., 1896, i, 323). It yields very little amido-derivative, or tolusafranine chloride, when its alcoholic solution is allowed to remain in contact with ammonia for several days at the ordinary temperature, being merely hydrolysed. Aniline only reacts with the acetyl derivative when kept in contact with it for 14 days. The *platino-chloride* of the acetyl derivative,  $(C_{22}H_{20}N_3O)_2PtCl_6$ , and the *nitrate*,  $C_{22}H_{20}N_4O_4 + H_2O$ , are described.

On account of the similarity between methylaposafranine and rosinduline, one of the following constitutions is suggested for the former,



in both of which the quinoid double bonds are on the heavier or basic side of the molecule. Monomethylaposafranine chloride is readily diazotised when suspended in 10 per cent. hydrochloric acid and treated with sodium nitrite; the diazotisation requires a longer time when a more dilute acid is employed. *Phenyltoluphenazonium* is obtained as its *iron double salt*,  $C_{19}H_{15}N_2FeCl_4$ , when the chloride is diazotised and the diazo-solution added to alcohol, and, at the end of 2 hours, precipitated with a saturated solution of ferric chloride in dilute hydrochloric acid, and may be best purified by washing with glacial acetic acid and subsequent crystallisation from the same solvent; it forms thick, brownish-red prisms melting at 150°, and dissolves readily in cold water and in hot acetic acid. The *nitrate*,  $C_{19}H_{15}N_2NO_3$ , obtained by precipitating the iron with ammonium carbonate, then adding dilute nitric acid, and salting out with solid sodium nitrate, also forms reddish-brown crystals. When the iron double salt is dissolved in alcohol (80 per cent.), and then treated with an excess of concentrated aqueous ammonia, a mixture of two isomeric methylaposafranines is obtained; the chief product is the methylaposafranine already described, but a small quantity of an isomeric substance is also formed, the chloride of which is more soluble in water, and crystallises in bronzy, glistening needles.

It is practically impossible to isolate pure dimethylaposafranine from Geigy's compound; even after repeated crystallisation, it always contains a quantity of the monomethyl derivative. When the impure dimethyl derivative is treated in the manner described above for the monomethyl derivative, a mixture of the double iron salts of methyl- and *dimethyl-phenylphenazonium chlorides* is formed. The dimethyl compound,  $C_{20}H_{17}N_2FeCl_4$ , is readily freed from the monomethyl compound, as it is much less soluble in glacial acetic acid; it crystallises in large, pale brown plates melting at 190°, and is readily soluble in water, but only sparingly in alcohol or acetic acid. The *nitrate*,  $C_{20}H_{17}N_2NO_3$ , and *platinochloride*,  $(C_{20}H_{17}N_2)_2PtCl_6$ , are also described. A concentrated solution of the iron double salt in alcohol (80 per cent.), when treated with an excess of concentrated ammonia and allowed to remain for 24 hours, yields *dimethylaposafranine*, the chloride of which crystallises in dark brown needles; its solutions in water or alcohol

have a magenta-red colour, and the latter exhibits a bright red fluorescence. The *platinochloride*,  $(C_{20}H_{18}N_3Cl)_2PtCl_4$ , and *acetyl* derivative are described.

J. J. S.

**Change of Position of the Double Linkings in Azonium Derivatives and its Causes.** By FRIEDRICH KEHRMANN (*Ber.*, 1898, 31, 977—984).—Numerous facts seem to indicate that the quinoid double-bonds in azonium compounds can change their position; this supposition is rendered absolutely necessary if it be conceded that amines and alkalis always react with azonium compounds yielding derivatives with the substituting groups in the quinoid nucleus (that is, in the benzene ring to which the double bonds are attached). The latter conclusion receives support from the fact that quinones themselves react with amines, yielding derivatives in which the substituting groups are attached to the same benzene nucleus as that to which the quinone oxygen atoms are attached.

The author compares the change in position of the quinoid bonds in azonium compounds to the mutual oxidation and reduction of quinones and quinols, the reaction being regarded as an intramolecular oxidation and reduction. It is shown that the same generalisations hold for the two cases. Several examples are given in illustration of the change in position of double linkings.

J. J. S.

**2 : 4-Tetrachloro-1 : 3-diketotetrahydronaphthalene.** By E. C. THEODOR ZINCKE and G. EGLY (*Annalen*, 1898, 300, 180—205).—  
**2 : 4-Tetrachloro-1 : 3-diketotetrahydronaphthalene**,  $C_6H_4\begin{array}{c} CO \\ \diagdown \\ CCl_2 \\ \diagup \\ CO \end{array}CO_2$ , is obtained as a hydrate by passing chlorine into a suspension of the anilide,  $C_6H_4\begin{array}{c} C(NHPh) \\ \diagdown \\ CCl \\ \diagup \\ COCl \end{array}CO_2$  (Zincke and Kegel, *Abstr.*, 1889, 268), in glacial acetic and hydrochloric acids. The *hydrate*, which contains  $3H_2O$ , is also produced by the action of chlorine on 1 : 3-dihydroxynaphthalene, and crystallises in thin, colourless plates; it sinters at  $80^\circ$ , melts to a clear liquid at about  $90^\circ$ , and intumesces at  $100^\circ$ . The anhydrous ketochloride, which is formed on exposing the hydrate to a vacuum, or to a temperature of  $100$ — $110^\circ$ , crystallises in stellate groups of prisms, and melts at  $92^\circ$ .

The *methoxy*-compound,  $C_6H_4\begin{array}{c} C(OH)(OMe) \\ \diagdown \\ CCl_2 \\ \diagup \\ CO_2 \end{array}H_2O$ , is obtained by boiling a solution of the hydrate in methylic alcohol; it begins to sinter at  $86^\circ$ , melts to a clear, red liquid at  $156^\circ$ , and decomposes at  $160^\circ$ .

**2 : 4-Dichloro-1 : 3-dihydroxynaphthalene (dichloronaphtharesorcinol).**  $C_6H_4\begin{array}{c} C(OH) \\ \diagdown \\ CCl \\ \diagup \\ CO_2 \end{array}H_2O$ , prepared by heating a solution of the hydrate in glacial acetic acid with concentrated hydrochloric acid and stannous chloride, crystallises from glacial acetic acid in colourless needles or nacreous leaflets, and melts at  $138$ — $139^\circ$ . The *diacetyl* derivative melts at  $136^\circ$ . Phenylhydrazine gives rise to the compound,  $C_6H_4\begin{array}{c} C(OH) \\ \diagdown \\ CCl \\ \diagup \\ C(N:NPh) \\ \diagdown \\ CO_2 \end{array}H_2O'$ , which melts at about  $190^\circ$ ; the *diacetyl* derivative melts at  $150^\circ$ .

*Orthodichloracetylphenyldichloracetic acid*,  $\text{CHCl}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_2\cdot\text{COOH}$ , obtained by the action of sodium carbonate on the ketohydrate, crystallises from benzene in colourless needles and small prisms, and melts at  $106-107^\circ$ . The *methyl*c salt forms colourless needles, and melts at  $114-115^\circ$ . On heating the acid or the ketohydrate with sodium carbonate,  $\beta$ -dichloro- $\alpha$ -ketohydroxyhydrindene carboxylic acid,  $\text{CO} \begin{array}{c} \text{CCl}_2 \\ \diagdown \\ \text{C}_6\text{H}_4 \end{array} > \text{C}(\text{OH})\cdot\text{COOH}$  (Zincke and Gerland, Abstr., 1888, 1199), is produced.

*Orthotrichloracetylphenyldichloracetic acid*,  $\text{CCl}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CCl}_2\cdot\text{COOH}$ , is prepared by treating the ketohydrate with a solution of bleaching powder ; it crystallises from benzene in colourless needles, or in monoclinic plates and melts at  $135^\circ$ , beginning to decompose at  $150-160^\circ$ . The *sodium* salt forms needles, and the *methyl*c salt melts at  $108-109^\circ$ ; the *anhydride* sublimes at  $160^\circ$  and melts at  $224^\circ$ , yielding dichloromethylene phthalyl. The action of hot sodium carbonate converts the acid into *trichloracetophenone carboxylic acid*,  $\text{CCl}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ , which melts at  $139^\circ$ ; alkalis eliminate chloroform. The *hydroxylactone* of orthotrichloracetylphenyldichloracetic acid,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{OH})(\text{CCl}_3)\cdot\text{O} \\ \diagdown \\ \text{CCl}_2 \end{array} \text{CO}$ , is produced on boiling the acid with water, and forms large, monoclinic crystals ; it melts and decomposes at  $139^\circ$ . The *acetyl* derivative crystallises from benzene in colourless prisms, melting at  $170^\circ$ . The hydroxylactone yields dichloromethylene phthalyl (Zincke and Cooksey, Abstr., 1890, 784) when heated with sodium acetate.

*Orthocarboxyphenyldichloracetic (dichlorohomophthalic) acid*,

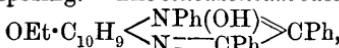


obtained on the action of potash on orthotrichloracetylphenyldichloracetic acid dissolved in methylic alcohol, crystallises from hot, dilute nitric acid in white needles, and from benzene in colourless plates melting at  $141^\circ$ , with formation of the *anhydride*, which melts at  $130^\circ$ . Aqueous alkalis convert the acid into orthocarboxybenzoylformic acid.

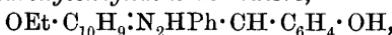
M. O. F.

**Reduction Products of Azo-compounds. VIII.** By PAUL JACOBSON and ANDREW TURNBULL (*Ber.*, 1898, 31, 890-906. Compare Abstr., 1896, i, 23).—It has previously been shown that whereas benzeneazophenetoil readily yields an orthosemidine on reduction with a hydrochloric acid solution of stannous chloride, benzeneazo-metacresetoil undergoes the same transformation much less readily, the difference having been ascribed to the presence of the methyl group in the ortho-position relatively to the azo-group. On the other hand, Witt and Helmholz have found (Abstr., 1894, i, 606) that benzeneazo- $\alpha$ -naphthylid ethylic ether very readily yields an orthosemidine derivative when it is reduced with stannous chloride, and the product then treated with hydrochloric acid. The authors have applied this method of reduction to all three compounds, and have found that, under these circumstances also, the orthosemidine forms 81 per cent. of the total semidine derivatives obtained from benzeneazophenetoil, 50 per cent. of the total obtained from benzeneazometacresetoil, and 100 per cent. of that from benzeneazonaphthylid ethylic ether; thus showing that the reaction is not influenced by the substitution of the naphthalene ring for the

simpler benzene ring. Benzeneazo-*ar*-tetrahydronaphthalic ethylic ether, however, behaves in a similar manner to the metacresetoil derivative, the orthosemidine amounting to only 50 per cent. of the total semidines obtained. The reduced ring of the naphthalene molecule, therefore, exerts an influence similar to that of a methyl group. *Benzeneazo-ar-tetrahydronaphthalic ethylic ether*,  $\text{PhN}_2 \cdot \text{C}_{10}\text{H}_{10} \cdot \text{OEt}$ , prepared by the action of sodium ethoxide and ethylic iodide on the corresponding naphthol, crystallises in orange-red prisms which have a golden lustre and melt at  $91\cdot 5^\circ$ . That this compound actually has the constitution assigned to it, is shown by the fact that benzeneazo-*ar*-tetrahydronaphthol, from which it is prepared, is converted by reduction, followed by oxidation, into tetrahydro-*a*-naphthaquinone. On reduction, it yields the ortho- and para-semidine derivatives, as well as a smaller amount of *paramido-ar-tetrahydronaphthalic ethylic ether*, which crystallises from light petroleum in long, colourless needles melting at  $60^\circ$ . The orthosemidine derivative, *4-amido-3-anilido-1-ethoxy-1':2':3':4'-tetrahydronaphthalene*,  $\text{C}_6\text{H}_8 \begin{array}{c} \text{C(OEt)} : \text{CH} \\ \diagdown \\ \text{C}(\text{NH}_2) : \text{C} \cdot \text{NHPH} \end{array}$ , crystallises from light petroleum in colourless plates or needles, which become pink on exposure to the air and melt at  $168\text{--}169^\circ$ . The corresponding *azimide*,  $\text{OEt} \cdot \text{C}_{10}\text{H}_9 \begin{array}{c} \text{NPh(OH)} \\ \diagdown \\ \text{N} = \text{C} \cdot \text{CPh} \end{array}$ , crystallises in colourless, oblique tablets, melts at  $125\text{--}126^\circ$ , and can be sublimed without decomposing. The *stilbazonium base*,



forms yellow prisms and melts at  $151\cdot 5^\circ$ . The *methenyl* compound,  $\text{OEt} \cdot \text{C}_{10}\text{H}_9 \begin{array}{c} \text{NPh} \\ \diagdown \\ \text{N} = \text{CH} \end{array}$ , which is obtained by heating the base with formic acid, crystallises in thin plates melting at  $139^\circ$ , and yields a sparingly soluble nitrate. The carbon bisulphide derivative,  $\text{OEt} \cdot \text{C}_{10}\text{H}_9 \begin{array}{c} \text{NPh} \\ \diagdown \\ \text{N} = \text{C} \cdot \text{SH} \end{array}$ , is only slowly formed and melts at  $269\text{--}270^\circ$ , whilst the *ortho**hydroxybenzylidene* derivative,



prepared from salicylaldehyde, crystallises in yellow prisms melting at  $130\text{--}131^\circ$ . The orthosemidine is converted by oxidation with ferric chloride into *anilidotetrahydro-a-naphthaquinone*,  $\text{C}_6\text{H}_8 \begin{array}{c} \text{CO} \cdot \text{CH} \\ \diagdown \\ \text{CO} \cdot \text{NHPH} \end{array}$  which forms brownish-red crystals melting at  $164^\circ$ .

The parasemidine derivative, *paramidophenylparethoxytetrahydro-ar-a-naphthylamine*,  $\text{C}_6\text{H}_8 \begin{array}{c} \text{C(OEt)} = \text{CH} \\ \diagdown \\ \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2) \end{array} \begin{array}{c} \text{CH} \\ \diagup \\ \text{C} \end{array}$ , crystallises in colourless prisms, melts at  $87\text{--}88^\circ$ , and becomes bluish on exposure to the air. The *sulphate* is only very sparingly soluble in water, whilst the *hydrochloride* dissolves more readily. This base gives the characteristic reactions of a parasemidine with nitrous acid, ferric chloride, chromic acid, and lead peroxide. The *monacetyl* derivative,  $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$ , crystallises in colourless needles melting at  $177\text{--}178^\circ$ , and the *thiocarbamide*,  $(\text{OEt} \cdot \text{C}_{10}\text{H}_{10} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH})_2\text{CS}$ , crystallises in plates melting at  $201^\circ$ .

*Tetrahydronaphthalis-azobenzene*, OH·C<sub>10</sub>H<sub>9</sub>(N<sub>2</sub>Ph)<sub>2</sub>, is formed in the preparation of benzeneazo-*ω*-tetrahydro-*α*-naphthol, and melts at 156°.  
A. H.

**Orientation in the Terpene Series : Conversion of Monocyclic Terpenes into the corresponding Derivatives of Benzene.** By ADOLF VON BAAYER and VICTOR VILLIGER (*Ber.*, 1898, 31, 1401—1405).—The authors have devised a general method by which monocyclic terpenes may be converted into the corresponding derivatives of benzene; it depends on the ultimate bromination of the terpene dihydrobromide, followed by reduction of the product with zinc and hydrochloric acid. It is found more convenient to brominate the dihydrobromides with bromine in presence of iodine, it being then unnecessary to raise the temperature as in using the halogen in presence of iron.

On this principle, paracycne and metacycne have been obtained from limonene and carvestrene respectively.

The passage from carone to carvestrene is now explained. Caronic acid has been recently synthesised by Perkin and Thorpe (*Proc.*, 1898, 107), in a manner which proves that it has the constitution assigned to it by von Baeyer (*Abstr.*, 1897, i, 83). The production of dihydrocarvone, CHMe< $\text{CO}-\text{CH}_2>\text{CH}\cdot\text{CMe}:\text{CH}_2$ , from carone CHMe·CO·CH>CMe<sub>2</sub>, on the one hand, and the conversion of carylamine,  $\text{CH}_2-\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}>\text{CMe}_2$ , into carvestrene,  $\text{CH}_2-\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}>\text{CMe}_2$ ,



on the other, represent the two directions which the rupture of the trimethylene ring is capable of following. M. O. F.

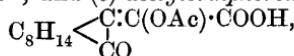
**Action of Sulphuric Acid on *l*-Terebenthene.** By GUSTAVE BOUCHARDAT and J. LAFONT (*Compt. rend.*, 1897, 125, 111—114).—By the action of sulphuric acid on laeo-terebenthene, and subsequent treatment with alcoholic potash, a number of products are obtained, among which are two potassium salts both readily soluble in water. The less soluble of the two, *potassium terebenthene sulphate*, C<sub>10</sub>H<sub>16</sub>SHKO<sub>4</sub>, crystallises in colourless plates somewhat resembling boric acid. Its rotatory power in alcoholic solution is [α]<sub>D</sub> = -25. Its aqueous solution is stable in the presence of a little alkali, but in neutral or acid solution readily undergoes decomposition, yielding potassium hydrogen sulphate and *l*-borneol. Nitric acid oxidises it to *l*-camphor melting at 203°. The second potassium salt has the same composition, but crystallises in silky needles, and its rotatory power is [α]<sub>D</sub> = +10°. It is decomposed in neutral or acid aqueous solution, yielding sulphuric acid and the alcohol melting at 45°, previously called isoborneol, but which the authors state to be *d*-fenchol. Nitric acid oxidises this potassium salt or the alcohol obtained from it to liquid camphor, identical with that obtained by the oxidation of synthetical isoborneol. J. J. S.

**Ethereal Oil of Pine Wood.** By PETER KLASON (*Bied. Centr.*, 1898, 27, 137—138; from *Svensk. kem. tidskr.*, 1897, 9, 138—140).—The oil obtained by the steam distillation of pine resin was found to be almost pure pinene. On the other hand, the oil extracted from pine wood by means of acid sulphite solution proved to be cymene. No terpenes are present in pine wood oil. N. H. J. M.

**A Crystalline Dicamphe Hydride.** By ALEXANDRE ÉTARD and GEORGES MEKER (*Compt. rend.*, 1898, 126, 526—529).—Terebenthene hydrochloride (100 parts) is heated until it just melts, sodium (15 parts) is introduced in one lot and the mixture well shaken so as to granulate the molten sodium; the reaction should take place slowly and at as low a temperature as possible. When the reaction is complete, the mixture is extracted with benzene and then fractionated, when two portions, one distilling at 150—160°, and a second at 320—330°, are obtained. The heavier fraction is mixed with a little benzene and agitated with fuming sulphuric acid. After well washing first with Nordhausen, then with concentrated sulphuric acid, and finally with water, the substance is distilled, when, if the liquid is well cooled, 15—20 per cent. of a crystalline substance is obtained. These crystals consist of *dicamphe hydride*, C<sub>20</sub>H<sub>34</sub>, and belong to the regular system, sp. gr. = 1·001 at 15°; it melts at 75°, boils at 326—327° (uncorr.), and has specific rotatory power [α]<sub>D</sub> = +15° 27'. [Letts obtained in this way a crystalline dicamphe hydride, C<sub>20</sub>H<sub>34</sub>, melting at 94°, and boiling at 321—323·6° (*Abstr.*, 1880, 669); to this no reference is made.—A. J. G.] J. J. S.

**The Rhodinol Question.** By JULIUS BERTRAM and EDUARD GILDEMEISTER (*Ber.*, 1898, 31, 749).—Poleck has no right to complain (this vol., i, 263) that the name of *geraniol* has been substituted for his name of *rhodinol*. What Eckart called rhodinol was a mixture of 70 per cent. of geraniol with 20 of *l*-citronellol and 10 of non-alcoholic substances of unknown composition. C. F. B.

**Action of Ethylic Oxalate on Camphor. III.** By J. BISHOP TINGLE (*Amer. Chem. J.*, 1898, 20, 318—342. Compare *Trans.*, 1890, 652; *Abstr.*, 1897, i, 484).—When camphoroxalic acid is boiled with acetic anhydride, there are produced, in small amounts, (a) a substance crystallising in clusters of colourless, slender needles melting at 242—242·5°, the nature of which has not been ascertained; (b) a substance, probably an anhydride, crystallising from light petroleum in slender needles melting at 190°; and (c) *acetylcamphoroxylic acid*,



crystallising from benzene in reticulated, stellate, needle-shaped prisms melting at 133·5—134·5°. It reacts speedily with bromine vapour, liquefying, and then gradually giving off hydrogen bromide, but no crystalline compound could be obtained.

Bromine vapour acts on camphoroxalic acid, producing a *bromo-acid*, C<sub>12</sub>H<sub>15</sub>O<sub>4</sub>Br, as an oil which gradually solidifies to crystalline nodules melting at 130°. The *silver* and *copper* salts are described. Magnesium amalgam removes the bromine from the acid, giving a substance melting

at 84—84·5°, which resemble camphoroxalic acid in general properties. The crystals are, however, not identical and will be further examined.

Camphoroxalic acid reacts with benzoic chloride, forming a substance melting at 192—193°, apparently identical with the supposed anhydride produced by the action of acetic anhydride as stated above; with benzoic anhydride, camphoroxalic acid reacts at 150° with evolution of carbonic anhydride, but no definite product could be isolated.

When quickly distilled under ordinary pressure, camphoroxalic acid evolves carbonic anhydride, and some camphor is formed, but the major portion passes over unchanged. Heating with barium hydroxide in a current of dry hydrogen causes hydrolysis to take place at the double linking, with production of barium oxalate and camphor.

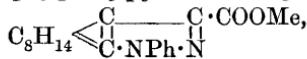
*Phenylhydrazine camphoroxalate*, prepared by the interaction of the components, separates from alcohol in minute, colourless needles darkening when heated to 205°, and melting and evolving gas at 214—215°; its alcoholic solution gives a red coloration with ferric chloride and a purple with concentrated nitric acid.

When camphoroxalic acid is heated in sealed tubes with dilute sulphuric or hydrochloric acid at 135—150° for several hours, an *acid*, C<sub>12</sub>H<sub>20</sub>O<sub>6</sub>, is formed which crystallises from benzene in clusters of colourless needles melting at 92—93°. It differs from camphoroxalic acid in not yielding any sparingly soluble salts, in not dissolving readily in light petroleum, and in giving a deep blue coloration with alcohol and ferric chloride.

Pure *ethylic camphoroxalate*, prepared by heating the acid with very dilute alcoholic hydrogen chloride, crystallises from light petroleum in fern-like aggregates of long needles melting at 40·5°. It does not form a copper salt, and is miscible with ether in all proportions. With dry ammonia, it gives a sparingly soluble, white *substance*, darkening when heated to 200°, and melting at 225°; with hydroxylamine, a *substance* crystallising from a mixture of toluene and light petroleum in colourless slender needles, melting at 120—121°; with acetic anhydride, acetylcamphoroxalic acid; with bromine, an *additive* compound, which evolves hydrogen bromide, forming a substance resembling the bromocamphoroxalic acid already described. With benzoic chloride or benzoic anhydride, however, no benzoyl derivative could be obtained, thus indicating a greater stability of the ethylic salt than of the free acid.

*Methylic camphoroxalate*, C<sub>8</sub>H<sub>14</sub> <math>\begin{array}{c} \text{C:C(OH)\cdot COOMe} \\ \diagdown \quad \diagup \\ \text{CO} \end{array}</math>, prepared by the

action of methylic oxalate on camphor, according to instructions given in a previous paper (*loc. cit.*), separates from light petroleum in long, arborescent needles melting at 74·5—75°; it resembles the ethylic salt in general properties. The *phenylhydrazide* forms slender, white needles melting at 204—205°, which, when acted on by glacial acetic acid, give *methylic camphylphenylpyrazolecarboxylate*,



crystallising in colourless needles, and melting at 80·5—81·5°. The

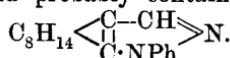
sodium salt is without marked physiological action, whereas the sodium salt of camphoroxalic acid is rapidly toxic.

*iso-Amylic camphoroxalate* separates in needle-shaped crystals melting at 98·5—99·5°. It gives a sparingly soluble *phenylhydrazide*.

A comparison of the crystallographic characters of camphoroxalic acid and its methylic and isoamyllic salts shows that the grade of symmetry of the crystals becomes lower as the molecular weight increases.

The compound obtained by the interaction of phenylhydrazine and camphoroxalic acid is shown to be a phenylhydrazide, as it is readily oxidised with mercuric oxide to give a substance crystallising in colourless, monoclinic plates melting at 112°.

When camphylphenylpyrazolecarboxylic acid is distilled with barium hydroxide, a yellowish-green oil passes over, which gives Knorr's pyrazoline reaction, and probably contains camphylphenylpyrazole



A. W. C.

Substances contained in Sesame Oil, and their Relation to the Characteristic Colour Reactions of the Oil. By VITTORIO VILLAVECCIA and GUIDO FABRIS (*Chem. Centr.*, 1897, ii, 772—773; from *Ann. Lab. chim. centr. delle Gabelle*, 3, 13—26).—Baudouin's colour reaction for sesame oil with hydrochloric acid and cane-sugar is also readily obtained with all those sugars which easily yield furfuraldehyde, and the authors assume this substance to be the cause of the reaction. As a test for sesame oil, they use a 1 per cent. solution of furfuraldehyde in 95 per cent. alcohol with hydrochloric acid, which forms an intense red coloration with the oil. From sesame oil, they have isolated the following substances. (1) *Sesamin*,  $(\text{C}_{11}\text{H}_{12}\text{O}_3)_2$ , crystallises from alcohol in long, colourless needles, from chloroform in prisms, is insoluble in water, light petroleum, ether, alkalis, and mineral acids, easily soluble in chloroform, benzene, and glacial acetic acid, melts at 123°, has a specific rotatory power  $[\alpha]_D = 68\cdot36$  at 22°, does not give the furfuraldehyde reaction, does not combine with iodine, forms neither acetyl nor phenylhydrazine derivatives, and is not attacked by potassium hydroxide, hydrochloric acid, or oxidising agents, but, with nitric acid of sp. gr. = 1·4, yields two crystalline compounds which melt at 235° and 145° respectively. (2) A higher alcohol,  $\text{C}_{25}\text{H}_{44}\text{O} + \text{H}_2\text{O}$ , which crystallises from alcohol in colourless leaflets having a nacreous lustre, melts at 137·5°, has a specific rotatory power  $[\alpha]_D = -34\cdot23$  at 20°, does not give the furfuraldehyde reaction, combines readily with bromine and iodine, yields an acetyl derivative which is a crystalline powder insoluble in water, very easily soluble in benzene, melts at 130—131°, and is easily saponified. (3) A viscous, odourless oil, which is very easily soluble in alcohol, ether, chloroform, and glacial acetic acid, insoluble in water and mineral acids, and very slightly soluble in alkalies. This substance gives the colour reaction with furfuraldehyde and hydrochloric acid.

E. W. W.

*Aloins.* By EUGÈNE LEGER (*Compt. rend.*, 1897, 125, 185—188).—Analyses of barbaloin made by the author agree best with Groenewold's formula (*Abstr.*, 1890, 639); it always crystallises with  $1\text{H}_2\text{O}$ . When treated in pyridine solution with benzoic chloride, it yields an

amorphous dibenzoyl derivative,  $C_{16}H_{14}Bz_2O_7$ , which is readily soluble in alcohol or ether. A diacetyl derivative may be obtained in a similar manner. Barbaloïn, partially purified by crystallisation from methylic alcohol, contains another aloin, apparently isomeric with barbaloïn, and crystallising from methylic alcohol in yellow, opaque plates containing  $3H_2O$ .

J. J. S.

**Aromatic Principles of Capsicum annuum, L., and Capsicum fastigiatum, Bl.** By JOHANNES MÖRBITZ (*Chem. Centr.*, 1897, ii, 593; from *Pharm. Zeit. Russ.*, 36, 299—301, 313—316, 327—331, 341—346, 369—376).—The cayenne fruit contains 0·05—0·07 per cent. of *capsacutin*,  $C_{35}H_{54}N_3O_4$ , which is obtained by freeing the powdered fruit from fat by means of light petroleum, extracting with ether, hydrolysing the residue left on evaporating the extract, again extracting with ether, evaporating, and finally crystallising the residue from boiling light petroleum. Capsacutin has an extremely pungent taste, which may be detected in a solution containing only 1 part in 11,000,000; it is only slightly soluble in water and light petroleum, but soluble in the ordinary solvents. It is neither a glucoside nor an acid.

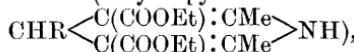
E. W. W.

**2-Methylpyrrolidine.** By GOTTFRIED FENNER and JULIUS TAFEL (*Ber.*, 1898, 31, 906—914).—The 2-methylpyrrolidine prepared from methylpyrrolidone by reduction with amylic alcohol and sodium (Neugebauer and Tafel, *Abstr.*, 1889, 1015) probably contained a little piperidine derived from impurities in the amylic alcohol and the authors have therefore prepared the pure compound by the same method, but using amylic alcohol which had been carefully purified, and have compared the properties of this substance with those of the 2-methylpyrrolidine derived from the 1:2-dimethylpyrrolidine, which is formed by the action of hydrochloric acid on dimethylpiperidine (Merling, *Abstr.*, 1891, 1506; Ladenburg, Mugdan and Brzostovicz, *Abstr.*, 1894, i, 555), the two compounds being found to be in all respects identical. 2-Methylpyrrolidine has a sp. gr. = 0·84 at 20°/20°, and boils at 95·5—96·5° under a pressure of 744 mm. The hydrochloride is very deliquescent, and melts at the temperature of the water bath, whilst the *oxalate* melts at 178—179°; the *platinochloride*,  $(C_5H_{12}N)_2PtCl_6$ , has no definite melting point, and the *aurochloride*,  $C_5H_{12}NAuCl_4$ , melts at 158—161°. Dimethylpyrrolidine boils at 96—96·5°, and yields 2-methylpyrrolidine when its hydrochloride is heated in hydrogen chloride. Both methyl- and dimethyl-pyrrolidine are converted by methylic iodide into the methiodide of dimethylpyrrolidine, whilst the corresponding methochloride is formed by molecular change from dimethylpiperidine hydrochloride. *Trimethylpyrrolidineammonium platinochloride* forms yellow, octahedral crystals, and decomposes at 240—250°, whilst the *aurochloride* begins to decompose at 204°. The aurochloride  $(C_5H_{12}NCl)_2AuCl_3$ , which was formerly ascribed to methylpyrrolidine, is in reality derived from piperidine.

A. H.

**Condensing Action of Ammonia and Organic Amines in Reactions between Aldehydes and Ethylic Acetoacetate.** By EMIL KNOEVENAGEL (*Ber.*, 1898, 31, 738—748).—The author's conclusions are reproduced below.

I. Nitrogenous products (dihydropyridine derivatives,



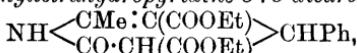
are obtained: (1) from an aldehyde, ethylic acetoacetate, and free ammonia; (2) from an aldehyde-ammonia and ethylic acetoacetate (Hantzsch's dihydropyridine synthesis), or from a hydramide [trialkylidenediamine,  $(\text{R}\cdot\text{CH}_3)_3\text{N}_2$ ] and ethylic acetoacetate together with ammonia; (3) from an aldehyde and ethylic  $\beta$ -amidoerotonate; (4) from ammonia and a mixture of an ethylic alkylideneacetoacetate,  $\text{CHR}:\text{CAC}\cdot\text{COOEt}$ , with ethylic acetoacetate; (5) from an ethylic alkylideneacetoacetate and  $\beta$ -amido- or a  $\beta$ -monalkylamido-crotonate.

II. Non-nitrogenous products (at low temperatures, ethylic alkylidene-acetoacetates,  $\text{CHR}:\text{CAC}\cdot\text{COOEt}$ ; at higher temperatures, ethylic alkylidenediacetoacetates,  $\text{CHR}(\text{CHAC}\cdot\text{COOEt})_2$ ), are obtained: (1) from a mixture of an aldehyde and ethylic acetoacetate under the influence of a mon- or di-alkylamine (or of ammonia at a low temperature); (2) from an alkylidenebisdialkylamine,  $\text{R}\cdot\text{CH}(\text{NR}_2)_2$ , and ethylic acetoacetate; (3) from an aldehyde and an ethylic  $\beta$ -dialkylamidoerotonate; (4) from an ethylic alkylideneacetoacetate and ethylic acetoacetate, under the influence of alkyl- and dialkyl-amines; (5) from an ethylic alkylideneacetoacetate and an ethylic  $\beta$ -dialkylamidoerotonate.

It appears that in Hantzsch's dihydropyridine synthesis, the aldehyde-ammonia first reacts with the ethylic acetoacetate to form ethylic ethylideneacetoacetate, ammonia being liberated, and the ammonia converts the second molecule of the acetoacetate into ethylic  $\beta$ -amidoerotonate, which reacts with the ethylideneacetate to form ethylic dihydrocollidinedicarboxylate. All these separate stages can be realised, at any rate to a certain extent. If this view be correct, one of the weightiest arguments in favour of Riedel's pyridine formula,  $\text{CH} \begin{array}{c} \text{CH}:\text{CH} \\ \swarrow \quad \searrow \\ \text{CH}:\text{CH} \end{array} \text{N}$ , is seriously impaired.

*Ethylic  $\beta$ -piperidocrotonate*,  $\text{C}_5\text{NH}_{10}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$ , is described for the first time. It is made by mixing piperidine (1 mol.) with ethylic acetoacetate (1 mol.), removing the oil after 3 hours, drying it over dehydrated sodium sulphate, and distilling it under diminished pressure. It boils at  $169^\circ$  under 15 mm. pressure. C. F. B.

Syntheses in the Pyridine Series. I. An Extension of Hantzsch's Dihydropyridine Synthesis. By EMIL KNOEVENAGEL and A. FRIES (*Ber.*, 1898, 31, 761—767).—When ethylic benzylidene-malonate,  $\text{CHPh}:\text{C}(\text{COOEt})_2$  (1 mol.), is heated with ethylic  $\beta$ -amidoerotonate,  $\text{NH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$  (1 mol.), for 9 hours at  $130$ — $150^\circ$  in a reflux apparatus under 40 mm. pressure, the product is *ethylic 6-oxy-4-phenyl-2-methyltetrahydropyridine-3:5-dicarboxylate*,



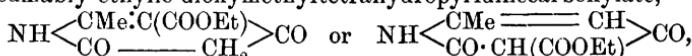
or the corresponding enolic form, and the yield of the crude substance is 75 per cent. of the theoretical. The new compound, which melts at  $149.5$ — $150^\circ$ , is hardly soluble in acids or alkalis, and when boiled with strong hydrochloric acid for 10 hours, yields  $\gamma$ -acetyl- $\beta$ -phenyl-

butyric acid,  $\text{COMe}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COOH}$  (Vorländer, Abstr., 1894, i, 528).

When the heating is continued for 18 hours at  $130-150^\circ$ , and then for 9 hours at  $150-170^\circ$ , there is obtained, besides the substance described above, a compound which apparently has the constitution  $\text{CMe} \begin{array}{c} \text{C}(\text{COOEt}) \\ \swarrow \\ \text{NH} \end{array} \text{---} \begin{array}{c} \text{CHPh} \\ \searrow \\ \text{CO} \end{array} > \text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$ , and must have been formed by the action of 2 mols. of the amidocrotonate on 1 mol. of the benzildienemalonate ; this compound melts at  $179-180^\circ$ , and also yields acetylphenylbutyric acid when it is boiled with hydrochloric acid. Two other products, melting at  $206-206.5^\circ$  and  $262-263^\circ$  respectively, were obtained in addition ; these have been shown (following abstract) to be identical with the products of the action of ethylic malonate itself on ethylic  $\beta$ -amidocrotonate.

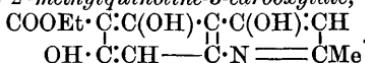
Ethylic ethylenemalonate reacts in a similar manner to the benzylidene analogue, yielding with ethylic  $\beta$ -amidocrotonate a compound,  $\text{NH} \begin{array}{c} \text{CMe}\cdot\text{C}(\text{COOEt}) \\ \swarrow \\ \text{CO}\cdot\text{CH}(\text{COOEt}) \end{array} > \text{CHMe}$ , which is closely related to the substance obtained by Collie (Trans., 1897, 301, 303 ; compound A) by heating the hydrochloride of ethylic  $\beta$ -amidocrotonate. C. F. B.

**Syntheses in the Pyridine Series. II. Action of Ethylic Malonate on Ethylic  $\beta$ -Amidocrotonate.** By EMIL KNOEVENAGEL and A. FRIES (*Ber.*, 1898, 31, 767-776. Compare preceding abstract). —When pure ethylic malonate (1 mol.) is heated with ethylic  $\beta$ -amidocrotonate (1 mol.) and alcoholic sodium ethoxide (1 mol.) for 7-9 hours in a sealed tube at  $140-150^\circ$ , a product is obtained which is presumably ethylic dioxymethyltetrahydropyridinecarboxylate,



or the enolic form of either of these. It melts at  $206-206.5^\circ$ , and has both acid and basic properties ; its rather unstable hydrochloride, with  $3\text{H}_2\text{O}$ , melts at  $152^\circ$  when heated quickly ; further, it yields a monobromo-substitution derivative which melts and decomposes at  $245^\circ$ , and also a compound containing very much more bromine (70.5 per cent.) ; it forms a dioxime, which carbonises at  $245-255^\circ$  ; and when boiled with aqueous or alcoholic potash, or strong hydrochloric acid, or when its hydrochloride is heated alone, 4 : 6-dihydroxy-2-methylpyridine (Collie, Trans., 1891, 617 ; 1892, 723) is obtained. This substance has feeble basic, but pronounced acid properties ; the potassium salt crystallises with  $1\text{EtOH}$ .

If the heating be carried out in a reflux apparatus at  $130-150^\circ$  under a pressure of 40 mm., 2 mols. of the amidocrotonate appear to react with 1 mol. of the malonate, the product being *ethylic 2 : 4 : 4'-trihydroxy-2'-methylquinoline-3-carboxylate*,



This melts at  $262-263^\circ$ , dissolves in strong hydrochloric acid, but not in alkalis, and loses carbonic anhydride when boiled with alcoholic or aqueous potash, the product, which remains unmelted at  $360^\circ$ , being presumably *2 : 4 : 4'-trihydroxy-2'-methylquinoline*. C. F. B.

**Syntheses in the Pyridine Series. III. Some Acetylpyridines and Acetyl-dihydropyridines.** By EMIL KNOEVENAGEL and WALTER RUSCHHAUPT (*Ber.*, 1898, 31, 1025—1033).—*3 : 5-Diacetyl-4-phenyl-2 : 6-dimethyl-Δ<sub>2,5</sub>-dihydropyridine*, C<sub>5</sub>NH<sub>2</sub>Me<sub>2</sub>PhAc<sub>2</sub>, is obtained by heating benzylideneacetylacetone (Abstr., 1895, i, 50) (1 mol.) with amidoacetylacetone (1 mol.) for 2 hours on a boiling water bath; it is yellow, melts at 180°, and boils at 225—235° under 25 mm. pressure. Dilute nitric acid at 60—70° oxidises the two hydrogen atoms, forming *3 : 5-diacetyl-4-phenyl-2 : 6-dimethylpyridine*, which melts at 188°.

*Ethylic 3-acetyl-4-phenyl-2 : 6-dimethyl-Δ<sub>2,5</sub>-dihydropyridine-5-carboxylate* is obtained by heating either ethylic benzylideneacetoacetate (Abstr., 1896, i, 232) with amidoacetylacetone, or ethylic β-amido-crotonate with benzylideneacetylacetone; it is yellow, melts at 167°, and boils at 210—230° under 25—30 mm. pressure. Dilute nitric acid, at temperatures slightly below 40°, oxidises it to *ethylic 3-acetyl-4-phenyl-2 : 6-dimethylpyridine-5-carboxylate*, which melts at 85—86°.

*Ethylideneacetylacetone*, CHMe·C(CMeO)<sub>2</sub>, was obtained by passing gaseous hydrogen chloride for  $\frac{1}{2}$  hour into a dilute chloroform solution of acetaldehyde (1 mol.) and acetylacetone (1 mol.), and then distilling off the chloroform under diminished pressure at 0°; it boils at 87°, 92°, and 97° under 10, 13, and 18 mm. pressure respectively. When it is mixed with amidoacetylacetone, *3 : 5-diacetyl-2 : 4 : 6-trimethyl-Δ<sub>2,5</sub>-dihydropyridine* is obtained; this is yellow, melts at 152°, and boils with some decomposition at 220—230° under 20 mm. pressure.

*Methylamidoacetylacetone*, NHMe·CMe·CH·CMeO, prepared by mixing 33 per cent. aqueous methylamine with acetylacetone, melts at 45°, and boils at 200°. When mixed with ethylideneacetylacetone, it forms *3 : 5-diacetyl-1 : 2 : 4 : 6-tetramethyl-Δ<sub>2,5</sub>-dihydropyridine*, which is greenish-yellow and melts at 118°.

When diacetyltrimethylidihydropyridine, or ethylic acetyltrimethylidihydropyridinecarboxylate, is boiled for 4 hours with 10 per cent. caustic potash, it is converted into 1 : 3-dimethyl-Δ<sub>2</sub>-ketotetrahydrobenzene (Hantzsch, Abstr., 1883, 84; Knoevenagel, Abstr., 1895, i, 52):—NH<<sub>CMe·CAC</sub>>CHMe + 3H<sub>2</sub>O = NH<sub>3</sub> + 3CH<sub>3</sub>·COOH + CH<<sub>CO—CH<sub>2</sub></sub>>CHMe. Diacetylphenyldimethylidihydropyridine and ethylic acetylphenyldimethylidihydropyridinecarboxylate are scarcely attacked. With 40 per cent. caustic soda, ethylic acetyltrimethylidihydropyridinecarboxylate yields, in addition to the product mentioned above, a substance which melts at 86° and boils at 155—160° under 15 mm. pressure, and appears to be somewhat impure ethylic trimethylidihydropyridinecarboxylate.

Methylenediacetylacetone (Scholtz, this vol., i, 43) was obtained in crystals incidentally; it melts at 87°.

C. F. B.

**Action of Concentrated Alkalies on Ethylic Dihydrocollidine-dicarboxylate [2 : 4 : 6-Trimethyl-Δ<sub>2</sub>-dihydropyridinedicarboxylate].** By OTTO COHNHEIM (*Ber.*, 1898, 31, 1033—1037).—When this substance is heated with 60—75 per cent. aqueous potash, the

volatile products distill, over at once, more water being added as required; the main product is ethylic trimethyldihydropyridine-carboxylate, which is a solid, melting at 89—90°, and boiling at 140—160° under 15 mm. pressure when still impure, and possessing scarcely any basic properties, unlike the isomeride which Hantzsch obtained, employing hydrochloric acid instead of potash, which was a basic oil. Some 3:5-dimethyl- $\Delta_2$ -ketotetrahydrobenzene (compare preceding abstract) is formed in addition. When an upright tube 60 cm. long is inserted between the flask and the condenser, so that only the more volatile products escape at once from the action of the potash, a small quantity of an oil is obtained which seems to be a mixture of trimethyldihydropyridine with a little trimethylpyridine.

C. F. B.

**Action of Formaldehyde on Tetrahydroquinoline.** By CARL GOLDSCHMIDT (*Chem. Zeit.*, 1897, 21, 243).—A compound,  $\text{CH}(\text{C}_9\text{NH}_{10}\text{Cl})_3$ , is formed when a solution of tetrahydroquinoline in concentrated hydrochloric acid is warmed for 10 minutes on the water bath with the requisite quantity of formaldehyde and ferric chloride. It is salted out, filtered, and washed with water, and further purified by solution in alcohol and precipitation with ether. It dyes silk green, and unmordanted cotton a greenish-blue, but not of a sufficiently strong tint to be of use. It is readily soluble in hot water, and with alkalis yields a brown base.

J. J. S.

**Action of Tannin and of Gallic Acid on Quinoline Bases.** By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1897, 125, 37—38. Compare Abstr., 1897, i, 447, 570).—Pure dry tannin readily dissolves in freshly distilled lepidine, and a red colour is only produced after prolonged exposure to the air and light. Gallic acid reacts in a similar manner, and no difference is observed when solutions of lepidine in absolute alcohol or in dry ether are employed. An aqueous solution of tannin immediately yields a white, curdy precipitate with pure lepidine. Quinoline and quinaldine react in exactly the same manner as lepidine, and in this respect resemble pyridine bases and various volatile alkaloids.

J. J. S.

**Amido-2'-hydroxylepidine and Lepidinic Acid.** By EMIL BESTHORN and H. BYVANCK (*Ber.*, 1898, 31, 796—804).—When meta-phenylenediamine (1 mol.) is heated with ethylic acetoacetate (rather more than 1 mol.) in a sealed tube for 5—6 hours up to 130°, *amido-2'-hydroxylepidine* (*amido-2'-hydroxy-4'-methylquinoline*), [NH<sub>2</sub> = 2, or perhaps 4] is formed; it melts at 270°. From metatolyenediamine, *amido-2'-hydroxymethyllepidine* is obtained in a similar manner; it melts above 300°. When the amidohydroxylepidine is boiled with phosphorus oxychloride, a pale yellow *amido-2'-chlorolepidine* is obtained; this melts at 142—143°, and can be converted into 2'-chlorolepidine by first transforming it into the hydrazine hydrochloride, and then boiling the free hydrazine base with copper sulphate in aqueous solution. By diazotising the amidohydroxylepidine and then heating the solution (see also below), pale yellow *hydroxy-2'-chlorolepidine* is obtained; this melts at 214—215°, and is oxidised by alkaline permanganate to

*2'-chlorolepidinic acid*, which melts and decomposes at 181—182°, crystallises with 2H<sub>2</sub>O, and is reduced by boiling with hydriodic acid, potassium iodide, and amorphous phosphorus to lepidinic (4-methyl-pyridine-5:6-dicarboxylic) acid.

When amido-2'-chlorolepidine is diazotised and the solution heated, *dihydroxylepidine* is formed, in addition to chlorhydroxylepidine; this is also formed when amido-2'-hydroxylepidine is diazotised, and the aqueous solution heated; it decomposes at 270°. Oxidation with alkaline permanganate converts it into *2'-hydroxylepidinic acid*, melting and decomposing at 252—253°, but the yield is poor. C. F. B.

**Morpholine Derivatives.** By RICHARD STOERMER and MAX FRANKE (*Ber.*, 1898, **31**, 752—760; compare *Abstr.*, 1897, i, 473).—1':2'-*Dimethylphenomorpholine*, C<sub>6</sub>H<sub>4</sub><sup>O—CH</sup><sub>2</sub>—NMe·CHMe, was obtained in the

following manner. 2'-Methylphenomorpholine is allowed to remain for several days with methylic iodide, and the product is made alkaline and extracted with ether. The extract is then freed from ether by distillation, and the residue is benzoylated and shaken with ether and hydrochloric acid, when benzoylmethylphenomorpholine remains dissolved in the ether and the dimethylphenomorpholine in the acid. The latter boils at 259—261°, has an odour like that of naphthalene, and gives a carmine coloration with ferric chloride; the *hydrochloride* melts at 170°, the brownish-yellow unstable *platinumchloride* at 144—146° with decomposition (in the presence of excess of platinum tetrachloride, another reddish-white salt, melting at 116° is formed), and the greenish-yellow *picrate* at 136°. By acidifying with hydrochloric acid the alkaline liquid that is left after the extraction with ether described above, evaporating to dryness, extracting the dry residue with absolute alcohol, and precipitating with ether, *trimethylphenomorphonium iodide*, C<sub>6</sub>H<sub>4</sub><sup>O—CH</sup><sub>2</sub>—NMe<sub>2</sub>I·CHMe, melting at 170°, is obtained.

The tertiary base, C<sub>9</sub>H<sub>13</sub>NO<sub>3</sub> or C<sub>9</sub>H<sub>12</sub>NO<sub>3</sub>, formed along with methylphenomorpholine when orthonitrophenoxyacetone, in boiling alcoholic solution, is reduced with tin and hydrochloric acid (*loc. cit.*), is now found to contain chlorine, and is shown to be *3-chloro-2'-methylphenomorpholine*; for it can be synthesised by boiling the potassium salt of nitrochlorophenol [OH : Cl : NO<sub>2</sub> = 1 : 3 : 6] with chloracetone and acetone, and reducing the *chloronitrophenoxyacetone* formed (which melts at 86°, its *semicarbazone* at 195°) in boiling alcoholic solution with tin and hydrochloric acid. Its *hydrochloride* melts at 105—106°, and is readily decomposed by water; the lemon-yellow *nitrosamine* melts at 96.5°, and the *phenylcarbamide*, NHPh·CO·C<sub>8</sub>NOH<sub>6</sub>MeCl, at 148°.

*2-Nitro-1-naphthoxyacetone*, NO<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·O·CH<sub>2</sub>·COMe, is obtained by heating the potassium salt of 2-nitro-1-naphthol with chloracetone and acetone for 12 hours at 100° in a sealed tube; it is yellowish and melts at 145°; the yellow, unstable *phenylhydrazone* melts at 120°, the yellowish-white *semicarbazone* at 208°, and the *oxime* at 158°. When reduced in boiling alcoholic solution with tin and hydrochloric acid, it yields *methylnaphthamorpholine*, C<sub>10</sub>H<sub>6</sub><sup>O—CH</sup><sub>2</sub>—NH·CHMe, melting at 95.5°;

the *hydrochloride* melts at 229°, and is readily decomposed by water; the unstable, brownish-yellow *platinochloride* melts at 237°, the lemon-yellow *nitrosamine* (only to be obtained by adding the calculated quantity of amylic nitrite to an alcoholic solution of the base containing a little hydrochloric acid) at 190—195° with decomposition, the *phenylcarbamide* at 180°, and the *acetyl* and *benzoyl* derivatives at 124° and 183.5° respectively.

C. F. B.

**Mercury Haloid Compounds of Antipyrine.** By M. C. SCHUYTEN (*Chem. Centr.*, 1897, ii, 614—615; from *Bull. Acad. roy. Belg.*, [iii], 33, 821—842).—The mercuric chloride compound,  $C_{11}H_{12}N_2O \cdot HgCl_2$ , is most soluble in alcohol and water, least soluble in ether, and dissolves in hot benzene, toluene, and carbon bisulphide; the solutions are neutral. When the aqueous solution is evaporated, small, crystalline needles separate, from the other solutions only amorphous residues are obtained. The mercuric bromide compound,  $C_{11}H_{12}N_2O \cdot HgBr_2$ , is obtained as a white, amorphous precipitate on mixing alcoholic solutions of the two substances; when heated, it melts at 103°, then turns slowly garnet-red, finally charring and giving off fumes of mercuric bromide. It dissolves in alcohol, benzene, and toluene, and is slightly soluble in water, chloroform, ether, and carbon bisulphide.

The mercuric cyanide compound,  $C_{11}H_{12}N_2O \cdot HgCy_2$ , obtained by mixing hot concentrated aqueous solutions of the components, crystallises in transparent prisms which, on heating, become opalescent at 160—165° and melt at 224°; the yellow, molten mass, on further heating, chars and emits white fumes. The mercury is only incompletely precipitated by sodium peroxide, whilst from the other mercury compounds complete precipitation is effected. According to the author, in these compounds one atom of halogen is directly united to nitrogen, since (1) only one molecule of antipyrine is contained in the compound, whereas other similar mercury haloid compounds usually contain two; (2) with mercurous chloride, antipyrine forms the hydrochloride, mercury, and mercuric oxide; and (3) mercuric iodide, which is not as easily dissociated as the other haloids, does not combine with antipyrine.

E. W. W.

**Generalisations as to Melting Points among Pentacyclic Nitrogen Compounds.** By EDGAR WEDEKIND (*Ber.*, 1898, 31, 949—953).—The author points out that, just as in the case of substituted malonic acids, so with the phenyl derivatives of tetrazole, the symmetrical compounds melt at relatively higher temperatures than the less symmetrical derivatives.

Malonic acid .....	134°	Tetrazole .....	156°
Methylmalonic acid .....	130	N-(1)-Phenyltetrazole .....	an oil
Dimethylmalonic acid .....	180	C-(3)-Phenyltetrazole ...	212—213
Methylisopropylmalonic acid	106—107	Diphenyltetrazole.....	106—107

Another generalisation is that phenyl derivatives of 5-ring nitrogen compounds, in which the phenyl group is attached to nitrogen, melt at a much lower temperature than the isomeric compounds in which the phenyl group is attached to carbon.

Pyrazole .....	70°	Glyoxalin.....	90°
N-(1)-Phenylpyrazole.....	11	N-Phenylglyoxalin.....	13
C-(3)-Phenylpyrazole .....	78	N-Phenylpyrroline.....	62
C-(4)-Phenylpyrazole .....	228	C-Phenylpyrroline .....	129

The same generalisation applies to alkyl, &c., derivatives.

Pyrroline .....	131°	Glyoxaline .....	89°
N-(1)-Methylpyrroline .....	113	N-Methylglyoxaline .....	-5
C-(2)-Methylpyrroline ( $\alpha$ ) .....	148	C-Methylglyoxaline .....	137
C-(3)-Methylpyrroline ( $\beta$ ) .....	143		
Triazole .....	121	Tetrazole .....	156
C-Methyltriazole .....	94	N-Methyltetrazole .....	145

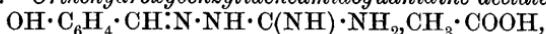
The introduction of nitrogen in place of carbon in a cyclic compound tends to raise the melting point.

Pyrroline (1N), liquid ; pyrazole (2N), m. p. 70° ; glyoxaline (2N), m. p. 89° ; triazole (3N), m. p. 121° ; tetrazole (4N), m. p. 156°. An exception to this is osotriazole, which melts at 22°, and yet has a very symmetrical formula.

The molecular weights of tetrazole, C-amidotetrazole, and of diphenyltetrazole have been determined, and the numbers indicate that each compound is monomolecular.

J. J. S.

Decomposition of 2:5-Diphenyltetrazole into Bladin's N-Phenyltetrazole. By EDGAR WEDEKIND (*Ber.*, 1898, 31, 942—948).—*Orthohydroxybenzylideneamidoguanidine acetate*,



is obtained as follows. Amidoguanidine nitrate (11.2 grams) is dissolved in the least possible quantity of cold water, and the solution then well shaken with salicylaldehyde (10 grams), and finally with concentrated potassium hydroxide, until it has an alkaline reaction ; when the odour of the aldehyde has disappeared, the solution is acidified with concentrated acetic acid, and on rubbing the sides of the vessel, the acetate is deposited in the form of a crystalline powder. It is best purified by suspending it in hot benzene and then bringing it into solution by the addition of hot alcohol ; at the end of 24 hours, large, colourless crystals are obtained, which, after several recrystallisations, melt at 191—192°. The salt is readily soluble in warm water or alcohol, and sparingly in benzene, acetone, chloroform, or light petroleum ; its aqueous solution gives a green coloration with ferric chloride, and with phenyldiazonium chloride it yields a red, gelatinous precipitate melting at 176—177°. This compound, when treated with concentrated nitric acid at 85°, yields an extremely explosive nitro-derivative. 5-Paramidodiphenyltetrazole,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\begin{array}{l}\diagdown \\ \diagup\end{array}\text{N}\cdot\text{NPh}$ , is

obtained when the finely powdered nitro-derivative (this vol., i, 336) is reduced with stannous chloride and hydrochloric acid ; it is extracted from the alkaline liquid by the aid of chloroform, and purified by repeated recrystallisation from dilute alcohol ; it crystallises from ether or dilute acetone in colourless prisms melting at 156°. Its hydrochloride crystallises in long, colourless needles, and is practically insoluble in water ; the nitrate, acetate, and sulphate, melting at 224—225°, are also described. When diazotised and the diazo-solu-

tion boiled with water, 5-*parahydroxydiphenyltetrazole* is obtained, and, after several recrystallisations from hot water, melts at 190—191°; it crystallises from ether in colourless, glistening needles, is readily soluble in alkalis or warm ammonium hydroxide, dissolves in benzene, alcohol, warm ether, acetone, chloroform, or acetic acid, and is sparingly soluble in warm water, nitric acid, or light petroleum. Bladin's phenyltetrazolecarboxylic acid,  $\text{COOH}\cdot\text{C} \begin{array}{l} \text{N}\cdot\text{NPh} \\ \swarrow \\ \text{N}=\text{N} \end{array}$ , is obtained when amidodiphenyltetrazole nitrate is oxidised with potassium permanganate. 2-Phenyltetrazole is obtained when the carboxylic acid is heated in an oil bath at 150—170°.

J. J. S.

Action of Diphenyltetrazochloride on Acetoacetic Acid, and on Benzaldehydephenylhydrazone. By EDGAR WEDEKIND [and PAUL BLUMENTHAL] (*Annalen*, 1898, 300, 239—258. Compare Abstr., 1897, i, 443).—*Cycloformazyl methyl ketone*,  $\text{COMe}\cdot\text{C} \begin{array}{l} \text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4 \\ \swarrow \\ \text{N}=\text{N} \end{array}$ , prepared by the action of diphenyltetrazochloride on acetoacetic acid, is a brownish-red, amorphous powder without definite melting point. The *phenylhydrazone*, which crystallises from a mixture of chloroform and petroleum, melts at about 205—210°; it is insoluble in alkali, and the solution in concentrated sulphuric acid is brownish-red. Phenylhydrazine also yields another compound, which melts at 197°, and dissolves in alkali; it forms a carmine-red solution in concentrated sulphuric acid.

*Paraphenylformazylbenzene (formazyldiphenyl),*  
 $\text{NHPH}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Ph}$ ,

obtained by the action of diphenyltetrazochloride on benzaldehydephenylhydrazone under the influence of alcoholic potash, is a greenish-violet, crystalline powder with bronze reflex, and melts at 174°. The solution in concentrated sulphuric acid is red, and becomes yellowish-brown when heated.

*Paraphenylhydroxyazobenzene*,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Ph}$ , is produced on adding an alcoholic solution of diphenyltetrazochloride to a solution of phenol in caustic potash; the solution in concentrated sulphuric acid is carmine-red. It begins to sinter at about 240°.

*Diformazylbenzene*,  $\text{C}_{12}\text{H}_8(\text{N}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}\cdot\text{NPh})_2$ , prepared by the action of diphenyltetrazochloride on the phenylhydrazone of benzoyl-formic acid, crystallises from dilute alcohol in needles, and melts at 153°. Oxidation converts it into *bistriphenyltetrazolium hydroxide*, which sinters at 260—278°, remaining solid at 285°; alkaline reducing agents regenerate diformazylbenzene.

M. O. F.

Derivatives of Cinchonine. By EDOUARD GRIMAUX (*Compt. rend.*, 1898, 126, 575—578).—The bromomeroquinine hydrobromide,  $\text{C}_9\text{H}_{14}\text{BrNO}_2 + \text{HBr}$ , obtained by Koenigs by the action of bromine on the crude product of the oxidation of cinchonine and quinine, loses only one atom of bromine when treated with silver nitrate at the ordinary temperature. When treated with picric acid or potassium picrate, it yields the salt  $\text{C}_9\text{H}_{14}\text{BrNO}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{OH}$ , which crystallises in yellow lamellæ melting at 203—204°, and is only slightly soluble in

cold water. The nitroso-derivative,  $C_9H_{13}BrNO_2 \cdot NO$ , obtained by the action of nitrous acid on the hydrobromide, forms nacreous crystals which melt at  $87\frac{1}{2}$ — $88^\circ$ . When the hydrobromide is heated with concentrated aqueous potash, it yields nacreous plates of the compound  $C_9H_{14}BrNO_2 + KBr$ .

By heating the hydrobromide with water and zinc powder, impure meroquinene is obtained, and this yields an acetyl derivative,  $C_9H_{14}NO_2Ac$ , which forms small, white crystals melting at  $112\frac{1}{2}^\circ$ .

Hydroxymeroquinene is obtained by the action of excess of silver hydroxide on the hydrobromide; it crystallises from a mixture of methylic alcohol and ether in small, white crystals insoluble in ether and chloroform, but very soluble in water and methylic and ethylic alcohols. It decomposes without melting, and its solutions have an alkaline reaction.

C. H. B.

**Yohimbe Bark and Yohimbine.** By HERMANN THOMS (*Chem. Centr.*, 1897, ii, 978—979; from *Ber. pharm. Ges.*, 7, 279—283).—From a sample of bark named Yumbehoa, the author obtained 0·54 per cent. of a mixture of two alkaloids, from which Spiegel's yohimbine (*Chem. Zeit.*, 1896) was separated by means of benzene. The other alkaloid forms a green fluorescent solution in chloroform, but could not be obtained in a crystalline state. According to Prof. Schumann, this bark is almost certainly identical with yohimbe bark. The leaves of the Yumbehoa tree also contain yohimbine. E. W. W.

**An Oxyptomaine.** By WILLIAM OESCHNER DE CONINCK (*Compt. rend.*, 1898, 126, 651—653).—The ptomaine,  $C_8H_{11}N$  (Abstr. 1888, 730 and 1118), when treated with very dilute hydrogen peroxide in the dark, yields an oxyptomaine,  $C_8H_{11}NO$ , together with yellowish, resinous products. The oxyptomaine is a non-deliquescent, white solid, which softens at  $250^\circ$ , melts at a slightly higher temperature, and decomposes suddenly at about  $260^\circ$ . It dissolves readily in acids, and forms a crystallisable hydrochloride,  $C_8H_{11}NO \cdot HCl$ , and a corresponding platinochloride, both of which are gradually decomposed when boiled with water.

When heated with zinc powder, the oxyptomaine yields the original base,  $C_8H_{11}N$  which is a collidine, and hence the oxy-derivative may be called *collidone*. It is the higher homologue of the oxypyridines previously described.

C. H. B.

**A New Enzyme—Caroubinase.** By JEAN EFFRONT (*Compt. rend.*, 1897, 125, 116—118).—The carbohydrate caroubin (this vol., i, 398) is readily hydrolysed by dilute acid, and also by a special diastase, *caroubinase*, which is produced during the fermentation of the seeds; the secretion of the enzyme is somewhat slow during the actual period of fermentation, and increases with the formation of chlorophyll. Alcohol precipitates the active principle from infusions of the growing germs. Caroubinase acts energetically at  $40^\circ$ , its maximum activity being at about  $45$ — $50^\circ$ , but becoming very feeble at  $70^\circ$ , and the enzyme is completely destroyed at  $80^\circ$ . An addition of 0·01—0·03 per cent. of formic acid increases the hydrolytic power of the enzyme. The sugar obtained by the hydrolysis of caroubin with this enzyme is not identical with that formed under the influence of dilute acids.

J. J. S.

**Peptone Salts from Glutin.** By CARL PAAL (*Ber.*, 1898, **31**, 956—966. Compare *Abstr.*, 1892, 895).—The author has made further experiments with three peptone hydrochlorides of different composition obtained from glutin. The peptone salt (20 grams), dissolved in 5 times its weight of water, was dialysed during 3 days into a litre of water, which was renewed daily; the contents of the dialyser and of the outer vessel were then separately evaporated in platinum vessels, and the residues dried by heating their methylic or ethylic alcoholic solutions in a vacuum. About 12 grams of one salt was found to have diffused; this portion was readily soluble in ethylic alcohol, whereas the salt which had not diffused was practically insoluble in ethylic alcohol but dissolved readily in cold methylic alcohol. The two salts also differed materially in their composition and also in molecular weight.

The author has succeeded in isolating the substances which are not precipitated when the peptone salts are treated with phosphotungstic acid; these were obtained in the form of a thick syrup, and were partially precipitated by alcohol, and completely by ether, in yellowish lumps. The dried substance gave 6·26 per cent. of ash, which consisted entirely of lime obtained from the barium hydroxide used. The substance gave a strong biuret reaction.

Glutin peptone barium ( $\text{Ba} = 9\cdot25$  per cent.) and ferropeptone were obtained from the peptone contained in the phosphotungstic acid precipitate. When the peptone salt is boiled with absolute ethylic alcohol and saturated with hydrogen chloride, a salt is obtained containing a rather higher percentage of hydrogen chloride, probably brought about by the water produced during etherification, as it has already been shown that peptone hydrochlorides are fairly readily etherified.

J. J. S.

**Crystallisation of Animal Proteids.** By F. GOWLAND HOPKINS and STANISLAW N. PINKUS (*J. Physiol.*, 1898, **23**, 130—136).—If an equal bulk of saturated solution of ammonium sulphate is added to white of egg, the fixed alkali of the proteid liberates ammonia, and this interferes with the separation of crystals; if, however, this is neutralised with acetic acid, the process of crystallisation is much accelerated; and still more is this the case if a slight excess of the acid is added. Evaporation is then unnecessary to obtain crystals, and there can be no confusion between them and crystals of ammonium sulphate; their affinity for carbol-magenta or methylene blue is also distinctive, should any confusion arise. Analogous results were obtained with serum albumin.

W. D. H.

**Action of Superheated Water on Proteid.** By RICHARD NEUMEISTER (*Zeit. Biol.*, 1898, **36**, 420—424).—The points of difference between Salkowski (this vol., ii, 173) and the author are explained as being chiefly due to the former's imperfect acquaintance with the published work of the latter.

W. D. H.