

Organic Chemistry.

Soluble Prussian Blue. By C. E. GUIGNET (*Compt. rend.*, **108**, 178—181).—Ordinary soluble prussian blue is a compound of prussian blue with potassium ferrocyanide. It is easily obtained by gradually adding to a boiling solution of 110 grams of potassium ferricyanide a hot solution of 70 parts of crystallised ferrous sulphate. The mixture is boiled for two hours, filtered, and the precipitate washed until the washings become dark blue. It is then dried at 100°, and has a fine deep-blue tint, and is very soluble in water. Admixed potassium ferrocyanide can be removed by washing with alcohol of 40 per cent. The compound is precipitated from its solution by sodium sulphate, sodium chloride, &c., but when the salts are removed by washing it redissolves. With salts of lead, zinc, and other metals, it yields, as Wyruboff observed, a series of well-defined blue compounds.

Colloidal prussian blue was obtained by Graham by dialysis. Pure soluble prussian blue is obtained by suspending purified prussian blue in a saturated solution of oxalic acid, filtering, and allowing the mixture to remain for two months. Prussian blue is completely precipitated, and the liquid is quite colourless. After thorough washing with dilute alcohol, the precipitate is readily soluble in pure water. The same result is obtained in a very short time by precipitating the oxalic acid solution with strong alcohol or by a concentrated solution of sodium sulphate, and washing the precipitate with dilute alcohol. Ammonium oxalate or tartrate can be used instead of oxalic acid.

If the oxalic acid solution is boiled, insoluble prussian blue is precipitated, a result due to the action of the acid and not to the rise of temperature. Dilute sulphuric acid has the same effect at the ordinary temperature, and the precipitate does not dissolve even after long washing. The soluble and insoluble modifications have the same composition.

When prussian blue is heated with water and molybdic anhydride, it yields a deep-blue solution which is not affected by boiling or by gelatin. It is precipitated by sulphuric or nitric acid, but if the precipitate, which retains a small quantity of molybdic anhydride, is well washed with dilute alcohol, it dissolves in pure water. Ammonium molybdate and tungstate will also dissolve prussian blue.

When prussian blue is treated with concentrated sulphuric acid, it yields a soft, white mass like starch-paste, and if the temperature rises is partially decomposed. Hydroferrocyanic acid is liberated and partially dissolves in the excess of sulphuric acid. If the liquid is filtered through glass-wool and the filtrate cooled, it deposits the acid in long needles. The same result is obtained with lead or copper ferrocyanide.

If prussian blue which has been treated with sulphuric acid, is treated with absolute alcohol, it re-acquires its blue colour and dissolves in the alcohol. The same solution is obtained by dissolving solid prussian blue in a mixture of equal volumes of sulphuric acid and alcohol. When mixed with water or with a large excess of strong

alcohol, the solution yields a precipitate of ordinary prussian blue, which retains sulphuric acid even after prolonged washing with dilute alcohol. Ethyl hydrogen sulphate does not dissolve prussian blue, and hence the phenomena just described cannot be attributed to the formation of this compound.

C. H. B.

Relative Stability of the Alkyl Bromides. By F. LENGFELD (*Amer. Chem. J.*, **71**, 40—66).—The stability of alkyl bromides when in solution with various reagents has been determined.

With sodium hydroxide, potassium hydroxide, and ammonia, the relative stability is (in order of increasing stability), ethyl, propyl, butyl, isoamyl, isobutyl, isopropyl.

With nitric and sulphuric acids, the order of increasing stability is isopropyl, ethyl, propyl and butyl (about equal), isoamyl, isobutyl, ethylene.

With argentic nitrate and argentic nitrate and nitric acid, the order of increasing stability is isopropyl, ethyl, propyl, isoamyl, isobutyl, ethylene.

Experiments carried out on the influence of light on the stability of alkyl bromides in contact with sodium hydroxide showed that it was without influence on the result.

With dilute sodium hydroxide, $n/40$ and less, the velocity of changes is inversely as the concentration.

The action of sodium hydroxide on the bromides dissolved in methyl alcohol is slower than in propyl alcohol, and slower in propyl than in ethyl alcohol.

In the case of excess of one reagent over another, similar effects are produced by similar excess of ether reagent.

J. W. L.

Analyses of Pure Sherry. By E. BORGmann and W. FRESENIUS (*Zeit. anal. Chem.*, **28**, 71—77).—The authors, having obtained 18 samples of genuine sherry of various qualities, have analysed them by recognised methods and give the results in a table. The chief feature worthy of notice is the high percentage of sulphates. The universal practice of plastering the must for the manufacture of sherry renders it necessary to adopt for that wine an admissible maximum different from that allowed in unplastered wines. The sulphates found (calculated as potassium sulphate) ranged from 2·5—8·8 grams per litre. The superior brands (with two exceptions) contained more than 4 grams, and the inferior (with one exception) less than 3 grams per litre. The maximum limit of 3 grams proposed by the German Imperial Commission would exclude the finer wines of this class. Plastering increases the proportion of potassium in the wine, but not that of calcium. Phosphoric acid, chlorine, and magnesium appear to rise with increasing sulphates. In most of the samples, a deposition of tartar occurred on keeping. This fact is of interest in connection with the dictum of Blitz, that in judging of a wine containing much sulphates, it is necessary to consider whether at the same time a sufficient amount of hydrogen potassium tartrate is present.

M. J. S.

Boiling Points of Secondary Alcohols with Secondary Radicles: Diisopropyl Carbinol. By G. POLETEÉFF (*J. Russ. Chem. Soc.*, **20**, 672—686).—The author finds that the boiling point of diisopropyl carbinol, as given by Münch (*Annalen*, 180, 331), that is, 131·5°, does not agree with Flavitzky's (*J. Russ. Chem. Soc.*, 1871, 815, and 1887, 369) method of calculating boiling points, and that a higher number might be expected. He very carefully prepared the pure carbinol and determined its physical constants and those of other compounds formed during its preparation. The calcium salt of isobutyric acid was subjected to dry distillation, and *diisopropyl ketone*, $C_7H_{14}O$, was obtained. Its (corrected) boiling point was found to be 123·7°, the sp. gr. = 0·8230 at 0° and 0·8063 at 20° (water at 4° = 1). The molecular refractive power = 55·03—55·24 (calculated 55·37), or for infinite wave-length = 33·46 (calculated 33·58). On reduction with sodium amalgam of 3 per cent., it yields *diisopropyl carbinol*, $C_7H_{16}O$, boiling at 140° (corr.), having the sp. gr. 0·8445 at 0° and 0·8288 at 20°, and the molecular refractive power = 57·64 (calculated 57·37), or for infinite wave-length = 34·82 (calculated 34·89). The *acetate* boils at 160° (corr.), and has the sp. gr. 0·8856 at 0° and 0·8676 at 20·5°. From this, after hydrolysis, the original alcohol was obtained boiling at 140·4°. On oxidation with chromic mixture, the alcohol yields diisopropyl ketone, isobutyric acid, acetone, and some acetic acid (formed from the last). It is shown that the correct boiling point of diisopropyl carbinol, 140°, is in better accord with Flavitzky's theory than that obtained by Münch, namely, 131·5°.

B. B.

Butyl Ethers. By E. REBOUL (*Compt. rend.*, **108**, 162—165; compare this vol., p. 366).—*Diisobutyl ether*, $O(CH_2\cdot CHMe_2)_2$, is readily obtained by the action of isobutyl bromide on the sodium-derivative of isobutyl alcohol. It is a mobile liquid only slightly soluble in water, and boils at 122—122·5° under a pressure of 760 mm.; sp. gr. at 15° = 0·7616. Concentrated hydrobromic acid converts it into isobutyl bromide boiling at 90—91°. The product of the action of isobutyl iodide on potassium isobutyl-oxide, which was believed to contain diisobutyl ether, is really a mixture of isobutylene and isobutyl alcohol in nearly equivalent proportions.

Secondary isobutyl ether, $CHMe_2\cdot CH_2\cdot O\cdot CHMe\cdot CH_2\cdot Me$, is formed, together with isobutylene and the secondary alcohol, by the action of isobutyl bromide on the sodium-derivative of the secondary alcohol. It is insoluble in water and boils at 121—122; sp. gr. at 15° = 0·7652. Hydrobromic acid resolves it into isobutyl bromide and secondary butyl bromide.

Tertiary isobutyl ether cannot be obtained by the action of isobutyl bromide on the sodium-derivative of trimethyl carbinol, nor by the action of tertiary butyl bromide on sodium isobutyl oxide. *Di-secondary butyl ether* is obtained in mere traces by the action of the secondary bromide on the sodium-derivative of the secondary alcohol, but the product consists mainly of the secondary alcohol and normal butylene. Secondary tertiary and ditertiary butyl ethers could not be obtained.

C. H. B.

Oxidation of Glycerol. By E. FISCHER and J. TAFEL (*Ber.*, **22**, 106--110; compare *Abstr.*, 1888, 1264).—*Trihydroxyisobutyric acid*, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{OH})_2\cdot\text{COOH}$, is obtained when glycerose (250 grams) is mixed with anhydrous hydrocyanic acid (30 grams) and allowed to remain for 12 hours at 50° and a second 12 hours at 60° in a well-closed vessel. After the removal of the excess of hydrocyanic acid, the product is concentrated to 150 c.c., saturated with hydrogen chloride in a freezing mixture, and allowed to remain two days at the ordinary temperature. It crystallises from alcohol in slender, colourless prisms, melts at 116° , and is readily soluble in water, sparingly soluble in alcohol, and almost insoluble in ether, benzene, and chloroform. The *calcium* salt, with 4 mols. H_2O , crystallises in slender, matted needles; the *lead* salt, with 1 mol. H_2O , crystallises in slender, colourless prisms; the normal *barium* salt could not be crystallised; the basic *barium* salt, $\text{C}_4\text{H}_6\text{O}_5\text{Ba}$, is precipitated from a hot solution of the acid in slender needles; the *strontium* salt crystallises in slender needles; the *sodium* salt in prisms. On reduction with hydriodic acid and amorphous phosphorus in a reflux apparatus, trihydroxyisobutyric acid is converted into a mixture of acids containing iodine, and these, by further reduction with zinc-dust and dilute sulphuric acid, yield isobutyric acid.

Diiodoisobutyric acid, $\text{C}_4\text{H}_6\text{O}_2\text{I}_2$, can be extracted by ether from the product obtained on reducing trihydroxyisobutyric acid with hydriodic acid and amorphous phosphorus. It crystallises from water in long, colourless needles, melts at 127° , and is very readily soluble in alcohol and ether.

In addition to trihydroxyisobutyric acid, a small yield of erythroglucic acid is also obtained on treating glycerose with concentrated hydrocyanic acid.

W. P. W.

Extraction of Sorbite. By C. VINCENT and DELACHANAL (*Compt. rend.*, **108**, 147—148).—The fermented juice of *Sorbus aucuparia* is concentrated in a vacuum to one-third of its volume, and 10 grams are heated with excess of sulphuric acid, evaporated to dryness, the residue calcined, and the combined sulphuric acid estimated. The amount of sulphuric acid required to convert into sulphates all the bases in the juice is calculated from this result, and this quantity of acid is added to the concentrated juice, which is then diluted with its own volume of water and twice the volume of alcohol. The calcium and potassium, which interfere with the crystallisation of sorbite, are thus almost completely precipitated in the form of sulphates. The liquid is filtered, the alcohol distilled off, and the residue exactly neutralised with barium hydroxide, evaporated to a syrup, and extracted with boiling alcohol of 95° , which dissolves almost pure sorbite, and leaves in combination with the barium the viscous acid substances which usually interfere greatly with crystallisation. When the alcoholic solution is concentrated, it leaves a syrup which after a few days deposits a large quantity of sorbite in long needles.

Sorbit may be estimated in the form of dibenzoic acetal (following Abstract) in the following manner. The juice is concentrated in a

vacuum to one-third its volume, mixed with excess of basic lead acetate, and the filtrate treated with hydrogen sulphide. The filtered liquid is concentrated in a vacuum to a thick syrup, mixed with its own weight of 50 per cent. sulphuric acid, and then with 80 per cent. of benzaldehyde. It rapidly becomes almost solid, owing to the formation of the acetal, which after 24 hours is thoroughly washed with water, dried, and weighed.

In order to separate sorbite from the acetal, the latter is heated with water which contains a few per cents. of sulphuric acid and benzaldehyde, and the liberated benzaldehyde is distilled off in a current of steam. The liquid is then treated with barium hydroxide to precipitate the sulphuric acid, and the barium present in the filtrate in the form of barium benzoate is exactly precipitated by addition of sulphuric acid. The liquid is then cooled, treated with ether in order to remove benzoic acid, and concentrated in a vacuum to a thick syrup, which after some days deposits crystals of sorbite.

C. H. B.

Dibenzoic Acetal of Sorbite. By J. MEUNIER (*Compt. rend.*, **108**, 148—149).—Sorbita when treated with benzaldehyde in presence of sulphuric or hydrochloric acid yields a dibenzoic acetal, $C_{20}H_{22}O_6$, which resembles the dibenzoic acetal of mannitol in constitution and properties. It is a white, confusedly crystalline substance, which melts at about 160° , is insoluble in water and almost insoluble in hot alcohol, but dissolves more readily in boiling benzene, chloroform, and acetic acid.

C. H. B.

Invert Sugar. By E. JUNGFLEISCH and L. GRIMBERT (*Compt. rend.*, **108**, 144—146; compare *Abstr.*, 1888, 1266).—The rotatory power of pure levulose does not agree with that calculated for levulose from measurements with invert sugar, using Tuchschnid's and Tollens' formulæ, and assuming that invert sugar contains dextrose and levulose in equal molecular proportions. The rotatory power of pure levulose is not altered by admixture with pure glucose, and the authors find that the observed differences are due to the action on the levulose of the acids which are used to produce inversion.

The rotatory power of a 10 per cent. solution of pure levulose increases from $[\alpha]_D = -94^\circ 66'$ to $-96^\circ 78'$ when heated for half an hour at 68° with 5 per cent. of hydrochloric acid. With a similar quantity of sulphuric acid, under the same conditions, the rotatory power rises to $-99^\circ 77'$. There is no sensible variation in the results when the liquid is neutralised before the measurements are made. The action of strong inorganic acids on levulose takes place at once at the ordinary temperature, oxalic acid behaves like the inorganic acids when heated, whilst formic and acetic acids of similar concentration do not affect the levulose. The rotatory power of glucose shows no variations of this kind.

The duration of the action of the acids used for inversion has long been known to affect the rotatory power of the product.

Comparative experiments with levulose and invert sugar under the conditions described show that the rotatory power of the levulose in the invert sugar, $[\alpha]_D = -96^\circ 52'$, agrees with that of pure levulose

which has been subjected to the same treatment, $[\alpha]_D = -96^\circ 78'$. Clerget's method of inversion by treating with 10 per cent. of hydro-chloric acid at 68° for 10 minutes, gives a levulose with a rotatory power of $[\alpha]_D = -101^\circ 30'$, whilst pure levulose treated in the same way has a rotatory power of only $[\alpha]_D = -97^\circ 44'$, which is practically the same as that obtained by treating levulose with hydro-chloric acid in the cold.

That these differences are due to the action of the inorganic acids is shown by the fact that if sugar is inverted by treatment with 5 per cent. of acetic or formic acid at 100° for 30 minutes, the rotatory power remains constant even after prolonged heating, and the rotatory power of the levulose which the product contains is identical with that of pure levulose. Addition of hydrochloric acid to this product at once alters the rotatory power of the levulose.

It is evident that the levulose contained in invert sugar which has been prepared in the usual way is not identical with pure crystallised levulose, but is a product of the alteration of the latter by the action of the mineral acids employed.

C. H. B.

Fermentation of Galactose, Arabinose, Sorbose, and other Sugars. By W. E. STONE and B. TOLLENS (*Annalen*, 249, 257—272).—Most of the results obtained by the authors have already been published (Abstr., 1888, 808). With yeast supplied with suitable nourishment, galactose ferments as completely as dextrose, but less rapidly. Sorbose ferments more slowly and less completely. Arabinose and milk-sugar ferment very slowly and incompletely. Pure yeast does not bring about the fermentation of arabinose.

W. C. W.

Formation of Furfuraldehyde and Non-production of Levulinic Acid from Arabinose: Formation of Furfuraldehyde as a Test for Arabinose: Formation of Arabinose and Xylose from Malt Residues. By W. E. STONE and B. TOLLENS (*Annalen*, 249, 227—245).—In addition to the results which have already been published (Abstr., 1888, 1060), the authors have obtained arabinose and xylose from the malt which has been used for brewing. Furfuraldehyde is formed when xylose is boiled with dilute acids.

W. C. W.

Mannose. By E. FISCHER and J. HIRSCHBERGER (*Ber.*, 22, 365—376).—The authors have simplified their method for the preparation of mannose (compare Abstr., 1888, 934) as follows:—Mannitol (3 kilos.) is heated at 40 — 45° with water (20 litres) and nitric acid of sp. gr. 1·41 (10 litres) with constant stirring. In four to five hours, evolution of gas commences, and, as soon as it is found that a small portion of the solution, after neutralising with sodium carbonate, gives a dense, yellowish precipitate with phenylhydrazine acetate, which is generally the case after five to six hours, the operation is brought to an end. The liquid is cooled to about 25° by throwing in ice, then made slightly alkaline with solid sodium carbonate to destroy the nitrous acid, and finally acidified with acetic acid. Phenylhydrazine (1 kilo.), dissolved in dilute acetic acid, is added to the solution, and after an hour's time the separated hydr-

azone is washed and pressed. About one-quarter of the product is boiled for about 15 minutes with water (5 litres), the filtered solution decolorised by heating with zinc dust and ammonia, and again filtered; the hydrazone separates in pale yellow plates, and the mother-liquors are employed for recrystallising another portion of the crude product, this process being repeated six or seven times until the whole is purified. The yield of hydrazone is, on the average, 10 per cent. of the mannitol employed.

The pure hydrazone (100 grams) is dissolved in hydrochloric acid of sp. gr. 1.19 (400 grams), and, after keeping for half an hour, the solution is cooled in a freezing mixture, and the crystals separated by filtration. The filtrate is diluted with water (2 vols.), neutralised with lead carbonate, and filtered; the yellow solution is made alkaline with baryta, extracted with ether to remove phenylhydrazine and coloured products, then treated with carbonic anhydride, decolorised with animal charcoal, and concentrated to about 300 c.c. The residue is treated with sulphuric acid to precipitate the barium, neutralised with lead carbonate, filtered, evaporated in a partial vacuum, and again filtered. The filtrate is evaporated to a syrupy consistency, dissolved in absolute alcohol (5 vols.), treated with hydrogen sulphide, and, after separating the lead sulphide, the mannose is precipitated by adding a large volume of ether. It is thus obtained in the form of a colourless syrup containing about 90 per cent. of sugar. 100 grams of the hydrazone yield 60 grams of the syrup.

Mannose is precipitated in amorphous, white flocks when ether is added to an alcoholic solution of the syrup; on keeping under absolute alcohol, the precipitate solidifies to a hard, colourless mass which, however, shows no distinctly crystalline structure. It is hygroscopic, deliquescent, and very readily soluble in water, but very sparingly in boiling absolute alcohol, and insoluble in ether. It does not produce a coloration in the magenta and sulphurous anhydride solution. Alcoholic potash precipitates a flocculent, hygroscopic substance from alcoholic solutions of the sugar; lead acetate and ammonia produce in aqueous solutions a precipitate which becomes yellow on keeping, or when warmed. The specific rotatory power is $[\alpha]_D = 12.96$, and 1 c.c. of Fehling's solution corresponds with 4.307 milligrams of mannose. The quantity of mannose present in the solutions employed for the determination of the rotatory power and reducing power was estimated by means of the phenylhydrazone; as, however, this compound is not quite insoluble in water, there is a slight error in both determinations. Cane-sugar, maltose, raffinose, trehalose, various kinds of molasses, manna, potato-starch, lichenin, gum tragacanth, gum arabic, quince seeds, linseed, fleabane, and Carragheen moss were tested for mannose, but in no case could the presence of this sugar be detected. Salep juice, however, as previously stated by Tollens and Gans, on inverting, yields mannose which can be isolated by means of the hydrazone. The yield of hydrazone is 5 to 6 per cent. of the bulbs employed.

When a dilute solution of mannose is heated at 110° for about four hours, humous substances are formed, and on distilling the filtered solution it yields furfuraldehyde.

Levulinic acid is formed, together with humous substances, when mannose phenylhydrazone is heated with fuming hydrochloric acid.

When mannose (0·25 gram) is heated for three hours with 7·5 per cent. hydrochloric acid (32 c.c.), small quantities of humous substances are formed, but only 0·07 gram of the mannose is decomposed. (Compare Sieben, *Zeit. anal. Chem.*, **24**, 138.)

Mannose (50 grams) dissolved in water (250 grams) was mixed with anhydrous hydrogen cyanide (18 c.c.) and a few drops of ammonia, and kept in a closed vessel at the ordinary temperature; a flocculent substance soon separates, and after three days the reaction is brought to an end by warming at 50° for four hours. The flocculent product seems, from its behaviour towards alkalis and iron salts, to be the amide of mannosecarboxylic acid; it is insoluble in hot water, and, after decolorising with animal charcoal, alcohol precipitates from the solution a white, amorphous powder melting at 182—183° with decomposition. The filtrate from this amide contains considerable quantities of the ammonium salt of the acid.

Barium mannosecarboxylate, $(C_7H_{13}O_8)_2Ba$, is prepared by evaporating the crude product of the action of hydrogen cyanide on mannose until free from hydrogen cyanide, adding water and baryta (80 grams), and again evaporating until the evolution of ammonia ceases. The residue is dissolved in water (4 litres), carbonic anhydride passed through it, the solution decolorised with animal charcoal, and evaporated until the barium salt commences to separate; further small quantities can be obtained by mixing the mother-liquor with alcohol and ether. The yield is almost theoretical. It is a colourless, semicrystalline compound, and is moderately soluble in hot water, but only very sparingly in cold water, and insoluble in alcohol.

The *lactone*, $C_7H_{12}O_7$, is obtained when a hot, aqueous solution of the barium salt is decomposed with the requisite quantity of sulphuric acid. It crystallises in needles, melts at 148—150°, and is very readily soluble in water, but only moderately in absolute alcohol, and insoluble in ether.

A second product, probably *mannosecarboxylic acid*, was sometimes obtained in small quantities in preparing the lactone; this substance has an acid reaction, melts at 167—169° with evolution of gas, and is more readily soluble in alcohol than the lactone.

Heptylic acid (normal) is formed when barium mannosecarboxylate (35 grams) is boiled for five hours with hydriodic acid boiling at 127° (250 grams) and amorphous phosphorus (10 grams). The product is diluted with water, extracted with ether, and the extract shaken with mercury to remove iodine. The oil (27 grams) which is obtained on evaporation is treated in the cold with zinc-dust and dilute sulphuric acid to reduce the iodine-compounds, which are present in considerable quantities, and then distilled with steam. The distillate contains heptylic acid (= 7 grams barium salt) and a neutral oil (2 grams) probably heptolactone.

Mannose is readily oxidised by bromine in aqueous solution; the acid obtained seems to be different from gluconic acid. It is also oxidised by nitric acid, but the acid has not yet been investigated.

The compound described as phenylmannosazone (*loc. cit.*) is identical with phenylglucosazone.

From the authors' experiments, it follows that mannose is the aldehyde of mannitol, and has, therefore, the same constitution as dextrose, with which it is physically isomeric. Since the phenylhydrazone of mannose and dextrose are totally distinct substances, both of which are readily converted into one and the same osazone, $N_2HPh\cdot CH\cdot C(N_2HPh)\cdot [CH\cdot OH]_3\cdot CH_2\cdot OH$, it must be assumed that the isomerism of the two sugars is determined by the carbon-atom which is directly combined with the aldehyde-group. As dextrose has a much greater specific rotatory power than mannose, the former must be looked on as the dextro-, the latter as the laevo-modification of the same system. The compounds which these sugars form with hydrogen cyanide are isomeric, as, probably, are also the corresponding carboxylic acids; as both sugars yield one and the same compound on reduction, some change must occur in the arrangement in space of the $COH\cdot CH\cdot (OH)$ -group. The difference in behaviour on reduction seems to show that mannose, in its physical as well as chemical structure, is the true aldehyde of mannitol, whilst dextrose is the aldehyde of a physically isomeric hexahydric alcohol. F. S. K.

Formation of Acrose from Formaldehyde. By E. FISCHER and F. PASSMORE (*Ber.*, **22**, 359—361).—Formose (compare Löw, *J. pr. Chem.*, **33**, 321), as the authors have previously shown, is a mixture of various aldehyde- and ketone-alcohols, which can be separated by means of the osazones.

Pure α -acrosazone can be isolated as follows:—Formaldehyde (100 grams) in 3 per cent. aqueous solution is first treated as described by Löw, the solution is then neutralised with acetic acid, and warmed on the water-bath for four hours with a mixture of phenylhydrazine (100 grams) and 50 per cent. acetic acid (100 grams). The cold solution is filtered, and the residual mixture of osazones dried on porous plates, and then extracted several times, first with cold benzene, and then with ether, to remove resinous products and the more readily soluble osazones. The dirty yellow, crystalline residue (20 grams) is extracted with water (6 litres) to remove phenylformosazone, washed twice with cold, absolute alcohol (10 c.c.), and then boiled twice for a long time with alcohol (10 c.c.). α -Acrosazone (1·1 gram) remains as a yellowish-green powder, and cannot be purified by recrystallisation. It is therefore converted into the osone by warming for one minute at 45° with fuming hydrochloric acid; the cold solution is separated from the phenylhydrazine salt, diluted with water (5 vols.), neutralised with lead carbonate, and filtered. The filtrate is warmed with phenylhydrazine acetate, and the osazone which is formed is obtained pure by recrystallising from a large quantity of hot alcohol. The compound thus prepared has all the properties of α -acrosazone.

The fact that acrose is very nearly related to the naturally occurring saccharoses lends considerable probability to Baeyer's views concerning the formation of grape-sugar in the vegetable kingdom.

F. S. K.

Compounds of Phenylhydrazine with Sugars. By E. FISCHER (*Ber.*, 22, 87—89; compare *Abstr.*, 1888, 1267).—The author proposes “osone” as a general term for compounds of the type of oxyglucose, and throughout the paper refers to this compound as glucosone.

Glucosone reacts with methylphenylhydrazine in alcoholic solution in the cold, forming *glucosone methylphenylhydrazone*,



which crystallises from water in slender, colourless scales, and melts at 171° when rapidly heated; with an excess of the hydrazine in acetic acid solution, however, *methylphenylglucosazone*, $\text{C}_{20}\text{H}_{26}\text{N}_4\text{O}_4$, is obtained, and this crystallises from benzene in slender, yellowish-red needles melting at 152° with decomposition. When treated in aqueous solution with solutions of orthodiamines free from acids, glucosone readily yields condensation compounds; thus, with orthotoluylenediamine, it forms *anhydroglucometaparadiamidotoluene*, $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4$, which crystallises in colourless, slender needles and melts at a few degrees above 180° with decomposition (compare Griess and Harrow, *Abstr.*, 1887, 930).

Glucosone decomposes into a mixture of humous substances and furfuraldehyde when heated in dilute aqueous solution at 140° for several hours, and into humous substances, carbonic anhydride, and a small quantity of levulinic acid when heated with hydrochloric acid. It is readily reduced by means of zinc-dust and acetic acid at 100° , and is thereby converted into levulose.

Galactosone and *rhamnosone* have been prepared from galactose and rhamnose (isodulcitol) by methods similar to that adopted for the preparation of glucosone.

W. P. W.

Synthetical Experiments in the Sugar-group. By E. FISCHER and J. TAFEL (*Ber.*, 22, 97—101; compare *Abstr.*, 1888, 358).— α -*Acrosone* is obtained when α -acrosazone is rapidly heated to 45° with 20 times its weight of fuming hydrochloric acid (sp. gr. = 1.19), maintained for one minute at this temperature until phenylhydrazine hydrochloride begins to crystallise out, then rapidly cooled to 25° and kept at this temperature for 5 to 10 minutes until the reaction is complete. The product is purified by the method employed in the case of glucosone (oxyglucose) (*Abstr.*, 1888, 1267), and the yield amounts to about 50 per cent. of that theoretically possible. It is a colourless syrup, which solidifies in the cold to a hard, amorphous mass, and in dilute aqueous solution reacts with phenylhydrazine acetate in the cold, forming α -acrosazone. On treatment with orthotoluylenediamine, α -acrosone is converted into a compound, which crystallises in slender needles, becomes brown at 180° and melts at 185° with decomposition, thus closely resembling *anhydroglucometaparadiamidotoluene* (compare preceding Abstract). When heated in aqueous solution for several hours at 140° , α -acrosone decomposes into humous substances and furfuraldehyde, and when heated with 18 per cent. hydrochloric acid at 100° for six hours it decomposes into humous substances and a small quantity (2½ per cent.) of levulinic acid.

α -Acrose, $C_6H_{12}O_6$, is formed by heating α -acrosone in dilute aqueous solution at 100° with zinc-dust and acetic acid. When the reduction is complete, the solution is freed from zinc by means of hydrogen sulphide, evaporated to dryness in a vacuum, and the residue extracted with absolute alcohol, the concentrated alcoholic solution being finally precipitated by ether. α -Acrose is a sweet syrup which reduces Fehling's solution, yields α -acrosazone on treatment with phenylhydrazine acetate at 100° , and is fermentable by yeast. On reduction with sodium amalgam, it is converted into acritol, $C_6H_{14}O_6$, which crystallises in spherical aggregates of thin plates, melts at $164-165^\circ$, has a sweet taste, does not reduce alkaline copper solution, is readily soluble in water, very sparingly soluble in alcohol, and, in short, differs only from mannitol in being optically inactive. W. P. W.

Rhamnodiazine. By B. RAÝMANN and K. CHODOÜNSKÝ (*Ber.*, **22**, 304—305).—Rhamnodiazine, $C_{18}H_{32}O_8N_2$, is formed when rhamnose is treated with ammonia and ethyl acetoacetate (2 mols.) at the ordinary temperature in methyl alcohol solution. It separates after a few days in long, soft needles, and is purified by recrystallising first from alcohol and then from hot water. It melts at 186° and is decomposed when heated more strongly; it is soluble in alcohol and hot water, but only sparingly so in chloroform, and insoluble in ether, light petroleum, and carbon bisulphide. It dissolves in large quantities in glacial acetic acid, with which it probably combines; the compound is, however, unstable, as rhamnose crystallises from the solution after a short time. It reduces Fehling's solution and a neutral solution of silver nitrate very readily, but ammoniacal silver nitrate solution is only very slightly acted on.

Other glucoses seem to yield similar compounds when treated with ethyl acetoacetate or ketones and ammonia as described above; these substances are not easily obtained in crystals. F. S. K.

Oxidation of Milk-sugar. By E. FISCHER and J. MEYER (*Ber.*, **22**, 361—364).—*Lactobionic acid*, $C_{12}H_{22}O_{12}$, is obtained when milk-sugar (1 part) dissolved in water (7 parts) is treated with bromine (1 part) at the ordinary temperature, the mixture being frequently shaken. The bromine dissolves in the course of one to two days and, after keeping for another 48 hours, a stream of air is passed through the solution to drive off most of the free bromine, the remainder being converted into hydrobromic acid by passing hydrogen sulphide into the cooled solution. The quantity of hydrobromic acid present having been ascertained by titrating a portion of the solution with silver nitrate, the calculated quantity of lead carbonate is added, and the hydrobromic acid remaining in the filtered solution is carefully precipitated with silver oxide. The solution is filtered, treated with hydrogen sulphide, and the filtrate evaporated. The acid, syrupy liquid thus obtained is agitated for a long time with large quantities of cold glacial acetic acid to remove reducing substances and other products, the colourless residue, the weight of which is about one-third that of the lactose employed, is dissolved in water and the warm solution precipitated with a hot, concentrated solution of basic

lead acetate. The solution of basic lead acetate is prepared by dissolving the neutral salt (2 parts) and lead hydroxide (1 part) in hot water (3 parts) and dissolving the crystals, which separate on cooling, in pure, hot water. The precipitated lead salt is quickly separated by filtration, washed with hot water, and then suspended in cold water and decomposed with hydrogen sulphide. The filtrate is evaporated on a water-bath in a partial vacuum, the residue treated with alcohol and ether to remove acetic acid, and finally dissolved in a small quantity of water and reprecipitated with alcohol and ether.

Lactobionic acid is a colourless, strongly acid syrup, and is very readily soluble in water but only very sparingly in alcohol and cold glacial acetic acid, and is insoluble in ether. It decomposes carbonates, but does not reduce Fehling's solution even on boiling. The calcium, $(C_{12}H_{21}O_{12})_2Ca$, barium, $(C_{12}H_{21}O_{12})_2Ba$, cadmium, and lead salts were prepared by warming an aqueous solution of the acid with the corresponding carbonate; they are all insoluble in alcohol, but readily soluble in water excepting the basic lead salt. On evaporating the aqueous solution over sulphuric acid, the salts are obtained in the form of syrups which gradually solidify but do not clearly show a crystalline structure.

Lactobionic acid is decomposed into galactose and gluconic acid when warmed with dilute mineral acids. The pure acid was heated at 100° for an hour with 5 per cent. sulphuric acid; the gluconic acid was then isolated by means of the barium salt, and identified by converting it into the calcium salt (Kilian, *Annalen*, **205**, 184). The filtrate was evaporated, and the galactose, which crystallised from the solution, identified by converting into the osazone.

The formation and decomposition of lactobionic acid confirm Fischer's conclusions (*Abstr.*, 1888, 1267) with regard to the constitution of milk-sugar.

An acid, isomeric with lactobionic acid, can most probably be obtained from maltose by the process described above; this compound, on inverting, should yield gluconic acid and dextrose. F. S. K.

Derivatives of Trimethylenediamine. By S. GABRIEL (*Ber.*, **22**, 224—226).— β -Hydroxytrimethylenediphthalimide (Goedeckemeyer, *Abstr.*, 1888, 1294) is best prepared by heating an intimate mixture of α -dichlorhydrin (13 grams) and potassium phthalimide (37 grams) at 140 — 150° ; as soon as the reaction commences, the mixture is cooled to about 100° and finally heated at about 160 — 180° for half an hour. The crude product is recrystallised from acetic acid, and washed first with dilute alcohol and then with water. The yield is 50 per cent. of the theoretical quantity. When β -hydroxytrimethylenediphthalimide is heated at 200° with concentrated hydrochloric acid, it yields hydroxytrimethylenediamine hydrochloride, and when treated in like manner with hydrobromic acid of sp. gr. 1·49, it is converted into the corresponding hydrobromide.

β -Bromotrimethylenediamine hydrobromide, $CHBr(CH_2\cdot NH_2)_2 \cdot 2HBr$, is obtained when the preceding compound (15 grams) is heated for four hours at 200 — 210° with hydrobromic acid (45 c.c.) saturated at 0° ; the product is dissolved in cold water, the filtered solution

evaporated to dryness, and the residue recrystallised from dilute alcohol. It crystallises in plates, decomposes at 210—215°, and is readily soluble in water but sparingly so or insoluble in absolute alcohol. The *picroate*, $C_3H_9BrN_2 \cdot 2C_6H_3N_3O_7$, melts at 215—217° with previous softening, and is soluble in hot water. The *aurochloride*, $C_3H_9BrN_2 \cdot 2HAuCl_4$, crystallises in plates. The *platinochloride*, $C_3H_9BrN_2 \cdot H_2PtCl_6$, crystallises in orange-yellow plates. The *ferrocyanide*, $(C_3H_9BrN_2)_2 \cdot H_4Fe(CN)_6$, is a colourless, granular, crystalline salt.

F. S. K.

Action of Sulphurous Anhydride on Tiglic Aldehyde. By F. H. HAYMANN (*Monatsh.*, **9**, 1055—1066; compare *Abstr.*, 1883, 570, and this vol., p. 121).—Excess of sulphurous anhydride was passed into water (50 c.c.) containing tiglic aldehyde (5 grams); the mixture being kept cool by means of ice. The saturated solution was placed in a closely stoppered bottle, well shaken and allowed to remain for three hours at the ordinary temperature, when the solution was neutralised in the cold with barium carbonate; on concentration in a vacuum at a temperature not above 35°, a quantity of barium sulphite separated, and on further concentration, a gummy mass remained, which consisted of a mixture of barium hydroxypentanedisulphonate and barium valeraldehydesulphonate. When the saturated solution was heated in sealed tubes for four hours at 65°, and then treated in a way similar to that above mentioned, the same results were obtained. Hydroxypentanedisulphonate was, however, completely converted into the mono-acid when heated at 100°.

On reduction with sodium amalgam in a solution always containing a small quantity of uncombined sulphuric acid, both valeraldehydesulphonic acid and hydroxypentanedisulphonic acid gave hydroxypentanesulphonic acid, $SO_3H \cdot CMeEt \cdot CH_2 \cdot OH$, the latter with formation of sulphurous anhydride. On heating with lime, sodium hydroxypentanesulphonate yielded a mixture of tiglyl alcohol and methylethylcarbin carbinol, $CHMeEt \cdot CH_2 \cdot OH$; whilst sulphovaleric acid was formed on oxidation with bromine-water.

G. T. M.

Metacetone. By E. FISCHER and W. J. LAYCOCK (*Ber.*, **22**, 101—105).—By distilling sugar with lime, Fremy obtained a compound boiling at 84°, which he termed metacetone, and to which he ascribed the formula $C_6H_{10}O$. An examination of the products obtained by distilling sugar with lime under the conditions described by Gottlieb (*Annalen*, **52**, 127) shows that metacetone does not exist, and that Fremy's substance is a mixture of propaldehyde, dimethylfuran, and a third hydrocarbon-like compound.

When sugar is distilled with three times its weight of lime, a distillate is obtained which separates into an aqueous and an oily layer. The aqueous layer contains much acetone. The oily layer can be separated into two fractions boiling at 30—115° and 115—280° respectively. The compounds contained in the first fraction were recognised by the hydrazones obtained by treating it with phenylhydrazine, and they comprised acetone, hydrocarbons, and further

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propaldehyde, dimethylfuran, and probably higher and lower homologues of these.

An examination of the "light oil" from wood-tar shows that propaldehyde and dimethylfuran are present.

W. P. W.

Chlorocrotonic Acids. By A. KOLL (*Annalen*, **249**, 303—326).—By the action of phosphorus pentachloride on the ethylic salt of methylacetooacetic acid, Isbert (*Abstr.*, 1886, 1010) obtained a mixture of ethyl mono- and di-chloromethylacetooacetates and α -methyl- β -chlorotetraacrylic acid. The author finds that the yield of acid is considerably increased by adding the ethyl salt of methylacetooacetic acid to an excess of phosphorus pentachloride, warming the mixture at 70° , and when cold, pouring the product into water. *Methyl* α -methyl- β -chlorotetraacrylate is a mobile liquid boiling at 158.5° (corr.), sp. gr. 1.131 at 15° . The ethyl, propyl, and isobutyl salts boil respectively at 171 — 172° , 189 — 190° , and 201 — 202° . The copper salt is not crystalline. The ethyl salt is decomposed by a strong solution of potassium hydroxide, yielding alcohol and ethyl methyl ketone. *Methyl* α -methyl- β -chlorotetraacrylate is acted on by sodium ethoxide and propoxide, yielding the *methyl* α -methyl- β -ethoxytetraacrylate and *methyl* α -methyl- β -propoxytetraacrylate respectively. The former boils at 203 — 204° and the latter at 215 — 216° .

α -Ethyl- β -chlorotetraacrylic acid is freely soluble in alcohol and ether. It crystallises in colourless needles, melts at 49.5° and boils at 215° . The *methyl* salt boils at 166 — 167° , sp. gr. 1.087 at 15° . The *ethyl* salt boils at 182 — 183° , the *propyl* salt at 197 — 198° , and the *isobutyl* salt at 207 — 208° . The *zinc* salt, $(C_6H_5ClO_2)_2Zn + \frac{1}{2}H_2O$, forms needles, and the *magnesium* salt, $(C_6H_5ClO_2)_2Mg + 2H_2O$, crystallises in plates. The copper salt is an insoluble amorphous powder. The potassium salt is decomposed by potassium hydroxide at 150° , forming methyl propyl ketone. Sodium methoxide and ethoxide act on the methylic salt of ethylchlorotetraacrylic acid, forming the methyl salts of α -ethyl- β -methoxy-, and α -ethyl- β -ethoxy-tetraacrylic acids boiling at 188 — 190° and 208 — 209° respectively.

The preparation of β -chloroquartenyllic acid has been described by Geuther and Frölich. The ethyl salt boils at 155 — 156° . It is converted into *ethyl* β -ethoxyquartenylate, $CH_2\cdot C(OEt)\cdot CH_2\cdot COOEt$, by the action of sodium ethoxide. This compound readily crystallises in rhombic plates. It melts at 29.5° and boils at 191 — 192° .

W. C. W.

Ketosulphides and Ketosulphide-acids. By A. DELISLE (*Ber.*, **22**, 306—309).—The compound obtained by treating ethyl acetooacetate with sulphur dichloride (compare *Abstr.*, 1887, 915) has the composition $C_{12}H_{18}O_6S$, and is identical with the substance prepared by Buchka (*Abstr.*, 1885, 1200) from ethyl sodacetooacetate and sulphur monochloride. It separates from benzene in well-defined crystals melting at 83 — 84° , but after recrystallising from alcohol it has no well-defined melting point. When treated with reducing agents, hydrogen sulphide is evolved, so that the constitution of this compound is probably $S(O\cdot CMe\cdot CH\cdot COOEt)_2$.

Acetonylphenyl sulphide, $C_9H_{10}OS$, is obtained by gradually adding the calculated quantity of chloracetone to a well-cooled mixture of ether and sodium thiophenoxyde ($NaSPh$), the whole being constantly shaken. It separates from ether in large, well-defined crystals, melts at $34-35^\circ$, boils at about $143-145^\circ$ (15 mm.), and is moderately soluble in alcohol, but only sparingly in light petroleum. It dissolves in concentrated sulphuric acid with a yellowish-red coloration, which turns dark-violet on warming. The hydrazone melts at $82-83^\circ$.

Phenylacetonylphenylsulphide, $C_{14}H_{12}OS$, prepared in like manner from bromacetophenone and sodium thiophenoxyde, crystallises from alcohol in colourless needles or plates, melts at $52-53^\circ$, and is very readily soluble in ether and acetone.

Ethyl β -thiophenyllevulinate, $C_{13}H_{16}O_3S$, can be obtained from sodium thiophenoxyde and ethyl bromolevulinate as described above; it is a liquid boiling at $196-197^\circ$ (15 mm.). F. S. K.

Molecular Weight of Pentic Acid. By R. MOSCHELES and H. CORNELIUS (*Ber.*, **22**, 243-244; compare *Abstr.*, 1888, 1272)—Determinations of molecular weight by Raoult's method made with ethyl pentate in glacial acetic acid solution gave the numbers: 153, 155, and 158, and thus confirm the formula $OEt\cdot C \begin{array}{c} \text{CEt}\cdot\text{CO} \\ \swarrow \quad \searrow \\ \text{CH}_2-\text{O} \end{array}$.

N. H. M.

Ketonic Acids. By J. SEISSL (*Annalen*, **249**, 272-303).—*Chlorolevulinic acid*, $C_5H_7ClO_3$, is the product of the action of phosphorus pentachloride on levulinic acid. It is a pale-yellow oil which cannot be distilled. No salts of the chlorinated acid could be obtained by neutralising the acid with bases or carbonates. Chlorine converts levulinic acid into *dichlorolevulinic acid*, $C_5H_6Cl_2O_3$; this is crystalline and melts at 77° . When phosphorus pentachloride acts on ethyl levulinate, a mixture of the ethyl salts of mono- and di-chlorolevulinic acids is formed.

Pyruvic acid is less readily attacked by chlorine at the ordinary temperature than levulinic acid. A mixture of the ethyl salts of mono- and di-chloropyruvic acids is formed by the action of phosphorus pentachloride on pyruvic acid. Under similar treatment, ethyl pyruvate appears to yield a mixture of ethyl tri- and tetra-chloropropionates.

W. C. W.

Potassium Antimony Oxalate. By R. WAGNER (*Chem. Zeit.*, **12**, 1726).—The crystals of potassium antimony oxalate resemble in form those of oxalic acid; it gives a clear solution with small quantities of hot water, but with much water it is partially decomposed, a basic antimony salt being deposited, whilst an acid salt remains in solution. The finely powdered salt loses 2·5 mols. H_2O at 75° , the rest of its water is given off at 130° , above which temperature further decomposition ensues.

Commercial crystalline potassium antimony oxalate has the composition $Sb_2(C_2O_4)_3 + 3K_2C_2O_4 + 8H_2O$; the salt prepared by Souchay and Lenssen's method has the same composition.

The antimony was estimated both volumetrically and gravimetrically.

cally. In the former case, excess of $\frac{N}{10}$ iodine solution was added to the neutral or feeble acid antimony solution, and titrated back with thiosulphate. Acid stannous solutions can be titrated in the same way under certain conditions.

D. A. L.

Symmetrical Dimethylsuccinic Acids. By C. A. BISCHOFF and E. VOIT (*Ber.*, **22**, 389—391; compare *Abstr.*, 1888, 254 and 1057).—Antidimethylsuccinic acid (m. p. 120°) is obtained, together with the isomeric acid, by hydrolysing ethyl dimethylethenyltricarboxylate, and the two products can be separated by recrystallising from water. Its solubility in water at 14° is 1 : 33·3, that of the para-acid 1 : 97. It is directly converted into pure pyrocinchonic acid when treated with bromine at 130°. The *ethyl* salt is a colourless oil, boils at 221—222°, and is decomposed into ether and the anhydride when heated at a high temperature. The *calcium* salt crystallises with 2 mols. H₂O and is insoluble in cold water. The *silver* salt is anhydrous and unstable. The anhydride, obtained by heating the acid at 200°, melts at 87°, and yields only the anti-acid when treated with water. It is converted into pyrocinchonic acid when heated at 90° with bromine in chloroform solution. The *imide* melts at 106°, and yields only the anti-acid when treated with potash. The *anil* crystallises from hot alcohol in small needles and melts at 146°. The *dianilide*, prepared by treating the chloride with aniline, crystallises from alcohol in colourless needles melting at 222°. It yields the anti-acid only when decomposed with potash.

When paradimethylsuccinic acid is heated at 180—196°, it yields an anhydride which melts at 87°, and is very similar to that obtained from the anti-acid. This anhydride yields a mixture of both acids, the relative quantities of which vary with the length of time during which the original para-acid was heated. When the para-acid is treated with acetic chloride, it gives an *anhydride* melting at 38°, from which only the original acid is obtained.

When the para-acid is heated with ammonia, it yields a mixture of imides which gives the anti-acid together with small quantities of the para-compound. The *imide* prepared by heating the para-ethyl salt with ammonia, crystallises from benzene, melts at 78°, and yields only the para-acid. An *anil*, melting at 126°, was obtained; it gives about equal quantities of the two acids when treated with alcoholic potash. The *anilide* melts at 235°, and is very similar to the anilide of the anti-acid; it yields only the para-acid when decomposed with alcoholic potash.

The para-acid yields pyrocinchonic acid when treated with bromine. No unsaturated acid, isomeric with pyrocinchonic acid, could be obtained either from the acid itself, or from the anhydride.

When ethyl dimethylethenylcarboxylate is treated with chlorine and the product hydrolysed, pyrocinchonic acid, dimethylethenylcarboxylic acid and the two isomeric dimethylsuccinic acids are obtained.

F. S. K.

Diacetylcarboxylic Acid (Kepitic Acid) and Diacetyl. By R. FITTIG, C. DAIMLER, and H. KELLER (*Annalen*, **249**, 182—214).

—Methods of preparing keptic acid have been described by the authors (Abstr., 1887, 362) and by Wislicenus (*ibid.*, 587).

When an excess of bromine is added to a well-cooled solution of ethyl kepitate in carbon bisulphide and the solution is kept in a cold place for 12 hours, *monethyl dibromo-kepitate*,



is deposited in transparent, colourless plates. The compound dissolves freely in chloroform and in water. It decomposes on exposure to the light or to a temperature of 70°. When bromine acts on a warm solution of ethyl kepitate in carbon bisulphide, *ethyl tetrabromo-kepitate* is formed; this substance crystallises in transparent prisms, soluble in carbon bisulphide. It melts at 119° and is not attacked by a solution of sodium carbonate at the ordinary temperature. Alcoholic ammonia decomposes the compound and yields oxamide and dibromacetamide. The ethyl salt of tetrachloro-keptic acid is formed when chlorine is passed into a boiling solution of ethyl kepitate in chloroform. Hantzsch and Zeckendorf (Abstr., 1887, 727) obtained this compound by acting on ethyl dihydroxyquinonedicarboxylate with chlorine. Ethyl kepitate forms, with 2 mols. phenylhydrazine, a crystalline compound, $\text{C}_2(\text{N}_2\text{HPh})_2(\text{CH}_2\cdot\text{COOEt})_2$, soluble in warm chloroform; it crystallises in pale yellow needles and melts between 160° and 180° with decomposition. Kepitic acid yields diacetyl or dimethyl diketone, $\text{CH}_3\cdot\text{CO}\cdot\text{C}\ddot{\text{O}}\cdot\text{CH}_3$, on dry distillation or on boiling with dilute sulphuric acid. Diacetyl is more conveniently prepared by the methods described by v. Pechmann (Abstr., 1888, 248 and 810). Hydroxylamine acts on diacetyl, forming the dioxime $\text{OH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$, a compound previously described by Schramm (Abstr., 1883, 573) under the name of ethylmethylacetoximic acid. The silver and copper salts of trimethylglyoxaline, $\text{C}_6\text{H}_9\text{N}_2\text{Ag}$ and $\text{C}_6\text{H}_9\text{N}_2\text{Cu}$, are precipitated when diacetyl is added to silver nitrate or cuprous chloride mixed with a large excess of ammonia. In the presence of a small quantity of ammonia, diacetyl deposits a mirror of metallic silver from a solution of the nitrate.

Dibromodiacetyl, $\text{C}_4\text{H}_4\text{Br}_2\text{O}_2$, prepared by adding bromine to a solution of diacetyl in carbon bisulphide, crystallises in flexible plates, melts at 116—117°, and is freely soluble in carbon bisulphide and chloroform. Diacetyl unites with hydrocyanic acid, forming the di-cyanhydrin $\text{CN}\cdot\text{CMe}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot\text{CN}$, a hygroscopic substance freely soluble in water, alcohol, and ether. It is decomposed by water at 100° into diacetyl and hydrocyanic acid, and is converted by strong hydrochloric acid at the ordinary temperature into dimethylracemic acid.

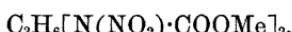
Dimethylracemic acid, $\text{COOH}\cdot\text{CMe}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot\text{COOH}$, forms colourless crystals containing 1 mol. H_2O , and bears a close resemblance to racemic acid and also to Böttiger's dimethyltartaric acid. It is very soluble in water. The anhydrous acid melts with decomposition at 178—179°. The following salts were prepared: $\text{C}_6\text{H}_8\text{O}_6\text{K}_2$, needle-shaped crystals, freely soluble; $\text{C}_6\text{H}_9\text{O}_6\text{K}$, sparingly soluble in cold water. The calcium and barium salts (containing $1\frac{1}{2}$ and 2 mols. H_2O respectively) are obtained as crystalline precipitates on the

addition of calcium or barium chloride to a solution of the normal potassium salt. W. C. W.

Some Nitramines and their Preparation. By A. P. N. FRANCHIMONT and E. A. KLOBBIE (*Rec. Trav. Chim.*, 7, 343—357).—*Methylurethane*, NH_2COOMe , is obtained by dissolving the methyl salt of the nitro-derivative of ethylenediamidoformic acid (this vol., p. 124) in a strong aqueous or alcoholic solution of ammonia. It crystallises from ether in large plates melting at 55—56°, and boils under a pressure of 760 mm. at 176·5—177·5°. Ethylenedinitramine is simultaneously formed, as also a compound of the nitramine with ammonia, which is insoluble in ether but very soluble in water, and melts with decomposition at about 155—157°. The action of ammonia on the above methyl salt takes place in accordance with the equation $\text{C}_2\text{H}_4[\text{N}(\text{NO}_2)\text{COOMe}]_2 + 2\text{NH}_3 = \text{C}_2\text{H}_4(\text{NH}\cdot\text{NO}_2)_2 + 2\text{NH}_2\text{COOMe}$.

By the action of methyl iodide (2 mols.) on ethylenedinitramine (1 mol.), a dimethyl-derivative, $\text{C}_2\text{H}_4(\text{NMe}\cdot\text{NO}_2)_2$, is obtained, melting at 137°. A monomethyl-derivative, melting at 121—122°, is formed at the same time. Both these substances can be crystallised from water or absolute alcohol, the latter of the two being the more soluble.

By the action of methyl carbonate (2 mols.) on trimethylenediamine (1 mol.), a white substance is obtained, crystallising from ether, in which it is but slightly soluble, in oblique rhombic plates melting at 74—75°. Analysis shows that it is *methyl trimethylenediamidoformate*, $\text{C}_3\text{H}_6\cdot(\text{NH}\cdot\text{COOMe})_2$. When treated with concentrated nitric acid, it is converted into *methyl trimethylenedinitramidoformate*,



which crystallises from alcohol in long needles or prisms melting at 89—90°. An aqueous solution of ammonia converts this last compound into a crystalline substance melting at 147°, which, when boiled with alcohol, loses ammonia and yields *trimethylenedinitramine*, $\text{C}_3\text{H}_6(\text{NH}\cdot\text{NO}_2)_2$. The melting point of this compound is 67°. It is very soluble in water and alcohol, less so in ether and chloroform. It crystallises in short, thick prisms. When boiled with water containing 2 per cent. of sulphuric acid, it loses nitrous oxide. It has an acid reaction and gives metallic derivatives.

By treating pentamethylenediamine in a similar manner, an analogous series of compounds were obtained. *Methyl pentamethylenediamidoformate* crystallises from water or alcohol in slender needles melting at 114°. *Methyl pentamethylenedinitramidoformate* crystallises from ether and alcohol in small prisms melting at 37°. *Pentamethylenedinitramine* crystallises in oblong plates melting at 59—60°. It is very soluble in water and alcohol, and when boiled with water containing sulphuric acid loses nitrous oxide, giving at the same time an oily substance which is volatile in steam.

By treating monomethylamine with an aqueous solution of methyl chloroformate, methyl methylamidoformate, $\text{NH}\cdot\text{Me}\cdot\text{COOMe}$, is obtained, which, on nitrating, subsequent treatment with ammonia and boiling in alcoholic solution, gives *methylnitramine*, $\text{NHMe}\cdot\text{NO}_2$. This

nitramine crystallises in long, colourless, flat needles melting at 38°. It has a very acid reaction. By the action of methyl iodide and alcoholic potash, it is converted into dimethylnitramine.

Ethynitramine, $\text{NHEt}\cdot\text{NO}_2$, may be similarly obtained from ethylamine. By evaporation of the alcoholic solution and cooling, crystals are obtained which melt at 3°.

The authors believe the method used for the preparation of the above nitramines from primary amines to be one of general application.

H. C.

Paradiethylbenzene. By A. VOSWINKEL (*Ber.*, **22**, 315—317).—Paradiethylbenzene boils at 182—183°, and when boiled with dilute nitric acid yields parethylbenzoic acid and terephthalic acid.

Cadmium paradiethylbenzenesulphonate, $(\text{C}_6\text{H}_3\text{Et}_2\cdot\text{SO}_3)_2\text{Cd} + \text{H}_2\text{O}$, crystallises very readily in flat, colourless prisms, whereas the salt of the corresponding meta-acid is very readily soluble in water. The *sulphonamide*, $\text{C}_6\text{H}_3\text{Et}_2\cdot\text{SO}_2\text{NH}_2$, crystallises in microscopic needles and melts at 85°.

Tetrabromoparadiethylbenzene, $\text{C}_6\text{Br}_4\text{Et}_2$, crystallises in needles melting at 112°. The *nitro*-compound, $\text{C}_6\text{H}_3\text{Et}_2\cdot\text{NO}_2$, is a heavy, brownish liquid boiling at 155° (23 mm.) with partial decomposition. The *amido*-derivative is a bright-yellow liquid boiling at 140—142° (20 mm.); the *hydrochloride*, $\text{C}_{10}\text{H}_{15}\text{N}\cdot\text{HCl}$, crystallises in colourless needles and turns reddish-brown on exposure to the air. *Acetoparadiethylanilide*, $\text{C}_6\text{H}_3\text{Et}_2\cdot\text{NHAc}$, crystallises in colourless plates and melts at 99°.

Paradiethylphenol, $\text{C}_6\text{H}_3\text{Et}_2\cdot\text{OH}$, prepared by melting the sulphonic acid with potash, is a yellowish liquid boiling at 126—127° (17 mm.). It is sparingly soluble in cold water, the solution having a burning taste and a phenol-like odour. Ferric chloride gives no coloration, but bromine-water produces a white precipitate in an aqueous solution.

Paradiethylthiophenol, $\text{C}_6\text{H}_3\text{Et}_2\cdot\text{SH}$, prepared by treating the sulphonic chloride with zinc-dust and reducing the salt obtained, is an almost colourless, disagreeably smelling liquid boiling at 113° (18 mm.).

F. S. K.

Nitrobromocymene and Nitrochlorocymene. By M. FILETI and F. CROSA (*Gazzetta*, **18**, 290—297).*—*Mononitrobromocymene* from thymol, $\text{C}_6\text{H}_5\text{PrMeBr}\cdot\text{NO}_2$ [1 : 4 : 2 : 5], is obtained pure by adding the bromocymene (parapropylmetabromotoluene) (1 part) rapidly to nitric acid of sp. gr. 1·48 (5 parts), cooled to 12—15°, keeping the temperature within these limits whilst the mixture is occasionally agitated; after an hour, the product is poured into water, the oil well washed, and distilled in a current of steam. If no more than 30 grams are operated on at a time, it does not contain either a dinitro-compound or unaltered bromocymene. The pure mononitro-derivative is an oil which is heavier than water; it is rapidly oxidised by boiling with

* The authors distinguish the bromine and chlorine derivatives obtained by the action of phosphorus perchloride or perbromide on *thymol* as chloro- or bromocymene from thymol, whilst those obtained from *cymene* by the action of bromine or chlorine are designated as chloro- or bromo-cymene from cymene.

nitric acid of sp. gr. 1·39, yielding bromonitrotoluic and melting at 199—200°. It dissolves in nitric acid of sp. gr. 1·52, cooled to 0°, with formation of two dinitro-derivatives.

Dinitrobromocymene (from thymol), $C_6H_2PrMeBr(NO_2)_2[1:4:2:5:?]$, is best prepared by allowing the bromocymene to drop slowly into nitric acid of sp. gr. 1·52 (5 parts), cooled to 0°. The product is then poured into water, the precipitate washed, pressed between filter-paper, and crystallised from alcohol. The crystals are a mixture of two isomeric dinitro-derivatives, which appear to be isomorphous, as they cannot be separated by crystallisation. Attempts to separate them by distillation with steam were equally fruitless. On agitating the finely powdered mixture with ether at the ordinary temperature, evaporating the solution and crystallising the residue repeatedly from alcohol, a compound was obtained with a constant melting point of 125—126°. The other isomeride, which seems to melt at about 94°, is also formed in small quantity along with bromonitrotoluic acid, when the mononitrobromocymene is treated with nitric acid of sp. gr. 1·39, as stated above. It could not be obtained in a pure state, however.

Mononitrochlorocymene (from thymol), $C_6H_2PrMeCl\cdot NO_2[1:4:2:5]$. This is prepared like the brominated derivative. Like the latter, it yields chloronitrotoluic acid melting at 180—181° when boiled with nitric acid of sp. gr. 1·39.

Dinitrochlorocymene (from thymol). Like the brominated derivative, the chlorocymene yields a mixture of two dinitro-derivatives, which could not be separated; one appears to melt at about 80°, the other was prepared in a pure state by Ladenburg and Engelbrecht by the action of phosphorus pentachloride on dinitrothymol.

Mononitrobromocymene (from cymene), $C_6H_2PrMeBr\cdot NO_2[1:4:3:?]$, is best prepared by allowing the bromocymene (parapropylorthobromotoluene) to drop slowly into cooled nitric acid, sp. gr. 1·48 (5 parts); the two liquids should be left in contact with occasional agitation for 8 to 10 hours and then poured into water. The product is washed with sodium carbonate solution to remove a little bromotoluic acid formed at the same time, distilled in a current of steam, dried over sulphuric acid in a vacuum, and distilled under diminished pressure (b. p. 210—211° at 100 mm.). It is a red liquid which distils at the ordinary temperature at 289—291° with partial decomposition.

Dinitrobromocymene (from cymene), prepared as already described. The product is a dark-red liquid which, after a time, deposits crystals; these, when separated, pressed, and recrystallised, form bright-yellow prisms which melt at 95—96°. The red oil is an isomeric dinitro-compound containing some of the solid in solution.

Mononitrochlorocymene (from cymene), prepared like the brominated derivative, is a dark-red liquid. The *dinitrochlorocymene* crystallises in bright-yellow prisms which melt at 109—110°. A liquid isomeride seems to be formed at the same time.

There is a marked difference in the action of light on these dinitro-derivatives, those from cymene rapidly becoming red on exposure, whilst the corresponding compounds from thymol are unaffected.

C. E. G.

Oxidation of the Chlorocymene and Bromocymene from Thymol and from Cymene. By M. FILETI and F. CROSA (*Gazzetta*, **18**, 298—313).—In a former paper (Abstr., 1887, 37) the authors showed that the chlorocymene from thymol when oxidised by nitric acid of sp. gr. 1·24 to 1·29, gave metachlorocumic, orthochloroparatoluic, and chloroterephthalic acids, whilst the brominated derivative, with acid of sp. gr. 1·20, gave bromocumic acid, and with acid of sp. gr. 1·29 the same product, together with bromonitrotoluic acid, bromoterephthalic acid, and bromonitrocymene. Acid of sp. gr. 1·39 gave the two acids last mentioned with mere traces of bromocumic acid.

The authors have repeated Landolph's and Gerichten's experiments on the oxidation of the bromo- and chloro-cymenes from cymene (*Ber.*, **5**, 268; **10**, 1249; and **11**, 366), and confirm their results, except that they found that the chlorocymene boils at 216—218° instead of at 208—211°, as stated by Gerichten.

The *bromonitrotoluic acid*, $C_6H_2MeBr(NO_2)\cdot COOH$ [1 : 3 : 6 : 4], is more conveniently prepared by oxidising mononitrobromocymene with nitric acid of sp. gr. 1·39 (preceding Abstract), as in this case no other acid is formed at the same time. The *calcium* salt, with 5H₂O, crystallises in lustrous, yellowish prisms; and the *magnesium* salt, with 8H₂O, in large, yellow plates. When reduced with sodium amalgam, it yields *metamidotoluic acid*, which crystallises in long, colourless plates, belonging seemingly to the trimetric system. It melts at 164—165°, and is identical with the acid obtained by Ahrens (*Zeitschr. f. Chem.*, 1869, 104) from *metanitroparatoluic acid*.

Orthamidometanitroparatoluic acid, $C_6H_2Me(NO_2)(NH_2)\cdot COOH$ [1 : 2 : 4 : 5]. When the bromonitrotoluic acid is heated with alcoholic ammonia at 180° for a day in sealed tubes, it is converted into a mixture of the amido-acid with nitrometatoluidine. These two are separated by evaporating the alcohol, and treating the residue with aqueous ammonia, when the amido-acid dissolves, leaving the nitrometatoluidine. On acidifying the ammoniacal solution, the acid is thrown down as a voluminous, yellow precipitate, which can be purified by crystallisation from dilute alcohol, when it forms long, silky, yellow needles, which contain 1 mol. H₂O, and melt at 235—236°.

The *nitrometatoluidine*, $C_6H_3Me(NO_2)\cdot NH_2$ = [1 : 2 : 5], which may be more conveniently prepared by heating bromonitrotoluic acid with fuming hydrochloric acid at 180°, melts at 135—136°, and is identical with the compound obtained by Beilstein and Kuhlberg from acetometatoluidide. When reduced with tin and hydrochloric acid in the usual way, it yields *paratoluylenediamine* melting at 64°, and boiling at 273—274°.

Orthobromometamidoparatoluic acid, $C_6H_2Me(NH_2)Br\cdot COOH$ = [1 : 2 : 5 : 4]. When bromonitrotoluic acid is heated at 120° with alcoholic ammonium sulphide for a day in sealed tubes, it is converted into the amido-acid, but at the same time resinous substances are produced, from which it is very difficult to separate it. It is far better to use ferrous oxide as the reducing agent, by dissolving the acid (10 grams) in excess of ammonia, and adding the requisite amount (64 grams) of ferrous sulphate in aqueous solution. The acid is

only sparingly soluble in alcohol or ether, and moderately so in alcohol. It crystallises in plates which melt at 186—187°.

Paradibromoparatoluic acid, $C_6H_2MeBr_2\cdot COOH$ [1 : 2 : 5 : 4]. Bromoamidotoluic acid dissolved in alcohol is mixed with an alcoholic solution of nitrous anhydride and ether added, until a precipitate begins to form; in a few minutes, the diazoamido-derivative separates as a whitish crystalline powder, which after being repeatedly washed with ether is treated with a solution of hydrogen bromide saturated at 0°, and the mixture gently heated at first and finally boiled. The acid is purified by crystallisation from boiling benzene. It forms long, colourless needles, or short, yellowish prisms which melt at 200—201°.

The *ethyl salt* crystallises in colourless, slender needles, which melt at 49°. This acid is identical with the acid Schultz obtained by oxidising paradibromoparaxylene (*Ber.*, **18**, 1762). He gives the melting point as 195°, as is shown by its yielding paradibromoterephthalic acid by oxidation with potassium permanganate. The true melting point of the last-mentioned acid is 316—317°, and its ethyl salt melts at 124—125°.

Orthobromoparatoluic acid, $C_6H_3MeBr\cdot COOH$ = [1 : 3 : 4], obtained by decomposing the diazoamidobromotoluic acid by boiling it with alcohol, crystallises in slender, colourless needles melting at 140—141°. It is easily soluble in alcohol, ether, and benzene, but only sparingly in water. The acid obtained by Kelbe and Koschnitzky (*Abstr.*, 1886, 884) by oxidising a bromocymene with nitric acid, and described by them as orthobromoparatoluic acid, is either bromonitrotoluic acid or impure metabromotoluic acid, according as the bromocymene employed was derived from thymol or from cymene.

Chlorocymene from thymol, when oxidised with nitric acid of sp. gr. 1.39, yields a mixture of the two isomeric dinitrochlorocymenes already described (preceding Abstract) with chloronitrotoluic and chloroterephthalic acids; these two acids may be easily separated by taking advantage of the insolubility of the chloroterephthalic acid in benzene.

Chloronitrotoluic acid, $C_6H_2Me(NO_2)Cl\cdot COOH$ = [1 : (?) 2 : 5 : 4], crystallises in yellowish, flattened needles which melt at 180—181°. It is insoluble in water, moderately soluble in boiling benzene, soluble in alcohol and ether. The *barium salt* crystallises with $3\frac{1}{2}$ mols. H_2O in yellowish needles; the *magnesium salt*, with 8 mols. H_2O , forms large, yellowish tables.

Chloroterephthalic acid, $C_6H_3Cl(COOH)_2$, obtained by the oxidation of chlorocymene, cannot be purified by crystallisation; it is necessary to first convert it into the methyl salt, purify it, and recover the acid by hydrolysis. The *methyl salt* crystallises from aqueous alcohol in colourless needles which melt at 59—60°; the acid is a white powder consisting of microscopic needles which melt at 300°.

C. E. G.

Behaviour of Phenols and Hydroxy-acids towards the Alkali Hydrosulphides. By F. FUCHS (*Monatsh.*, **9**, 1143—1147). The hydrogen of the hydroxyl of hydroxy-acids and phenols containing neither halogens nor nitro-groups is not displaced by metal on

treatment with an alkaline hydrosulphide; which, however, readily turns out the hydrogen of a carboxyl-group (compare this vol., p. 463).

G. T. M.

Nitrometacresols. By W. STAEDEL (*Ber.*, **22**, 215—216).—The nitrometacresol melting at 56°, obtained by nitrating metacresol (compare *Abstr.*, 1883, 662), has the constitution [OH : Me : NO₂ = 1 : 3 : 6], and the nitro-compound (m. p. 129°) produced in the same reaction has the constitution [OH : Me : NO₂ = 1 : 3 : 4]. Salts and alkyl-derivatives of both of these substances have been prepared and will be fully described in a subsequent paper. The ethyl-derivatives yield one and the same dinitro-compound [OEt : Me : (NO₂)₂ = 1 : 3 : 4 : 6], from which dinitrotoluidine [NH₂ : Me : (NO₂)₂ = 1 : 3 : 4 : 6] was obtained. The nitrotoluidines [NH₂ : Me : NO₂ = 1 : 3 : 6] and [NH₂ : Me : NO₂ = 1 : 3 : 4] were also prepared, and the corresponding nitrotoluenes were obtained from the three nitramido-derivatives.

Paramidometacresol gives a chloroquinoneimide with calcium hypochlorite; the salts and acetyl-derivative were also prepared.

F. S. K.

Constitution of the Anilic Acids. By J. U. NEF (*Amer. Chem. J.*, **11**, 17—26).—Hydroxylamine hydrochloride reacts with nitranilic acid, *hydroxyammonium nitranilate*, C₆O₄(NO₂)₂(NH₄O), being formed. It is a yellow, crystalline solid, soluble in water. When heated to a high temperature, it explodes. With cold concentrated nitric acid, nitranilic acid is liberated. When boiled with hydroxylamine hydrochloride in excess, it is decomposed.

Sodium nitranilate reacts with bromine-water, bromopicrin, sodium bromide, hydrogen bromide, and oxalic acid being the products. This reaction takes place quantitatively, and must be carried out at 0°.

Methyl- and acetyl-derivatives of nitranilic acid could not be prepared, and the author believes that the anilic acids are derivatives of tetraketohexamethylene.

J. W. L.

Action of Methyl Iodide and Potash on Phloroglucinol. By O. MARGULIES (*Monatsh.*, **9**, 1045—1054).—The author has treated phloroglucinol (1 mol.) with potash (6 mols.) and methyl iodide, conducting the experiment in the same way as that adopted by Herzig and Zeisel (*Abstr.*, 1888, 822), and has isolated the following compounds:—

Pentamethylphloroglucinol, C₆HMe₅O₃ [Me₂ : Me₂ : Me = 2 : 4 : 6], contains neither hydroxyl- nor methoxyl-groups, thus differing in constitution from the chief product obtained by Herzig and Zeisel (*loc. cit.*) with ethyl iodide. After several recrystallisations from ether, it melts sharply at 80°. *Trimethylphloroglucinol*, C₆H₃O₃Me₃, and *bi-secondary tetramethylphloroglucinol*, C₁₀H₁₄O₃, are both soluble in potash, and each contains an hydroxyl-group. The former crystallises from methyl alcohol in plates melting at 184°; the latter in small needles melting at 114°.

G. T. M.

Aniline Chlorate and Perchlorate. By C. GIRARD and L. L'HOTE (*Compt. rend.*, **108**, 183—185).—When pure aniline is poured

into chloric acid, acicular crystals of aniline chlorate separate immediately, and can be dried on porcelain. At about 20°, the salt inflames and leaves a carbonaceous residue. It can also be obtained on a large scale from aniline hydrochloride by double decomposition, provided that the salt is carefully neutralised by agitating it with aniline. 100 grams of the hydrochloride are dissolved in 200 grams of water and mixed with a solution of 82 grams of sodium chlorate in 125 grams of water, and the white, crystalline product is drained on a funnel which is cooled to 0°. It is very soluble in water, and takes fire when brought in contact with fuming nitric acid, Nordhausen acid, or concentrated sulphuric acid, but not with ordinary nitric acid or with strong hydrochloric acid. With the two last mentioned, it yields coloured products.

Aniline perchlorate is obtained in brilliant lamellæ by the direct union of aniline and perchloric acid. It is also formed by adding a solution of 30 grams of sodium perchlorate in 50 grams of water to a solution of 30 grams of neutral aniline hydrochloride in 60 grams of water. It is very stable in the air at the ordinary temperature, but if heated in a tube, it deflagrates and deposits carbon. In contact with fuming nitric acid, it inflames, but ordinary nitric acid and strong sulphuric acid have no action in the cold. On heating, nitric acid forms coloured products, sulphuric acid expels the perchloric acid.

C. H. B.

Dehydrothiotoluidine. By P. JACOBSON (*Ber.*, **22**, 330—335).—*Dehydrothiotoluidine*, $C_{14}H_{12}N_2S$, is obtained when primuline (3 grams) (compare Green, *J. Soc. Chem. Ind.*, **7**, 179) is heated at 190—200° with phosphorus (1 gram) and hydriodic acid of sp. gr. 1·7 (12 grams). It can also be obtained by heating paratoluidine (100 grams) with sulphur (60 grams) at 180—190° for 18 hours, and then at 200—220° for six hours. The crude powdered product is extracted with hot hydrochloric acid, precipitated from the solution with water, and dissolved in hydrochloric acid; the filtered and diluted solution is neutralised with ammonia, and the precipitated base recrystallised from alcohol. It forms almost colourless needles, melts at 190—191°, and is moderately soluble in hot alcohol, benzene, and ether, but only sparingly in cold alcohol; all the solutions show a blue fluorescence. It dissolves in warm, concentrated hydrochloric acid with an orange coloration, but is precipitated in an impure condition on adding water.

This compound is identical with the “thiotoluidine” described in the German patent No. 35790 (Dahl & Co.), and a base of the same composition can be isolated from the insoluble portion of the melt obtained according to the directions given in the patent.

The phenol, $C_{14}H_{10}NS \cdot OH$, is obtained when dehydrothiotoluidine is diazotised and the product boiled with water. It crystallises from alcohol in colourless needles, melts at 255—256°, and is moderately soluble in hot alcohol, but almost insoluble in benzene and ether. The alcoholic solution is colourless, but alkaline solutions show a blue fluorescence. The *acetyl-derivative*, $C_{14}H_{10}NS \cdot OAc$, crystallises from alcohol in colourless needles, melts at 131—132°, and is readily soluble in glacial acetic acid and hot alcohol. (Compare also Green, *Trans.*, 1889, p. 228 *et seq.*.)

F. S. K.

Metamidoparacresyl Methyl Ether. By L. LIMPACH (*Ber.*, **22**, 348—353).—Metamidoparacresyl methyl ether crystallises from hot water, melts at 51°, boils at 235°, and is readily soluble in alcohol, ether, and benzene. (Compare Hofmann and v. Miller, *Abstr.*, 1881, 592.) The hydrochloride, $C_8H_{11}NO \cdot HCl + H_2O$, crystallises in prisms, and loses its water at 80—90°. The acetyl-derivative, $C_{10}H_{13}NO_2$, crystallises in plates, and melts at 110°. The formyl-derivative, $C_9H_{11}NO_2$, crystallises from alcohol in prisms, and melts at 86°.

Chlorocresyl methyl ether, [Me : OMe : Cl = 1 : 4 : 3], prepared from the amido-compound by Sandmeyer's reaction, is a yellow oil, boils at 210° (uncorr.), and is insoluble in alcohol, ether, and benzene.

Hydroxycresyl methyl ether, [Me : OMe : OH = 1 : 4 : 3], is obtained by diazotising the amido-compound, boiling the product with potash, and distilling with steam. It is a yellow, aromatic-smelling oil, boils at about 185° with partial decomposition, and is readily soluble in alcohol, ether, and benzene, but only moderately so in water.

The *hydrazine-derivative*, [Me : OMe : N_2H_3 = 1 : 4 : 3], is obtained by diazotising the amido-compound and reducing the diazo-chloride first in the cold with a solution of hydrogen sodium sulphite and then with warm acetic acid and zinc-dust; the boiling filtered solution is mixed with fuming hydrochloric acid, and the salt which separates is decomposed with soda. It is a crystalline compound melting at 45°.

Homomethylsalicylonitrile, [Me : OMe : CN = 1 : 4 : 3], is prepared from the amido-compound by Sandmeyer's method; the product is distilled with steam and fractionated. It is a yellow oil, which boils at 270°, and is converted into homomethylsalicylic acid when heated with potash. This acid crystallises in needles, melts at 70°, and is soluble in water, benzene, and light petroleum. The silver salt, $C_9H_9O_3Ag$, is moderately soluble in water. Since the methyl ether of this acid yields homosalicylic acid when treated with hydriodic acid, the constitution of amidoparacresyl methyl ether is [Me : OMe : NH_2 = 1 : 4 : 3].

Amidoazoparacresyl methyl ether,



is obtained when an alcoholic solution of amidocresyl methyl ether hydrochloride (5 grams), and the free base (10 grams) is treated with a solution of sodium nitrite (1·4 grams); hydrochloric acid is added, and the dark-red salt, which separates after a short time, is recrystallised from dilute hydrochloric acid and then decomposed with sodium carbonate solution. It crystallises from dilute alcohol in shining plates, melts at 156° with decomposition, and dissolves in acids with a red coloration.

F. S. K.

Oxidation of Orthophenylenediamine. By O. FISCHER and E. HEPP (*Ber.*, **22**, 355—359).—When trianilidonaphthalene, $[(NHPH)_3 = 1 : 2 : 4]$, is oxidised it is converted into rosinduline; a full account of the results will be published shortly.

It was observed by Griess (this Journal, 1872, 499) that ortho-phenylenediamine hydrochloride yields with ferric chloride a ruby-red, crystalline compound which he considered to be the hydrochloride of a base, $C_{12}H_{10}N_4$. The authors prove that this base has the composition assigned to it by Griess, because, when the ruby-red salt is dissolved in water and the largely diluted solution poured into hot ammonia, diamidophenazine, $C_{12}H_{10}N_4$, separates on cooling in small, yellow needles. (Compare Salkowski, *Annalen*, 173, 58.) No decomposition takes place as stated by Wiesinger (Abstr., 1884, 1322), and the results obtained by Rudolph (Abstr., 1880, 162) and Wiesinger (*loc. cit.*) are erroneous.

Diamidophenazine, the constitution of which is probably $NH_2 \cdot C_6H_3 \begin{array}{c} N \\ | \\ N \end{array} C_6H_3 \cdot NH_2$, can be obtained in long, brownish-yellow needles by pouring a boiling, very dilute solution of the pure and sparingly soluble sulphate (prepared by dissolving the precipitated base in very dilute sulphuric acid and crystallising) into hot ammonia. It sublimes in slender, yellow plates when heated carefully in small quantities, and dissolves in concentrated sulphuric acid with a grass-green coloration which turns orange-red on diluting with water. It dissolves in benzene and alcohol with a greenish-yellow fluorescence; alcoholic solutions of the salts show a dark, orange-red fluorescence. The *diacetyl-derivative*, $C_{16}H_{14}N_4O_2$, separates immediately in yellow needles when the base is dissolved in acetic anhydride (10 parts) and the solution warmed. It turns brown when heated at about 200° , melts at about 270° , and is very sparingly soluble in all ordinary solvents, but can be crystallised from 20 per cent. alcohol.

Amidophenazine, $C_{12}H_9N_3$, sublimes in red needles when an intimate mixture of the diamido-compound (1 part) and zinc-dust (4 parts) is carefully heated. It crystallises from alcohol in long, red needles, melts at 265° , and is a strong base. It dissolves in concentrated sulphuric acid, forming an unstable, green salt which, on diluting with water, is converted into a stable, red salt. Dilute solutions of the base show an orange-red, solutions of the neutral salts a saffron-red fluorescence. The *platinochloride*, $(C_{12}H_9N_3)_2 \cdot H_2PtCl_6$, crystallises from boiling water in feathery groups of brownish-red needles, and is very sparingly soluble in cold water.

When amidophenazine is treated with sodium nitrite and dilute sulphuric acid in alcoholic solution, it is converted into phenazine (azophenylene). Phenazine is also formed, together with amidophenazine, when the diamido-derivative (1 part) is distilled with zinc-dust (6—10 parts); it can be isolated by distilling with steam, as amidophenazine does not volatilise.

F. S. K.

Benzyl-derivatives of Hydroxylamine. By R. BEHREND and K. LEUCHS (*Ber.*, 22, 384—386).—When dibenzylhydroxylamine (m. p. 123°), prepared by treating hydroxylamine with benzylchloride according to Schramm's method (Abstr., 1884, 51), is heated at 130° with excess of benzyl chloride, the hydrochlorides of tribenzylamine and dibenzylamine are formed together with benzaldehyde and a basic oil, possibly tribenzylhydroxylamine.

Dibenzylbenzoylhydroxylamine, $\text{BzN}(\text{C}_7\text{H}_7)_2\text{O}$, is obtained when the dibenzyl-derivative is treated with benzoic chloride. It crystallises from alcohol in needles, melts at 97° , and is decomposed into dibenzyl-hydroxylamine and benzoic acid when boiled with alcoholic potash. *Benzoxycarbamide*, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OC}_7\text{H}_7$, crystallises from alcohol in needles and melts at 139° .

When benzylhydroxylamine is treated with benzyl chloride (1 mol.) in presence of sodium carbonate, it is partially converted into a compound having the composition of dibenzylhydroxylamine and a neutral oil which seems to consist principally of tribenzylhydroxylamine; the neutral compound reduces Fehling's solution on warming. The dibenzyl-derivative is also an oil, and differs from the isomeric compound referred to above in having more strongly marked basic properties, and in its behaviour towards reagents. The hydrochloride, $\text{NH}(\text{C}_7\text{H}_7)_2\text{O}, \text{HCl}$, is very sparingly soluble in water. F. S. K.

Some Derivatives of Orthazotoluene. By V. POSPÉCHOFF (*J. Russ. Chem. Soc.*, 1888, **20**, 608—610).—In a former paper (Abstr., 1888, 825) the author showed that orthazotoluene melts at 55° and not at 137° . On adding powdered orthazotoluene to fuming nitric acid of sp. gr. 1·400, it dissolves, and after some time the mixture solidifies to a crystalline mass. On treating this with water and recrystallising the product from alcohol, reddish-brown needles consisting of *mononitrazotoluene* are obtained; this melts at 87° and is soluble in alcohol, ether, benzene, and chloroform. If the nitric acid is stronger (sp. gr. 1·45), dark, reddish-brown crystals are obtained which are not perfectly homogeneous; they melt at 248 — 253° with volatilisation, and consist chiefly of *dinitrazotoluene*. B. B.

Orthonitrophenylhydrazine. By A. BISCHLER (*Ber.*, **22**, 240—241).—Orthonitrophenylhydrazine (Michael, Abstr., 1886, 699) is readily obtained by diazotising orthonitraniline and treating the product with stannous chloride and hydrochloric acid. It forms yellow needles of a silky lustre; the salts crystallise well.

Orthamidophenylhydrazine, prepared by reducing the above compound with stannous chloride and hydrochloric acid, forms white plates which soon become brown when exposed to air. N. H. M.

Azimido-compounds. By T. ZINCKE and H. ARZBERGER (*Annalen*, **249**, 350—372; compare Abstracts, 1887, 730—731, and 1888, 159).—*Bromazimidobenzene* is prepared by acting on an alcoholic solution of bromonitracetanilide [1 : 3 : 4] with dilute acetic acid and iron powder. When the reduction is accomplished, hot water is added to the mixture, the iron is precipitated by the addition of sodium carbonate, and the mixture is filtered hot. The filtrate is at once acidified with hydrochloric acid and mixed with sodium nitrite, when acetyl bromazimidobenzene is deposited as a yellowish-white precipitate. This compound is decomposed by boiling with strong hydrochloric acid, yielding crystals of bromazimidobenzene, $\text{C}_6\text{H}_5\text{BrN}_3\text{H}$. This melts at 158 — 159° , and is freely soluble in alcohol and in glacial acetic acid. It is also soluble in alkalis, but is reprecipitated

from its alkaline solutions by carbonic anhydride. It dissolves in sodium ethoxide, forming the sodium-compound $C_6H_3BrN_3Na$. Bromazimidobenzene forms compounds with acids as well as with metals. The hydrochloride and platinochloride, $(C_6H_3BrN_3H)_2, H_2PtCl_6$, are crystalline.

The acetyl derivative, $C_6H_3BrN_3Ac$, crystallises in needles, soluble in ether, benzene, and chloroform, and melts at 117—118°. Bromazimidobenzene unites with methyl iodide, forming *dimethylbromobenzeneazammonium iodide*, $C_6H_3BrN_3Me_2I$. This compound is decomposed by distillation in a vacuum, yielding methyl iodide and *methylbromazimidobenzene*, $C_6H_3BrN_3Me$; this is a crystalline compound which is soluble in alcohol, melts at 80° and forms a crystalline platinochloride. *Dimethylbromobenzeneazammonium chloride*, prepared by the action of silver chloride on the iodide, crystallises in needles. It is freely soluble in alcohol and in water, and melts with decomposition at 204°. The platinochloride crystallises in yellow needles and melts at 229°. The *chloriodine additive product*, $C_6H_3BrN_3Me_2Cl, ICl$, melts at 186—187°, and appears to crystallise in the monoclinic system.

Dimethylbromobenzeneazammonium bromide crystallises in needles soluble in alcohol and water; it melts at 206° with decomposition. The perbromide, $C_6H_3BrN_3Me_2Br, Br_2$, melts at 167°. *Dimethylbromobenzeneazammonium iodide* melts with decomposition at 200°. The periodide melts at 142—143°. *Dimethylbromobenzeneazammonium hydroxide* is known only in aqueous solution. It has a strongly alkaline reaction, and precipitates iron and copper salts from their solutions.

Benzylbromazimidobenzene, $C_6H_3BrN_3 \cdot C_7H_7$, and *dibenzylbromobenzeneazammonium chloride*, $C_6H_3BrN_3Cl(C_7H_7)_2$, are prepared by heating at 100° a mixture of methyl alcohol (3 parts), benzyl chloride (3 parts), and bromazimidobenzene (2 parts). The crude product is evaporated and the residue dissolved in ether. Repeated treatment with water removes the azammonium chloride from the ethereal solution. The residue which remains on evaporating the ether becomes crystalline when moistened with methyl alcohol. After treatment with ammonia, it is purified by recrystallisation from dilute hydrochloric acid and from alcohol. *Benzylbromazimidobenzene* crystallises in silky needles, melts at 108°, and is soluble in alcohol and benzene. The *platinochloride*, $(C_6H_3BrN_3 \cdot C_7H_7)_2, PtCl_6$, is crystalline. *Dibenzylbromobenzeneazammonium chloride* also forms a crystalline platinochloride.

Methylbenzylbromobenzeneazammonium iodide, $C_6H_3BrN_3(C_7H_7)MeI$, crystallises in needles and melts at 153—154°. The *chloriodochloride* melts at 123° with decomposition, and the *periodide* melts at 99°.

Trichlorobromazimidobenzene, $C_6Cl_3BrN_3H$, prepared by boiling the crude acetyl-derivative of bromazimidobenzene with nitrohydrochloric acid, melts between 246° and 250°, and is freely soluble in alcohol, benzene, and in acetic acid. This compound unites with bases but not with acids.

Methyltrichlorobromazimidobenzene, $C_6Cl_3BrN_3Me$, melts at 196°, and is insoluble in alcohol and acetic acid.

Dimethyltrichlorobromobenzeneazammonium iodide, $C_6Cl_3BrN_3Me_2I$,

melts at 185° , and forms needle-shaped crystals which are sparingly soluble in water and have an intensely bitter taste. W. C. W.

Theory of the Formation of Aniline-blue. By R. HIRSCH (*Chem. Zeit.*, **12**, 1725—1726).—The author endeavoured to prepare aniline-blue by heating together rosaniline and paratoluidine, and confirms Nietzki's statement that no blue is formed unless some organic acid is present. It was thought that the acids might form anilides, and that these reacted with the rosaniline to yield the blue; however, experiments with acetanilide and rosaniline, both with and without aniline, did not support this view. In another experiment, leucaniline, aniline, and benzoic acid were heated at 180° for two hours in a current of carbonic anhydride, when, contrary to expectations, the leucaniline remained unchanged, with the exception of a small quantity which became accidentally oxidised. The author thinks that the carbinol-group in the rosaniline takes some part in the formation of the blue.

D. A. L.

Aldehyde-blue. By L. GATTERMANN and G. WICHMANN (*Ber.*, **22**, 227—236).—Aldehyde-blue can be prepared by dissolving para-rosaniline (5 grams) in a mixture of concentrated hydrochloric acid (55 grams) and water (55 grams), and, after adding aldehyde (22 grams) to the solution, keeping the mixture for 24 hours at the ordinary temperature. The whole is then diluted to 1 litre, the dye precipitated with sodium chloride, dried on porous plates, dissolved in absolute alcohol, and the filtered solution evaporated at the ordinary temperature. The same compound can also be prepared from pararosaniline and paraldehyde as described above; the yield is larger by this method, 10 to 12 grams of the pure substance being obtained from 10 grams of pararosaniline. It is a dark-blue powder, which on rubbing, or when compressed, shows a bronze-coloured metallic lustre. It is very hygroscopic and very readily soluble in water and alcohol, but insoluble in ether, benzene, and light petroleum. This dye is the hydrochloride of some base, but when treated with concentrated hydrochloric acid, it combines with a further quantity of acid, forming a reddish-yellow salt. The free base separates in light-red flocks when alkali is added to an aqueous solution of its salts. The salt shows all the properties of a rosaniline dye, and yields a colourless, amorphous leuco-base when reduced with zinc-dust and hydrochloric acid. The leuco-base dissolves in hydrochloric acid, forming a colourless solution which soon becomes blue on exposure to the air, and is rapidly converted into the original colouring matter by oxidising agents.

Aldehyde-blue yields a colourless, amorphous base when heated at 220° with concentrated hydrochloric acid; when heated alone, water and hydrogen chloride are evolved, but on raising the temperature a strong smell of quinoline is perceptible, and a heavy oil condenses and solidifies on the cooler portions of the tube. This substance, after purifying by dissolving in dilute hydrochloric acid, boiling with animal charcoal and reprecipitating, was obtained in colourless flocks; its composition is $C_{10}H_9N$, and it is probably a

2 l 2

polymeric quinoline, because when quinaldine hydrochloride is heated at about 220° , an amorphous substance, identical in properties with that obtained from aldehyde-blue, is formed. It is readily soluble in alcohol, and the hydrochloric acid solution gives precipitates with platinic chloride, mercuric chloride, and bromine-water.

The *picrate*, $(C_{10}H_9N)_3 \cdot 2C_6H_3N_3O_7$, is precipitated on adding picric acid to an alcoholic solution. The free base melts without decomposing, but has no well-defined melting point; when heated more strongly it is decomposed, but in a partial vacuum it boils without decomposition. The relationship between this base and Claus' diquinoline is shown also by the fact that both substances dissolve in hydrochloric acid with a red coloration. As this compound is probably a triquininaldine, aldehyde-blue is probably the chloride of *triquinaldylcarbinol*, $CCl(C_{10}NH_8)_3 \cdot HCl + 3H_2O$. This formula agrees fairly well with the analyses, and is also in accordance with the fact that nitronic acid has no action on aldehyde-blue.

A blue colouring matter, probably $C_{10}NH_3Me \cdot CCl(C_{10}NH_8)_2 \cdot HCl + 3H_2O$, is obtained by treating rosaniline with paraldehyde under the conditions stated above: this compound resembles aldehyde-blue in all its properties, and when heated, yields a compound very similar to triquininaldine.

Many attempts were made under various conditions to convert aldehyde-blue into aldehyde-green, but all were unsuccessful: when an aqueous solution of the blue is treated at 100° with hydrogen sulphide and sulphurous anhydride, a blue precipitate only is produced. Two distinct blue compounds are formed by the action of aldehyde on rosaniline: the sodium chloride filtrate from the aldehyde-blue contains a blue dye in solution. This substance is precipitated on adding alkali to the solution; it dissolves in hydrochloric acid with a blue coloration, and gives aldehyde-green when treated with hydrogen sulphide and sulphurous anhydride, but does not yield a blue precipitate. A light-green, amorphous base is precipitated when alkali is added to an aqueous solution of aldehyde-green; when this base is heated, the odour of both quinoline bases and sulphur-compounds is perceptible.

Aldehyde-blue can be suitably employed for staining microscopic preparations which have been hardened by alcohol.

A blue dye, different from aldehyde-blue, is obtained when aldehyde or paraldehyde and pararosaniline react at about 50° . This compound contains a larger proportion of chlorine and a smaller proportion of carbon than aldehyde-blue.

F. S. K.

Silico-organic Compound of a new Type. By J. E. REYNOLDS (*Proc. Roy. Soc.*, **45**, 39–40).—A well-defined crystalline substance, *silicotetraphenylamide*, $Si(NHPh)_4$, is obtained by the action of silicon tetrabromide on excess of aniline dissolved in benzene, aniline hydrobromide being also formed. If the aniline is not in excess, the liberated bromine forms a brominated compound with it. The crystalline substance is purified by evaporation of the benzene solution, and crystallisation of the residue from carbon bisulphide. It forms short prisms, which melt at 136 – 137° , and do not decompose at

210°. When distilled at 80 mm. pressure, aniline and a substance, seemingly the silicon analogue of carbodiphenylimide, are obtained. It is anticipated that compounds similar to the above will be obtained from the homologues of aniline.

H. K. T.

Aromatic Boron and Silicon Compounds. By A. MICHAELIS (*Ber.*, **22**, 241—243).—A reply to Gattermann (this vol., p. 344). Phenyl boron chloride, $BPhCl_2$, reacts with chlorobenzene and sodium with formation of *boron triphenyl*, which crystallises well and burns with a green flame when ignited. (Compare Michaelis and Becker, *Ber.*, **13**, 59, and *Abstr.*, 1882, 731; Michaelis, *Annalen*, **229**, 397.)

N. H. M.

Preparation of Terephthalaldehyde. By M. HÖNIG (*Monatsh.*, **9**, 1150—1153).—Paraxylenyl bromide, $C_6H_4(CHBr_2)_2$ [= 1 : 4], is obtained by acting on dry paraxylene, contained in a retort provided with an inverted condenser, and heated first at 140°, and eventually at 170° and 200°, with six times its weight of bromine previously dried over sulphuric acid. On cooling, almost the whole product crystallises in a mass of needles, the small quantity of oil remaining is removed by pressure, the crystals are washed with cold chloroform, and finally recrystallised from warm chloroform; the solution, on cooling, deposits large prisms which melt at 169°.

On heating paraxylenyl bromide with three times its weight of sulphuric acid (sp. gr. 1·825) at 120—130°, and pouring the product into water, terephthalaldehyde crystallises out in needles, which are quite pure after one recrystallisation from water. It melts at 116°, boils at 245—248°, and its compound with phenylhydrazine crystallises from alcohol in golden scales which melt with decomposition at 250°.

G. T. M.

Acetophenone-derivatives. By C. ENGLER and O. ZIELKE (*Ber.*, **22**, 203—207).—Ethyl paranitrobenzoylacetate is a solid substance melting at 54—55°.

Paranitracetophenone is best prepared by mixing ethyl nitrophenyl-propiolate with concentrated sulphuric acid, and keeping the mixture at 35—40° for 10 to 12 hours; the solution is then poured into water, boiled until the evolution of carbonic anhydride ceases, and the product recrystallised from carbon bisulphide and dilute alcohol. The *hydrazone* is crystalline, and melts at 132°.

Bromoparanitracetophenone, $NO_2C_6H_4COCH_2Br$, is obtained by gradually mixing equivalent quantities of bromine and nitracetophenone in glacial acetic acid, then boiling, and lastly precipitating the ketone by adding water. It crystallises from a mixture of benzene and light petroleum, in needles, melts at 98°, and is soluble in acetone, glacial acetic acid, carbon bisulphide, ether, and hot alcohol. The *hydrazone* crystallises in yellow needles.

Paranitrobenzoyl carbinol, $NO_2C_6H_4COCH_2OH$, is prepared by boiling the bromide with sodium acetate, first in glacial acetic acid and then in dilute acetic acid solution; it is a crystalline compound, melts at 121°, is readily soluble in warm alkalis, and yields a reddish, crystalline *hydrazone*.

Dibromoparacacetophenone, $\text{NO}_2\text{C}_6\text{H}_4\text{COCHBr}_2$, is formed when a glacial acetic acid solution of nitracetophenone is boiled with rather more than the calculated quantity of bromine. It crystallises from a mixture of benzene and light petroleum in large, quadratic plates, which melt at $67\cdot4^\circ$, and probably contain benzene; it is readily soluble in carbon bisulphide, acetone, glacial acetic acid and ether, but only sparingly in cold alcohol, and is not decomposed when boiled with water. When boiled with sodium carbonate, it yields para-nitrobenzoic acid, parazoxybenzoylformic acid, and bromoform, but when treated in the cold with the calculated quantity of very dilute potash it is partially converted into nitrobenzoic acid and paranitromandelic acid (compare this vol., p. 508).

Parazoxybenzoylformic acid, $\text{N}_2\text{O}(\text{C}_6\text{H}_4\text{CO}\text{COOH})_2$, is formed when dibromonitracetophenone is boiled with alkalis, and can also be obtained by boiling ethyl paranitromandelate with a concentrated solution of sodium carbonate, and decomposing the resulting sodium salt with hydrochloric acid. It separates from ether in yellow, nodular crystals, melts at 190° , and explodes when heated more strongly. The potassium and ammonium salts are readily soluble, but the sodium salt is only sparingly soluble in water. The methyl salt, $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_7$, crystallises in yellow needles, melts at $173-175^\circ$, and is moderately soluble in benzene and glacial acetic acid, but only sparingly in alcohol. The acid gives a cherry-red coloration with strong sulphuric acid and benzene containing thiophen, and on diluting with water greyish-blue flocks are precipitated. When warmed with strong sulphuric acid, a gas, probably carbon monoxide, is evolved.

F. S. K.

Derivatives of Phenylacetic Acid and Phenylglyoxylic Acid. By G. HAUSKNECHT (*Ber.*, **22**, 324—330).—*Phenylacetodiethylamide*, $\text{CH}_2\text{PhCONEt}_2$, is prepared by treating phenylacetic chloride with diethylamine in very dilute ethereal solution. It crystallises in nacreous plates, melts at 86° , and boils at $295-297^\circ$ (corr.). It is not changed when treated with sodium ethoxide and benzyl chloride or with sodium ethoxide and isobutyl bromide.

Phenylacetodiphenylamide, $\text{CH}_2\text{PhCONPh}_2$, prepared in like manner from phenylacetic chloride and diphenylamine, crystallises in small, yellowish needles melting at 72° . The hydrogen-atom in the methylene-group is not replaceable by alkyl radicles. The hydrogen in the methylene-group in the methyl salts of ortho- and para-nitrophenylacetate is not replaceable by alkyls.

Paranitrophenylacetic acid is oxidised to paranitrobenzoic acid when treated with nitrous acid in alkaline solution.

Methyl dinitrophenylacetateazotoluene, $\text{C}_{16}\text{H}_{14}\text{O}_6\text{N}_4$, prepared by treating methyl dinitrophenylacetate with diazotoluene (compare p. 516), crystallises in bright red needles, melts at 168° , and is sparingly soluble in cold alcohol.

Methyl dinitrophenylacetateazo-xylene, $\text{C}_{17}\text{H}_{16}\text{O}_6\text{N}_4$, crystallises in dark red needles melting at 159° .

Methyl dinitrophenylacetateazonaphthalene, $\text{C}_{19}\text{H}_{14}\text{O}_6\text{N}_4$, crystallises in dark brown prisms, and melts at 94° . The last three compounds are all insoluble in aqueous alkalis.

Sodium methyldinitrophenylacetateazobenzenesulphonate,

crystallises in small, yellow plates, and is readily soluble in water but insoluble in alcohol.

Diazobenzene chloride has no action on the two nitrophenylacetic acids.

The silver salts of ortho- and para-nitrobenzyl cyanide were obtained in an impure condition in the form of brownish-black precipitates, by treating the respective cyanides with potash and silver nitrate in alcoholic solution. Lead orthobenzyl cyanide is yellowish-brown, the copper salt is green. The lead salt of the para-compound is brown, the copper salt dark green.

Paranitrobenzoylphenylhydrazine, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}_2\text{H}_2\text{Ph}$, is formed, with evolution of hydrogen cyanide, when paranitrobenzoic cyanide or chloride (1 mol.) is treated with phenylhydrazine (2 mols.). It crystallises in small, yellowish-red needles, melts at 198° , and is readily soluble in hot alcohol. It dissolves in alcoholic potash with a dark-violet coloration, which disappears on exposure to the air or on adding acid. It dissolves in warm, concentrated sulphuric acid with a blue coloration.

Paranitrobenzoyl cyanide gives a red coloration with an aqueous solution of sodium acetate, but no evolution of hydrogen cyanide takes place.

Benzoylphenylhydrazine (m. p. 169°) is formed when benzoic cyanide is treated with phenylhydrazine. F. S. K.

Nitrohydroxycinnamic Acids. By G. LUFF (*Ber.*, **22**, 291—299).—Metamidocinnamic acid (30 grams) dissolved in sulphuric acid (5 parts) and well cooled, was gradually treated with the calculated amount of potassium nitrate; the solution was then poured into water, and an excess of sodium nitrite added. The diazotised solution was afterwards boiled and filtered hot.

Orthonitrometahydroxycinnamic acid, [COOH : OH : NO₂ = 1 : 3 : 6], separates from the solution obtained as just described in yellow flakes. It melts at 216° , and dissolves very readily in alcohol, very sparingly in hot water, ether, and acetic acid.

Orthonitrocoumaric acid, C₉H₇NO₅ [COOH : NO₂ : OH = 1 : 2 : 3], is obtained from the filtrate from the above acid by boiling with basic zinc carbonate, decomposing the zinc salt with sulphuric acid, and extracting with ether. It melts at 218° , dissolves readily in hot water, ether, and dilute alcohol, sparingly in benzene, and hardly at all in chloroform. The zinc salt forms very slender, pale yellow needles, very readily soluble in alcohol. The acid has an intensely sweet taste.

Symmetrical metanitrohydroxycinnamic acid, [COOH : OH : NO₂ = 1 : 3 : 5], is obtained by evaporating the mother-liquor from the above zinc salt, and treating the zinc salt which separates with dilute sulphuric acid. It forms lustrous crystals rather readily soluble in hot water, alcohol, and ether.

On repeating the above operations, the acid (m. p. 216°) was not

again obtained; metahydroxybenzaldehyde was found in the product. The acid (m. p. 216°) is formed if the metamidocinnamic acid is first converted into the acetyl-compound.

Metahydroxycinnamic acid was prepared by suspending the amido-acid hydrochloride in water, diazotising with an excess of sodium nitrite, boiling the product, and filtering from resin. The yield was 75 per cent. of the theoretical.

Paranitrometahydroxycinnamic acid, [COOH : OH : NO₂ = 1 : 3 : 4], is obtained by slowly treating a solution of metahydroxycinnamic acid in glacial acetic acid with a slight excess of nitric acid (sp. gr. = 1.4); after some time reddish-brown crystals separate, and are crystallised from alcohol. It crystallises in gold-coloured needles melting at 248°, is extremely sparingly soluble in water, cold alcohol, and ether, practically insoluble in benzene and chloroform. Orthonitrocinnamic and metanitrometahydroxycinnamic acids are also formed.

The constitution of all four nitrohydroxycinnamic acids, as given, was determined by conversion into the corresponding nitrohydroxybenzoic acids.

N. H. M.

Action of Methyl Iodide on Ethyl Phenylamidocrotonate. By M. CONRAD and F. ECKHARDT (*Ber.*, **22**, 83—86).—When ethyl phenylamidocrotonate (anilacetooacetate) is heated with methyl iodide at 130—140° for seven hours, it yields a product which on treatment with dilute ammonia divides itself into an oily and an aqueous layer. The oily layer contains ethyl acetate, aniline, and a compound, possibly dimethyltoluidine, boiling at 208°. The aqueous layer contains phenyllutidonecarboxylic acid; this acid, when heated at 270° until carbonic anhydride ceases to be evolved, is converted into phenyl-lutidone, which crystallises from water with 1 mol. H₂O (compare *Abstr.*, 1887, 500).

W. P. W.

Preparation of Nitromandelic Acids. By C. ENGLER and O. ZIELKE (*Ber.*, **22**, 207—209).—Orthonitromandelic acid (compare Engler and Wöhrle, *Abstr.*, 1887, 948) can be prepared as follows:— Hydrochloric acid is gradually poured into a well-cooled mixture of dry potassium cyanide and an ethereal solution of orthonitrobenzaldehyde, the whole being constantly shaken; excess of methyl alcohol is then added, and hydrogen chloride passed into the solution. The hydrochloride of the imido-ether which separates is washed with ether, dissolved in water, and the solution filtered; after a short time, methyl orthonitromandelate separates from the solution. The free acid, obtained by hydrolysing the ethereal salt with sulphuric acid, is identical with the compound previously obtained from acetophenone. The yield is 15 to 20 per cent. of the theoretical quantity. The methyl salt melts at 74.5°, and is readily soluble in alcohol and ether, but only sparingly in light petroleum.

Paranitromandelic acid (compare p. 506) is easily obtained from paranitrobenzaldehyde as described above; the resulting methyl salt is hydrolysed with a mixture of equal volumes of water and concentrated sulphuric acid, and the free acid is extracted with ether. It crystallises from a mixture of ether and light petroleum, melts at 126°,

and is readily soluble in acetone, glacial acetic acid, alcohol, and hot water, but only sparingly in chloroform, carbon bisulphide, and benzene. When treated with cold dilute alkalis, or when boiled with sodium carbonate, it is to a large extent converted into parazoxybenzoylformic acid, and when heated with concentrated sulphuric acid, carbon monoxide is evolved. The salts of the alkalis and alkaline earths are readily soluble. The *silver* salt is very sparingly soluble and is unstable. The *ethyl* salt, prepared by decomposing the imido-ether hydrochloride, crystallises from light petroleum in colourless needles melting at 75–76°. The *methyl* salt crystallises from benzene in prisms and melts at 87°.

F. S. K.

Tautomeric Compounds. By J. U. NEF (*Amer. Chem. J.*, **11**, 1–17).—*Ethyl quinonedimidotetra carboxylate*, $C_6(NH)_2(COOEt)_4$, is prepared by adding bromine to a cooled solution of ethyl diamido-pyromellitate.

It is a yellow solid, crystallising from alcohol in prisms which melt at 161°. It is volatile without decomposition, and dissolves readily in chloroform, benzene, and hot alcohol, with a pure yellow colour and without fluorescence. The alcoholic solution gives no coloration with ferric chloride; with zinc-dust and acetic acid, it is readily reduced to ethyl diamidopyromellitate.

With a view to determine whether the metal or alcohol radicle in the salts of ethyl quinol-tetracarboxylate is united to carbon or to oxygen, the following compounds were prepared and studied:—

Ethyl sodioquinol-tetracarboxylate, $C_6O_2Na_2(COOEt)_4$, prepared by the action of sodium ethoxide on ethyl quinol-tetracarboxylate, separates as a red, gelatinous precipitate from the mixture. When dry, it is perfectly stable. With solutions of barium chloride, lead acetate, and cupric sulphate it forms yellow precipitates; silver nitrate is instantly reduced; with hydroxylamine hydrochloride, the original ethyl salt is regenerated. With methyl iodide, it forms a *dimethyl*-derivative, $C_6(MeO)_2(COOEt)_4$, melting at 95°; this crystallises in colourless needles, and is volatile without decomposition; its solutions fluoresce; with ferric chloride, it gives no coloration.

The corresponding *diacetyl*-derivative, $C_6(AcO)_2(COOEt)_4$, prepared by the action of acetic chloride on the dry sodium salt, is a colourless substance, volatile without decomposition, insoluble in alkalis, and melting at 120°. Its solutions show no fluorescence, and give no coloration with ferric chloride. It does not react with bromine.

In a similar series of experiments carried out with ethyl para-diketohexamethylenetetracarboxylate, the *sodium*-derivative was obtained by the action of sodium ethoxide on the diketo-compound. It is a pale-rose-coloured substance, and reacts with metallic salts and hydroxylamine in a manner exactly corresponding with the sodium-derivative of the quinol-compound. With bromine-water, it forms no additive compound, but is converted into the quinol-derivative. The *diacetyl*-derivative, $C_6(HO)_2Ac_2(COOEt)_4$, crystallises from alcohol in colourless needles melting at 142°. It gives a blood-red coloration with ferric chloride, dissolves in soda and sodium carbonate solutions, and its salts give reactions entirely analogous to those of the phenols.

With bromine-water, a product melting at 155° and containing no bromine is formed; it is not the diacetyl salt of the quinol-derivative. It forms an acetyl-derivative with acetic chloride, and reduces silver nitrate in the cold.

J. W. L.

Derivatives of Resorcinoldisulphonic Acid. By F. UHLER (*Monatsh.*, **9**, 1127—1131).—The author finds that the nitrogenous compound, which Fischer (*Abstr.*, 1881, 1147) obtained in small quantity by the action of potassium nitrite on potassium resorcinoldisulphonate, is a salt of nitrosoresorcinoldisulphonic acid. It may be readily prepared in quantity by allowing a solution of potassium nitrite (20 grams) to drop slowly into a solution of potassium resorcinoldisulphonate (100 grams) in water (400 c.c.) and acetic acid (15 c.c.), the containing vessel being frequently shaken during the addition of the nitrite, after which it is allowed to remain in a warm place for several hours, and is cooled in ice-water, when violet-coloured crystals of *potassium nitrosoresorcindisulphonate*, $\text{NO}\cdot\text{C}_6\text{H}_4(\text{OH})(\text{SO}_3\text{K})_2\cdot\text{OK}$, are deposited.

On oxidation of potassium nitrosoresorcinoldisulphonate with 3 per cent. hydrogen peroxide or 2 per cent. permanganate, *potassium nitroresorcinoldisulphonate*, $\text{C}_6\text{H}(\text{SO}_3\text{K})_2(\text{OH})_2\cdot\text{NO}_2$, is obtained. It crystallises in golden-yellow prisms, its aqueous solution gives a deep blood-red coloured solution with ferric chloride, and on carefully warming with fuming nitric acid it furnishes styphnic acid. The corresponding *amidoresorcinoldisulphonic acid*, $\text{C}_6\text{H}(\text{SO}_3\text{H})_2(\text{OH})_2\cdot\text{NH}_2 + 3\text{H}_2\text{O}$, is obtained on reduction of the nitro-compound with tin and hydrochloric acid. It crystallises in silky needles which decompose at 240° without previously melting.

G. T. M.

Preparation of Tetramethyldiamidotriphenylmethane. By M. NENCKI (*Monatsh.*, **9**, 1148—1149; compare O. Fischer, *Abstr.*, 1880, 40).—This base may readily be prepared in quantity by the following method:—A mixture of benzaldehyde (40 grams), dimethyl-aniline (100 grams), and 93 per cent. alcohol (40 grams) is placed in a large flask heated in a water-bath and provided with an inverted condenser. Phosphorus oxychloride (65 grams) is added very slowly from a dropping funnel, and the mixture is then heated for about half an hour, after which the product is dissolved in warm water, the solution filtered, and, when cold, treated with excess of soda. The oil thus obtained solidifies on standing, and on recrystallisation from alcohol furnishes pure tetramethyldiamidotriphenylmethane, the yield being nearly theoretical.

G. T. M.

Diphenyl Ether and Dinitro diphenyl Ether. By R. HIRSCH (*Ber.*, **22**, 335—336).—Diphenol can be easily obtained by diazotising benzidine and boiling the product with water; 50 grams of benzidine yield 40—42 grams of diphenol.

Diphenyl ethyl ether, prepared by boiling diphenol (20 grams) with ethyl iodide (35 grams) and potash (12 grams) in alcoholic solution (150 grams), crystallises from glacial acetic acid in needles, melts at

174—176°, and is moderately soluble in hot alcohol, but insoluble in water.

Dinitrodiphenyl ethyl ether, obtained by nitrating the ether in glacial acetic acid solution, crystallises from alcohol, melts at 192—193°, and is converted into dinitrophenol when boiled with alcoholic potash.

Dianisidine can be prepared by boiling a glacial acetic acid solution of the dinitro-compound with tin and hydrochloric acid, and treating the product with nitrous acid. It yields colouring matters with naphthol- and naphthylamine-sulphonic acid.

F. S. K.

Action of Nitrous Acid on Tetramethyldiamidobenzophenone and Analogous Compounds. By E. BISCHOFF (*Ber.*, **22**, 337—346; compare *Abstr.*, 1888, 1197).—*Nitrosotetramethyldiamidobenzophenone picrate*, $C_{17}H_{19}N_3O_2C_6H_3N_3O_7$, prepared by treating the ketone with picric acid in alcoholic solution, crystallises in orange-red needles melting at 150—152°. It is readily soluble in warm alcohol, but only sparingly in hot water, and insoluble in the cold. The *hydrochloride*, $C_{17}H_{19}N_3O_2\cdot 2HCl$, is precipitated when hydrogen chloride is passed into a benzene solution of the ketone; it is decomposed by water. The *mercurochloride* is a granular, crystalline compound. The *hydrazone*, $C_{23}H_{25}N_5O_3$, crystallises from hot alcohol in red needles, melts at 148°, and is soluble in hot alcohol, benzene, and hydrochloric acid, but insoluble in water.

Nitrosodimethamidobenzophenone, $COPh\cdot C_6H_2(NMe_2)\cdot NOH$, is obtained when sodium nitrite (2 15 grams) is gradually added to a dilute and well-cooled hydrochloric acid solution of dimethamidobenzophenone (7 grams); the oily product, which is precipitated on adding dilute sodium carbonate solution, is purified by dissolving in ether and shaking the solution with animal charcoal. It is a reddish-yellow oil, gives the nitroso-reaction, and yields an unstable hydrochloride. When reduced with tin and concentrated hydrochloric acid, it is converted into dimethamidobenzophenone.

Paradimethamidobenzoic acid (compare Michler, this Journal, 1876, ii, 68) is best prepared by heating an intimate mixture of tetramethyldiamidobenzophenone (1 part) and soda-lime (2—3 parts) at 340° for two hours, or distilling the mixture until no more dimethyl-aniline passes. The crude product is extracted with hot water, precipitated from the concentrated solution with dilute acetic acid, and recrystallised from alcohol. The *calcium salt* crystallises in yellowish plates.

Nitrosoparadimethamidobenzoic acid. $COOH\cdot C_6H_2(NMe_2)\cdot NOH$, is obtained when the preceding compound is treated with nitrous acid as described above. It crystallises from warm alcohol in yellow plates, melts at 224°, and is readily soluble in benzene, chloroform, and light petroleum, but only sparingly in ether. The *picrate*,



crystallises in yellow needles melting at 168°. The *hydrochloride*, $C_9H_{10}N_2O_3HCl$, crystallises in colourless needles, and is stable in the air. The *oxalate* melts at 178—181°. It also forms salts with platinic and mercuric chlorides. The nitroso-compound is reconverted into

paradimethylamidobenzoic acid when heated with stannous chloride and concentrated hydrochloric acid.

Methyl paradimethamidobenzoate, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\text{COOMe}$, crystallises from hot alcohol in plates, melts at 102° , and is readily soluble in benzene, ether, and chloroform, but only moderately so in dilute alcohol, and insoluble in alkalis.

Methyl nitrosoparadimethamidobenzoate, $\text{OH}\cdot\text{N}(\text{C}_6\text{H}_4(\text{NMe}_2))\cdot\text{COOMe}$, crystallises from alcohol in golden-yellow plates, melts at 101° , and is readily soluble in ether and hot alcohol, but insoluble in water. It gives Liebermann's nitroso-reaction, is readily converted into the corresponding acid when boiled with alcoholic potash, and yields paradimethamidobenzoic acid when warmed with stannous chloride and concentrated hydrochloric acid. The *hydrochloride*, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3 \cdot \text{HCl}$, crystallises in short, colourless needles. The *picrate*,



crystallises in golden-yellow needles and is readily soluble in warm alcohol, but insoluble in water. The methyl salt also forms a platino-chloride.

F. S. K.

Derivatives of Deoxybenzoïn. By E. BISCHOFF (*Ber.*, **22**, 346—348).—*Propyldeoxybenzoïn*, prepared from sodiodeoxybenzoïn and propyl bromide, crystallises from alcohol in moss-like needles, melts at 33° and boils at 328 — 331° (corr.). The *oxime*, $\text{CHPr}=\text{Ph}\cdot\text{CPh}\cdot\text{NOH}$, crystallises from alcohol in needles and melts at 100° . *Isopropyldeoxybenzoïn*, melts at 48° and boils at 324 — 326° (corr.). The *oxime* crystallises in needles and melts at 69 — 70° . The *hydrazone* crystallises in needles, melts at 72° , and decomposes on exposure to the air.

Hexyldeoxybenzoin crystallises from alcohol in needles or plates, melts at 59° , and boils at 344 — 346° (corr.).

The *oxime*, $\text{C}_6\text{H}_{13}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{NOH}$, crystallises in needles and melts at 89° .

Octyldeoxybenzoïn melts at 61° and boils at 350 — 355° (corr.). The *oxime*, $\text{C}_8\text{H}_{17}\cdot\text{CHPh}\cdot\text{CPh}\cdot\text{NOH}$, crystallises in long needles and melts at 101° .

F. S. K.

Benziles. By R. STIERLIN (*Ber.*, **22**, 376—383).—In preparing anisoin by Bosler's method (*Abstr.*, 1881, 421), it is best, as soon as the mixture has been boiled sufficiently, to cool directly and at the same time shake well for 15—20 minutes; the anisoin then separates immediately in considerable quantities.

α -*Anisildioxime*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is precipitated when anisil is boiled for a long time with excess of hydroxylamine hydrochloride in methyl alcohol solution. It is a crystalline powder, melts at 217° , and resembles α -benzildioxime in properties. It is soluble in hot glacial acetic acid and in dilute soda, but almost insoluble in alcohol, ether, and benzene. The *diacetyl*-derivative, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_6$, crystallises in prisms, melts at 139° , and is sparingly soluble in cold alcohol and glacial acetic acid.

β -*Anisildioxime* is obtained, together with the monoxime and other

impurities, when the filtrate from the α -compound is evaporated. The pure compound is prepared by heating the α -derivative (1 part) at 160—170° with absolute alcohol (2—3 parts), or by heating a mixture of anisil (2 parts) and hydroxylamine hydrochloride (1·2 parts) at 170° with absolute alcohol (6 parts) and two drops of concentrated hydrochloric acid. It crystallises in slender, colourless needles, melts at 195°, and is readily soluble in alcohol, glacial acetic acid, and soda. The diacetyl-derivative melts at 130° and is more readily soluble in alcohol and glacial acetic acid than the corresponding derivative of the α -oxime.

Anisiloxime, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NOH})\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is formed when an alcoholic solution of anisil (2 parts) is boiled for 10 minutes with hydroxylamine hydrochloride (1·2 parts). It separates from alcohol in crystalline aggregates, melts at 130°, and is readily soluble in ether, benzene, chloroform, and glacial acetic acid.

Paratoluoin (*diparamethylbenzoïn*) $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained by boiling paramethylbenzaldehyde (10 parts) with potassium cyanide (2 parts) and 50 per cent. alcohol (30 parts) for about two hours, and then shaking the solution until the crystalline product separates. It crystallises in yellowish prisms, melts at 88—89°, and is readily soluble in alcohol, ether, benzene, chloroform, and glacial acetic acid, but only sparingly in hot water. It turns green when treated with fuming sulphuric acid. The *acetyl*-derivative, $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Ac}$, melting at 100°, and the *benzoyl*-derivative, $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Bz}$, melting at 119°, are colourless, crystalline compounds readily soluble in alcohol and ether.

Paratolil, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared by boiling tolouoin (1 part) with concentrated nitric acid (2 parts), crystallises from alcohol in yellowish plates, melts at 104—105°, and is soluble in ether, benzene, and glacial acetic acid. It gives a violet coloration when boiled with potash and absolute alcohol, and when treated with hydroxylamine hydrochloride, as described above, it yields two isomeric dioximes. The α -*dioxime*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises in plates or needles, melts at 217°, and is only sparingly soluble in alcohol, ether, and glacial acetic acid; the *acetyl*-derivative, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4$, crystallises in prisms melting at 133—134°. The β -*dioxime* crystallises in needles, melts at 225°, and is readily soluble in alcohol; the *acetyl*-derivative melts at 144°.

Deoxytolucin, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}$, prepared by reducing tolouoin with zinc and hydrochloric acid in boiling alcoholic solution, crystallises in needles, melts at 102°, and is readily soluble in ether and benzene, but insoluble in water; it is turned brownish-red by sodium ethoxide. The *benzyl*-derivative, $\text{C}_{23}\text{H}_{22}\text{O}$, crystallises in needles, melts at 92—93°, and is readily soluble in alcohol, ether, and benzene.

F. S. K.

Nitration of Naphthionic Acid. By R. NIETZKI and J. ZÜBELEN (*Ber.*, **22**, 451—453).—When sodium naphthionate is heated with acetic anhydride, it is readily converted into an acetyl-derivative which, on nitration in the cold, yields acetylaminonitronephthalenesulphonic acid; the ammonium salt of this acid, $\text{NO}_2\cdot\text{C}_{10}\text{H}_5\cdot(\text{NHAc})\cdot\text{SO}_4\text{NH}_4$,

crystallises in yellow needles. *Nitronaphthylaminesulphonic acid*, $\text{NO}_2\cdot\text{C}_{10}\text{H}_5(\text{NH}_2)\cdot\text{SO}_3\text{H}$, is obtained by heating the acetylated derivative with dilute aqueous potash; it crystallises in colourless needles, yields red crystalline salts with alkalis, is readily diazotised, forming a diazo-compound yielding azo-dyes on treatment with amines or phenols, and is converted by the action of alkali into nitronaphthylamine (m. p. = 119°). It follows, therefore, that the constitution of the acid is [$\text{NH}_2:\text{SO}_3\text{H}:\text{NO}_2 = 1:4:4'$].

W. P. W.

Action of Phosphorus Pentachloride on β -Hydroxynaphthoic Acid. By H. RABE (*Ber.*, **22**, 392—396).—The chloride, $\text{POCl}_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$, is prepared by treating β -hydroxy- α -naphthoic acid with phosphorus pentachloride; it crystallises in white, satiny needles melting at 38°. When treated with water, or, preferably, allowed to remain exposed to the air for two days, it is converted into α -carboxylnaphthyl- β -phosphoric acid, $\text{PO}(\text{OH})_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{COOH}$, which crystallises in tufts of white needles, melts at 156°, and is readily soluble in water, alcohol, and acetone, sparingly soluble in benzene, and almost insoluble in light petroleum. The silver salt, $\text{C}_{11}\text{H}_6\text{O}_6\text{PAs}_3$, was prepared; the ammonium salt, on boiling its aqueous solution, decomposes into phosphoric acid, carbonic anhydride, and β -naphthol.

The chloride, when treated with absolute alcohol, yields a diethyl salt, $\text{PO}(\text{OEt})_2\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{COOH}$, which forms colourless, rhombohedral crystals, melts at 113°, is soluble in alcohol and ether, and decomposes when boiled with water. Phosphorus pentachloride reacts with the dichloride under pressure at 180—190°, forming β -chloronaphthoic trichloride, $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{CCl}_3$, a dark-brown, fluorescent oil which on exposure to the air is converted into β -chloro- α -naphthoic acid, $\text{C}_{10}\text{H}_6\text{Cl}\cdot\text{COOH}$. This is crystalline, melts at 152—153°, is readily soluble in alcohol and ether, and dissolves in 1000 parts of water at 20°, and in 126 parts at 100°. The sodium salt crystallises in thin, lustrous scales; the calcium salt, with 2 mols. H_2O , dissolves in 75 parts of hot and 150 parts of cold water; the methyl salt crystallises in white, broad, brittle prisms and melts at 50°.

W. P. W.

Constitution of β -Naphthylamine- α -Sulphonic Acid. By C. IMMERHEISER (*Ber.*, **22**, 412—413).—The author points out that the formation of β -pyridinephenyleneketonesulphonic acid from β -naphthylamine- α -sulphonic acid (compare p. 527) is only possible if the compound is heteronucleal. Adopting the view ascribed to Cleve (*Ber.*, **20**, 75) and Forsling (*Ber.*, **20**, 2105) that β -naphthylamine- γ -sulphonic acid (Dahl's acid) has probably the constitution [$\text{NH}_2:\text{SO}_3\text{H} = 2:4'$], the author points out that the alternative formula [$\text{NH}_2:\text{SO}_3\text{H} = 2:1'$] must be that of β -naphthylamine- α -sulphonic acid.

W. P. W.

Note by Abstractor.—Both Cleve and Forsling (*l. c.*) adopt provisionally the formula 2 : 1' and not 2 : 4' for the Dahl acid, and therefore the author's conclusions, based on the assumption made by Cleve and Forsling, would point to the formula 2 : 4' and not 2 : 1' as that of β -naphthylamine- α -sulphonic acid. Since the publication of this

paper Armstrong and Wynne (Proc., 1889, 49, 50) have proved that the former acid has the constitution $2:4'$ and the latter $2:1'$.

W. P. W.

Constitution of β -Naphthol- α -Sulphonic Acid and β -Naphthol- α -Disulphonic Acid (R-Acid). By W. PFITZINGER and C. DUISBERG (*Ber.*, 22, 396—399).—When Bayer's β -naphthol- α -sulphonic acid is heated with ammonia in an autoclave, it is converted into so-called β -naphthylamine- α -sulphonic acid (Badische acid) which yields naphthalene- α -sulphonic acid when its amido-group is displaced by hydrogen by the hydrazine method. It follows, therefore, that each of these acids contains its sulphonic group in the α -position.

β -Naphthol- α -disulphonic acid (R-acid) when similarly treated yields Ebert and Merz's naphthalene- α -disulphonic acid, and consequently must contain a sulphonic group in a β -position in each nucleus.

W. P. W.

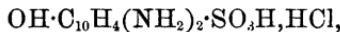
Note by Abstractor.—Since the publication of this paper, the constitution of the so-called β -naphthylamine- α -sulphonic acid (Badische acid) has been shown to be $[\text{NH}_2 : \text{SO}_3\text{H} = 2:1']$ (Armstrong and Wynne, Proc., 1889, 50); it follows, therefore, that β -naphthol- α -sulphonic acid has the constitution $[\text{OH} : \text{SO}_3\text{H} = 2:1']$. In the same paper (p. 53) it is also shown that Ebert and Merz's naphthalene- α -disulphonic acid has the constitution $2:2'$; consequently β -naphthol- α -disulphonic acid (R-acid) must have the constitution $[\text{OH} : \text{SO}_3\text{H} : \text{SO}_3\text{H} = 2:3:3']$.

W. P. W.

β -Naphthol- α -Sulphonic Acid. By R. NIETZKI and J. ZÜBELEN (*Ber.*, 22, 453—456).—Naphthalene- α -sulphonic acid is obtained when β -naphthylamine- α -sulphonic acid, derived from β -naphthol- α -sulphonic acid, is diazotised and boiled with alcohol (compare preceding Abstract). When warmed with dilute nitric acid, β -naphthol- α -sulphonic acid is converted into a *dinitro*-derivative (crocein-yellow) which forms a *dipotassium* salt, $\text{OK}\cdot\text{C}_{10}\text{H}_4(\text{NO}_2)_2\cdot\text{SO}_3\text{K}$, crystallising in golden-yellow scales, and a *potassium* salt,



crystallising in long, yellow needles. On reduction with stannous chloride and hydrochloric acid, the dinitro-derivative is converted into the *hydrochloride* of *diamidonaphtholsulphonic acid*,



which crystallises in colourless needles; it forms the *diimido*-derivative, $\text{C}_{10}\text{H}_8\text{SN}_2\text{O}_4$, on oxidation with ferric chloride, and yields a *diazo*-compound, $\text{OH}\cdot\text{C}_{10}\text{H}_4(\text{NH}_2)\text{N}_2^{\text{SO}_3}$, crystallising in sparingly soluble green needles.

W. P. W.

Unorganised Ferments. By N. KRAVKOFF (*J. Russ. Chem. Soc.*, 1888, 20, 623—632; comp. Abstr., 1888, 862).—In order to prepare diastase, barley-malt was ground and treated for half an hour with water at 35° to 40° ; the liquid was then strained and filtered, and the

solution saturated with powdered ammonium sulphate. The precipitate, after being collected, was washed with alcohol, treated with absolute alcohol for some time, dried at 35° to 40° and extracted with water. The solution thus obtained, when freed from salts by dialysis, was very limpid, gave none of the reactions of albuminoïds, and had a powerful action on starch. The following results in part confirm those obtained by Chittenden and Cummins (Abstr., 1885, 999), but in some respects are not in accordance with them. The mineral acids, hydrochloric, nitric, and sulphuric of 0·0002 per cent., and the organic acids, acetic and lactic, of 0·002 per cent., destroy the diastatic action of the ferment, and this action is not restored by 0·3 per cent. solution of sodium carbonate, or by albuminoïds; this action is found to depend on the strength of the acid, duration of action, and temperature. Carbonic acid in solution, but not gaseous carbonic anhydride, has a considerable retarding action. Alkalies show a retarding action merely; even a 5 per cent. solution of sodium carbonate does not stop the process. Neutral salts also act in the same way. In the stomach, however, owing to the presence of other compounds, especially albumins, globulins, and peptones, the action of diastatic substances is not stopped even in the presence of 0·2 per cent. hydrochloric acid (Schmidt), these substances having a protecting and sometimes even a stimulating action, as shown by direct experiment. For this purpose, the albuminoïd substance must be added first and then the acid, otherwise the fermentative process is stopped at once. This shows that starch may be actually converted into sugar in the stomach. It has been assumed hitherto, that ferments are incapable of diffusion through membranes; the author, however, shows that such a diffusion can take place, but that it depends on the medium below the dialysing membrane. Thus diastase diffuses very slowly into water, although its action on starch through a membrane is tolerably rapid; the action of pepsin and trypsin is much slower. The composition of diastase seems to be less complicated than that of trypsin and pepsin.

The author has found diastatic ferments in almost all animal tissues, and it seems that ferments may be regarded as products of decomposition of living protoplasm.

B. B.

Ring-formation with Elimination of a Nitro-group from the Benzene Nucleus. By V. MEYER (*Ber.*, **22**; 319—323).—The compound $C_6H_3(NO_2)_2\cdot C(COOMe)\cdot N\cdot NHPh$, melting at 182—183°, is obtained when methyl dinitrophenylacetate is treated with a solution of diazobenzene chloride (compare A. and V. Meyer, *Abstr.*, 1888, 693). If the yellowish-red alcoholic solution of this substance is mixed with a little potash (or soda), a deep blue solution of the salt $C_6H_3\cdot (NO_2)_2\cdot C(COOMe)\cdot N\cdot NKPh$ is formed; on keeping for a few minutes at the ordinary temperature, the blue solution turns bright-yellow and considerable quantities of a mixture of potassium nitrite and the benzopyrazole-derivative, $NO_2\cdot C_6H_4 < \begin{matrix} C(COOK) \\ \text{NPh} - \text{N} \end{matrix} \gg$, separates in the form of light-yellow crystals.

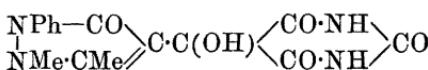
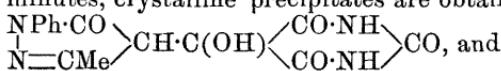
Nitrophenylbenzopyrazolecarboxylic acid (nitrophenylisindazolecar-

boxylic acid), $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{C}(\text{COOH})\text{NPh}-\text{N}\gg$, is obtained when the potassium salt is warmed for a long time with dilute sulphuric acid. It crystallises in small, pale-yellow needles, melts at 272° , turns brown at 265° , and is sparingly soluble in alcohol. The methyl salt is prepared by treating the acid with methyl alcohol and hydrogen chloride, first in the cold and then at a higher temperature; it crystallises in small, bright-yellow needles, melts at $191-192^\circ$, and gives a slight pyrazole-reaction. The compounds (hydrazones) which methyl dinitrophenyl-acetate yields with diazotoluene, diazo-xylene, and diazobenzenesulphonic acid, behave towards alkalis in the same way as that obtained from diazobenzene.

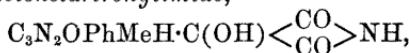
Methyl dinitrophenylacetate yields a deep-brown salt with alkalis, but no further change occurs under the conditions described above.

F. S. K.

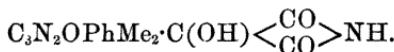
Compounds of Alloxan with Pyrazolic Bases. By G. PELLIZARI (*Gazzetta*, **18**, 340—344).—In a former memoir (Abstr., 1888, 142), the author showed that alloxan was capable of combining with amines with formation of new compounds; he has now investigated the compounds obtained by the action of phenylmethylpyrazolone and phenyldimethylpyrazolone (antipyrin). Aqueous solutions of alloxan dissolve these bases, and on heating the liquid to boiling for a few minutes, crystalline precipitates are obtained having the composition



respectively. The latter, *phenyldimethylpyrazolonetartronylcarbamide*, is but slightly soluble in water, and decomposes at 261° ; the former, *phenylmethylpyrazolonetartronylcarbamide*, crystallises from water in long, yellow needles containing 3 mols. H_2O , and decomposes at $170-180^\circ$. They combine both with acids and with bases. When dissolved in cold aqueous potash, ammonia is produced, and on adding acetic acid to the solution much carbonic anhydride is evolved, and white crystalline precipitates are produced consisting respectively of *phenylmethylpyrazolonetartronylimide*,



and *phenyldimethylpyrazolonetartronylimide*,



These compounds also have both basic and acid properties. The former is easily decomposable; the latter crystallises from alcohol or water in colourless needles which melt with decomposition at $245-250^\circ$.

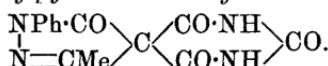
If instead of using cold aqueous potash, the substances just described are boiled with potash, a different reaction takes place. Under these circumstances, the antipyrin-derivative yields a substance of the composition $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_2$; this is far more easily obtained, how-

ever, by boiling either of the antipyrin-derivatives with concentrated hydrochloric acid for some hours, and concentrating the solution. On cooling it deposits the hydrochloride, $C_{12}H_{12}N_2O_2 \cdot HCl + H_2O$, in white, lustrous needles. This hydrochloride loses acid on repeated crystallisation from water, the base, which is insoluble in water, being deposited. The base is insoluble in ether and benzene, but dissolves in hot alcohol, from which it crystallises on cooling in colourless, transparent prisms melting at 238° with decomposition. It is not acted on by acetic anhydride or by reducing agents, and it does not form compounds with phenylhydrazine or hydroxylamine.

When the phenylmethylpyrazolone-derivatives are boiled with potash, they are converted into "*phenylmethylmethoxypyrazolone*" (phenylmethylpyrazolone carbinol), $C_3N_2OPhMeH \cdot CH_2 \cdot OH$, a substance crystallising in white nodules insoluble in water, ether, and benzene, but soluble in hot alcohol and in acetic acid. When heated at $180-185^\circ$, it loses a molecule of water, and is converted into *phenylmethylmethylenepyrazolone*, $C_3N_2OPhMe \cdot CH_2$; this substance is more conveniently prepared, however, by merely boiling the alcoholic or acetic acid solution. It forms long, orange-yellow needles which melt at 178° . By the reducing action of zinc and acetic acid, it is converted into a compound which crystallises in slender, colourless needles melting at about 120° . It is, in all probability, a *phenyldimethylpyrazolone* of the formula

$$\begin{array}{c} NPh \cdot CO \\ | \\ N=CMe \end{array} > CHMe.$$

When treated with hydrochloric acid, the phenylmethylpyrazolone-derivatives undergo a totally different change. On boiling the tartronylcarbamide for a short time with concentrated hydrochloric acid, a new compound is precipitated in orange-red needles which decompose at 250° without melting. It is insoluble in water, and but little soluble in alcohol. As analysis showed that it was formed from the tartronylcarbamide by the elimination of H_2O , it in all probability is *phenylmethylpyrazolonemalonylcarbamide*,



The oxidising action of nitric acid on these compounds completely destroys the alloxanic chain; in the case of the antipyrin-derivatives with formation of nitroantipyrin.

C. E. G.

Reduction of Quinoline-derivatives. By E. BAMBERGER (*Ber.*, **22**, 353—355).—Tetrahydroquinoline is not reduced by sodium and boiling amyl alcohol. When moist carbonic anhydride is passed into a solution of tetrahydroquinoline in light petroleum, a heavy, oily carbonate is precipitated, and gradually solidifies to a mass of colourless crystals.

β -Naphthaquinoline yields two isomeric octohydro-derivatives, which have probably the constitution $C_6H_4 < \begin{array}{c} CH_2 \cdot CH_2 \\ \backslash \quad / \end{array} > C_5NH_9$ and $C_6H_8 < \begin{array}{c} CH \cdot CH \\ \backslash \quad / \end{array} > C_5NH_7$. The former is produced in by far the larger quantity, and melts at 91° , the latter melting at 60° . Both compounds

are easily obtained in crystals, and differ fundamentally both in chemical and physiological properties.

α -Naphthaquinoline, when treated in like manner, yields a crystalline octohydride, $C_6H_8 < \begin{smallmatrix} CH:CH \\ C_5NH_7 \end{smallmatrix} >$, which in its properties resembles the β -derivative melting at 60° . F. S. K.

Quinoline-derivatives from Ethyl Orthonitrobenzoylmalonate. By C. A. BISCHOFF (*Ber.*, **22**, 386—388).—*Ethyl α -ethoxy- γ -hydroxy- β -quinolinecarboxylate*, $OEt \cdot C_9NH_4(OH) \cdot COOEt$ [$= 2' : 4' : 3'$], is formed when ethyl orthonitrobenzoylmalonate dissolved in absolute alcohol is treated in the cold with zinc-foil and hydrogen chloride. It crystallises in small, colourless needles, melts at 107° , and the solutions give a violet coloration with ferric chloride.

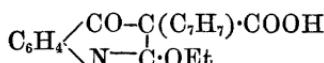
When ethyl orthonitrobenzoylmalonate is treated with hydrochloric acid and zinc-dust at the ordinary temperature, or if it is heated with zinc-dust and glacial acetic acid, various products are obtained, amongst which seem to be the ethereal salt described above, hydrogen ethyl salts, and *dihydroxyquinolinic acid*, $[(OH)_2 : COOH = 2' : 4' : 3']$. This acid, which could only be isolated in the form of the silver salt, is converted into α - γ -dihydroxyquinoline (compare Baeyer and Bloem, *Abstr.*, 1883, 197, and Friedländer and Weinberg, *Ber.*, **15**, 2683) when boiled for a long time with concentrated hydrochloric acid.

When ethyl orthonitrobenzoylmalonate is reduced with tin and hydrochloric acid in dilute alcoholic solution, α - γ -dihydroxyquinoline, α -ethoxy- γ -hydroxyquinoline, and various blue and green compounds are formed. The yield of the dihydroxy-derivative is 80 per cent.; none of the colouring matters are true dyes.

α -*Ethoxy- γ -hydroxyquinoline* crystallises in colourless needles and melts at 228° .

Azodihydroxyquinoline, $N_2[C_9NH_4(OH)_2]_2$ [$N_2 : (OH)_2 = 3' : 2' : 4'$], is obtained when nitrosodihydroxyquinoline is treated with hydrogen sulphide in ammoniacal solution. It is very stable, and dyes silk, wool, and unmordanted cotton-wool a bright orange-yellow.

Nitrodihydroxypyridinecarboxylic acid, $[NO_2 : (OH)_2 : COOH = 3 : 2 : 4 : 5$ or $3 : 2 : 4 : 6$], is formed when dihydroxyquinoline is treated with nitric acid. Ethyl benzylorthonitrobenzoylmalonate yields on reduction a hydrogen ethyl salt of a ketone acid. This compound melts at 147° , and has the constitution



F. S. K.

Methylquinaldone and Methyllutidone. By M. CONRAD and F. ECKHARDT (*Ber.*, **22**, 73—83).— γ -*Hydroxyquinaldine methiodide*, $C_{10}H_9NO, MeI + H_2O$, is obtained by heating sodium hydroxyquinaldine with methyl iodide and benzene at 140° for about three hours. It crystallises in long, satiny needles, and when anhydrous melts at 201° . When heated in aqueous solution with silver chloride, it is converted into the corresponding *chloride*, $C_{10}H_9NO, MeCl + H_2O$,

2 m 2

which crystallises in well-formed, prismatic crystals, melts at 217°, and yields a crystalline *platinochloride*, $(C_{11}H_{12}NO)_2PtCl_6$, melting at 240° with decomposition.

γ -*Methoxyquinaldine methiodide*, $C_{11}H_{11}NO, MeI$, is prepared by heating γ -methoxyquinaldine with benzene and the calculated quantity of methyl iodide at 80—100° for some hours. It crystallises in white, lustrous needles, melts when anhydrous at 201°, is sparingly soluble in cold water, and yields methyl- γ -quinaldone (Abstr., 1887, 680) on treatment with silver oxide suspended in water.

γ -*Chloroquinaldine methiodide* crystallises in greenish-yellow, needle-like forms.

Lutidone methiodide, C_7H_9NO, MeI , is formed by heating lutidone with methyl alcohol and an excess of methyl iodide at 140° for some hours. It is crystalline, melts when anhydrous at 242°, is readily soluble in water and methyl alcohol, and on decomposition with silver oxide is converted into methyllutidone (Abstr., 1887, 500).

Methoxylutidine is prepared by heating chlorolutidine at 150—160° with a solution of sodium methoxide in alcohol. It boils at 203°, and has a sp. gr. = 1.1011 at 24° compared with water at 15°. The *platinochloride*, $(C_8H_{12}NO)_2, H_2PtCl_6$, is a yellow, crystalline compound sparingly soluble in water; the *methiodide*, $C_9H_{14}NOI$, crystallises in long, white prisms, melts at about 204° with decomposition, and is converted into methyllutidone by treatment with silver oxide and water.

Ethoxylutidine is obtained by heating chlorolutidine with a solution of sodium ethoxide in alcohol. It is a colourless oil which boils at 215° without decomposition, and yields a crystalline *methiodide*, $C_{10}H_{16}NOI$; this melts at 196°, and on digestion with silver oxide is converted into methyllutidone.

W. P. W.

Metamidoquinaldine. By GERDEISSEN (*Ber.*, **22**, 244—254).—Ortho- and meta-amidoquinaldine are prepared from the corresponding nitro-derivatives. Dry quinaldine nitrate (100 grams) is gradually added to sulphuric acid (1 kilo.), and after half an hour the mixture is diluted with water (3 litres), and nearly neutralised with solid sodium carbonate. The very small amount of resin which separates on neutralising is readily removed; and on treating the acid solution with a small amount of aqueous soda (so that it still remains acid) the orthonitro-compound separates; it is then collected, treated with an excess of soda, and kept in a cool place. The yield is 37 grams of ortho- and 56 grams of meta-nitroquinaldine. The reduction to amido-derivatives is best effected by adding the nitro-compound (30 grams) to an amount of stannous chloride sufficient to reduce 40 grams, and boiling.

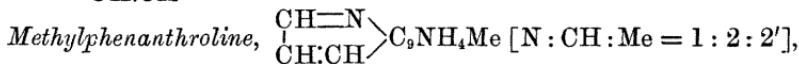
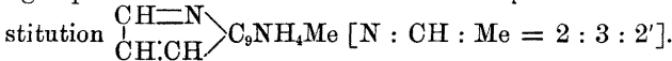
Methylphenanthroline, $\begin{array}{c} \text{CH}=\text{N} \\ | \\ \text{CH} \cdot \text{CH} \end{array} > C_9\text{NH}_4\text{Me}$ [$\text{CH} : \text{N} : \text{Me} = 1 : 2 : 2'$], is obtained together with an isomeride when a mixture of metamidoquinaldine (100 grams), glycerol (320 grams), and orthonitrophenol (75 grams), is gradually treated with sulphuric acid (270 grams). Amidophenol and hydroxyquinoline are also formed. The dark oily mixture of bases obtained is treated with hydrochloric acid, and the crystals covered with alcohol. The salt is then dissolved in water,

treated with ammonia, and extracted with benzene; the solution is dried with potash, distilled, and the crystalline residue extracted with ether, which dissolves only the methylphenanthroline. This is further purified by repeatedly crystallising the hydrochloride from alcohol. The free base, with 3 mols. H₂O, melts at 49—50°; it loses its water when kept over sulphuric acid, and then melts at 64—65°. It boils at above 360°, dissolves readily in cold benzene, and is soluble in boiling water, aqueous and absolute alcohol, and in ether, sparingly soluble in light petroleum. The *hydrochloride*, with 1 mol. H₂O, crystallises in needles, dissolves readily in hot water, and is soluble in hot aqueous alcohol, insoluble in ether; the *sulphate*, with 1 mol. H₂O, crystallises from alcohol in slender, silky needles; the *picrate* forms slender, sulphur-coloured needles melting at 216—217°; the *chromate* crystallises from water in very lustrous, red prisms; the *platino-chloride*, with 1 mol. H₂O, the *ethiodide* (with 2 mols. H₂O), melting at 100—110°, and the *platinochloride* of the *ethochloride*,



are described. When methylphenanthroline is oxidised with permanganate, a *phenanthrolinecarboxylic acid*, C₁₂H₇N₂COOH, is obtained. This crystallises in pale yellow needles which melt at 208—209°, and decompose at 210° with evolution of carbonic anhydride and formation of Skraup's phenanthroline.

The *isomeric base*, C₁₃H₁₀N₂ + 4H₂O, crystallises from dilute alcohol in lustrous, concentrically grouped needles melting at 81—82°; the anhydrous base melts at 108—109°. It dissolves readily in hot benzene and hot dilute alcohol, and is insoluble in cold ether and cold light petroleum. It distils without decomposition. It has the con-



prepared from orthamidoquininaldine, glycerol, orthonitrophenol, and sulphuric acid, crystallises with 2 mols. H₂O and melts at 53°; the anhydrous base melts at 75—76°. It dissolves very easily in hot benzene, readily in chloroform, rather readily in glacial acetic acid, and sparingly in ether and in light petroleum. It does not distil without decomposition.

N. H. M.

Metaquinaldineacrylic Acid and Metaquinaldinealdehyde.

By F. ECKHARDT (*Ber.*, **22**, 271—285).—*Metaquinaldineacrylic acid*, C₁₃H₁₁NO₂, is prepared by the action of strong hydrochloric acid (300 grams) on metamidocinnamic acid hydrochloride (60 grams) and paraldehyde (45 grams) at 150°. The product is treated with water, freed from resin, and evaporated. The crystals of the crude hydrochloride (12 grams) are dissolved in water and treated with a solution of sodium acetate (12 grams), and quickly filtered from the resin which separates; after some time the free acid separates. This is repeatedly crystallised from hot alcohol and decolorised by means of animal charcoal. It forms small, slightly yellowish, monoclinic prisms,

melts at 246° with decomposition, is very sparingly soluble in ether, chloroform, and light petroleum, more soluble in alcohol, benzene, and acetone. It has an acid reaction, and has at the same time basic properties, being readily soluble in dilute alkalis, less soluble in dilute acids. When heated, a small amount of a sublimate of slender needles melting at 223° is formed. The *hydrochloride*, $C_{13}H_{11}NO_2 \cdot HCl + H_2O$, crystallises in rhombic needles; it is easily dissociated; the *nitrate* (with 1 mol. H_2O) forms long, lustrous needles readily soluble in water; the *chromate* crystallises in orange-red needles; the *platinochloride* (with 2 mols. H_2O) crystallises in yellow needles; the *picrate* (with 1 mol. H_2O) separates from the alcoholic solution in groups of hair-like needles, soluble in alcohol, acetone, hot water, and acetic acid; the anhydrous salt melts at 150—152°. The *silver salt* (with 2 and 4 mols. H_2O) and the *calcium salt* (with $1\frac{1}{2}$ mol. H_2O), which crystallises in slender needles, are described. The neutral solution of the ammonium salt gives precipitates with various metallic salts which are described.

An isomeric *metaquinaldineacrylic acid* was obtained on one occasion from the alcoholic mother-liquor from the above acid. It crystallises in monoclinic plates (with 1 mol. H_2O) melting at 184°; it also crystallises with $\frac{1}{2}$ mol. EtOH and melts then at 204°. The *hydrochloride* crystallises in groups of very slender needles. The acid differs from that described above in the behaviour of its ammoniacal solution towards calcium and barium chlorides and magnesium sulphate: the one gives precipitates, the other does not.

Metaquinaldinealdehyde, $C_{11}H_9NO$, is obtained by dissolving the acid (10 grams) in sodium carbonate, diluting with water (500 c.c.), and adding benzene (250 grams); the whole is then cooled to 0° and gradually treated with a 6 per cent. solution of permanganate (10 grams). After 12 hours, it is filtered through calico, and the benzene separated and evaporated down; the oil thus obtained solidifies when cooled and is crystallised from light petroleum. It is purified by steam distillation. It forms white, matted hairs melting at 73°, which are readily soluble in benzene, ether, acetone, and alcohol, less so in light petroleum and hot water. The hot aqueous solution has a penetrating, unpleasant odour. The anhydrous salt melts at 61°. It reduces ammoniacal silver solutions, and yields a double compound with hydrogen sodium sulphite. The *hydrochloride* crystallises in pale-yellow needles; the *picrate* forms slender, matted needles, which blacken at 174°, and melt at 182° with decomposition; the *platinochloride*, $(C_{11}H_9NO)_2 \cdot H_2PtCl_6$, crystallises in orange-coloured, triclinic plates, melts at 211°, and is sparingly soluble in hot alcohol. When the aldehyde is heated with quinaldine and zinc chloride at 150°, a compound melting at 69° is formed. The *hydrochloride* of the phenyl-hydrazine-compound forms long, very thin, brick-coloured, matted hairs; the *sulphate*, $(C_{17}H_{15}N_3)_4 \cdot 3H_2SO_4 + 9H_2O$, crystallises in small, brick-red needles. When metaquinaldinealdehyde (0.5 gram) is boiled with silver oxide (from 2 grams of silver nitrate), it is converted into Döbner and v. Miller's metaquinaldinecarboxylic acid (Abstr., 1884, 1200).

Quinaldineacrylic acid (10 grams) was heated on a water-bath with

pure chloral (35 grams), and the pulverulent hydrochloride thus formed extracted with alcohol. On evaporating the alcohol, a black, resinous substance was obtained, which was treated with hydrochloric acid ; the light brown solution was precipitated with sodium carbonate, and the *trichloro-derivative*, $C_{12}NH_8O_2\cdot CH_2\cdot CH(OH)\cdot CCl_3$, which separated, crystallised from alcohol. It forms colourless prisms melting at 201° . The *hydrochloride*, $C_{15}NH_{12}Cl_3O_3\cdot HCl$, was repeatedly crystallised from alcohol and decolorised with animal charcoal. It crystallises in slender prisms melting above 300° . The *silver salt*, $COOAg\cdot CH\cdot CH\cdot C_9N_5\cdot CH_2\cdot CH(OH)\cdot CCl_3$, crystallises in slender, white needles. When the resinous condensation product is treated with strong instead of with weak hydrochloric acid, the hydrochloride of a compound is obtained which only dissolves in hot caustic alkalis. This *hydrochloride* melts at 217° ; the *free base*, which has the formula $C_{28}N_2H_{25}O_5Cl_5$, crystallises in needles melting at 128° .

α-Metaquinolinediacrylic acid, $C_9N_5(CH\cdot CH\cdot COOH)_2$, is obtained when the hydrochloride of the above trichlorinated derivative (9 grams) is heated on a water-bath with a solution of potassium carbonate (10 grams) in water (110 grains) for three hours, the product being filtered and fractionally precipitated with sodium carbonate. It melts at above 300° , is insoluble in water, sparingly soluble in hot alcohol.

N. H. M.

2' : 3'-Dimethylquinoline. By G. ROHDE (*Ber.*, **22**, 267—271). — $2' : 3'$ -Dimethylquinoline (*Abstr.*, 1887, 974) crystallises in the rhombic system and boils at 261° (uncorr.) under 729 mm. pressure (not 255 — 260°). The platinochloride blackens at 230° ; the picrate melts at 225° . The *chromate*, $(C_{11}H_{11}N)_2\cdot H_2Cr_2O_7$, crystallises in orange-coloured spear-heads which become brown at 150° and decompose completely at 185° ; the *hydrochloride*, $C_{11}H_{11}N\cdot HCl + 2H_2O$, forms concentrically grouped needles of a vitreous lustre, very readily soluble in water and alcohol; the *sulphate*, $C_{11}H_{11}N\cdot H_2SO_4 + H_2O$, crystallises in slender, concentrically grouped needles, extremely soluble in water, moderately soluble in alcohol, it melts at 235° ; the *nitrate* crystallises in prisms very readily soluble in water and alcohol. The *methiodide*, $C_{11}H_{11}N\cdot MeI + \frac{1}{2}H_2O$, crystallises from alcohol in groups of bright yellow, bent needles, melting at 218° . When $2' : 3'$ -dimethylquinoline dissolved in sulphuric acid is treated with sufficient chromic acid to oxidise one methyl-group, an acid is obtained which is identical with Friedländer and Göhring's *α-methylquinoline-β-carboxylic acid* (*Abstr.*, 1883, 1149).

The base obtained by the condensation of quinaldine with benzil (*loc. cit.*) has the formula $C_9NH_4Me\cdot CH\cdot CPh\cdot COPh$; it melts at 176° (not $173'$) and has a striking resemblance to acridine; the solutions of the salts show an intense green fluorescence. When heated for some hours at 180° , it is converted into a *polymeride*, which forms yellow crystals melting at 240° ; this is a very feeble base and is extremely insoluble in the usual solvents. All attempts to effect a condensation between the methyl-group of the dimethylquinoline and the carbonyl-group of the benzil were unsuccessful.

N. H. M.

Action of Acetone on Ortho- and Para-amidophenol. By C. ENGLER and A. BAUER (*Ber.*, **22**, 209—215).—*Orthohydroxy- α - γ -dimethylquinoline*, $C_9NH_4Me_2OH$ [= 2' : 4' : 1], is formed together with methane when dry orthamidophenol hydrochloride (1 mol.) is heated with acetone (3 mols.) for 48 hours at 170—180°. The crude product is extracted with hydrochloric acid and acetone, and the mixed solutions distilled with steam to remove acetone and condensation products. The solution is then concentrated, partially neutralised with soda, filtered from resinous products, and the basic substances precipitated with sodium carbonate, excess being carefully avoided. The precipitate is washed with hot water, dried, dissolved in absolute alcohol, and concentrated sulphuric acid added to the solution; the precipitated crystalline sulphate, a further quantity of which can be obtained by adding ether to the alcoholic solution, is washed with alcohol and ether, dissolved in water, and, after evaporating the alcohol, potassium dichromate is added to the cold solution. The crystalline dichromate is decomposed with dilute sodium carbonate, and the base, which is precipitated in a flocculent condition, is crystallised from ether. Hydroxydimethylquinoline crystallises in prisms, melts at 65°, and boils at 281° (uncorr.). It is readily soluble in ether, benzene, alcohol, acetone, and chloroform, but only sparingly in light petroleum, and almost insoluble in water. It is slightly volatile with steam, sublimes when heated, and has an intensely bitter taste and the peculiar odour of quinoline-derivatives. It dissolves in soda, the solution giving orange or red precipitates with diazochlorides; the colouring matter obtained with β -naphthylamine dyes silk yellowish-brown. In a neutral solution of the base, ferric chloride gives a green coloration, which disappears slowly on heating but immediately on adding acids. A yellow, crystalline substance is precipitated when water is added to a hot alcoholic solution which has been previously mixed with bromine. The sulphate, $C_{11}H_{11}NO_2H_2SO_4$, crystallises in slender needles and is soluble in water but only sparingly in hot absolute alcohol. The hydrochloride crystallises from hot concentrated hydrochloric acid or alcohol in yellowish, anhydrous plates, and is readily soluble in water but insoluble in ether; it sublimes without melting. The platinochloride, $(C_{11}H_{11}NO)_2H_2PtCl_6 + 2H_2O$, crystallises in bright-yellow needles and loses its water at 110°. The dichromate, $(C_{11}H_{11}NO)_2H_2Cr_2O_7$, crystallises in citron-yellow, microscopic needles containing water and is sparingly soluble in cold water. The picrate, $C_{11}H_{11}NO_2C_6H_3N_3O_7$, crystallises in plates or prisms, turns brown at 200°, melts at 207°, and is completely decomposed at 210°; it is almost insoluble in water, and only sparingly in hot alcohol, benzene, chloroform, and acetone. The yield of hydroxydimethylquinoline, by the method described above, is not more than 20 per cent. of the amidophenol employed. Better results are obtained when a mixture of acetone (1 mol.) and paraldehyde (1 mol.) is saturated with hydrogen chloride, kept for two to three days, and then heated at 100° for six hours with a concentrated hydrochloric acid solution of amidophenol ($\frac{2}{3}$ mol.). (Compare Beyer, *Abstr.*, 1885, 672 and 1246.) The product is purified as described above.

Several sulphonic acids are formed when α - γ -dimethylquinoline is

treated with fuming sulphuric acid; when the more sparingly soluble portion of the product is melted with soda, a mixture of substances is obtained, from which, in one experiment, a crystalline product melting above 70° was isolated. (Compare Beyer, Abstr., 1886, 629.) This substance is probably an orthohydroxyquinoline, but it is not identical with the orthohydroxy-derivative described above.

Parahydroxy- α - γ -dimethylquinoline is obtained, together with methane, when paramidophenol is heated with acetone for several days at 170—180°. The product can be purified as described in the case of the ortho-derivative or by means of the crystalline hydrochloride. The yield is only about 12 per cent. of the theoretical quantity, but better results are obtained by using a mixture of acetone and acetaldehyde as described above. It crystallises from alcohol in prisms or small plates, melts at 214° (uncorr.), and boils above 360° with partial decomposition. It is readily soluble in alcohol and acetone, but only sparingly in ether, and almost insoluble in benzene and hot water; it is readily soluble in acids and in alkalis but not in ammonia; the alkaline solutions are precipitated by carbonic anhydride and give coloured precipitates with diazochlorides. The acid alcoholic solution of the colouring matter obtained with β -naphthylamine dyes silk red. Ferric chloride produces a brown coloration in an alcoholic solution of the base, and with bromine an amorphous bromide is obtained. The hydrochloride, $C_{11}H_{11}NO \cdot HCl$, crystallises from alcohol in yellowish needles, is readily soluble in water and sublimes when heated. The platinochloride, $(C_{11}H_{11}NO)_2 \cdot H_2PtCl_6 + 2H_2O$, crystallises in yellow needles and is sparingly soluble in water and alcohol; it loses its water at 110° and decomposes when heated more strongly. The sulphate, $(C_{11}H_{11}NO)_2 \cdot H_2SO_4$, crystallises from water in colourless needles and is almost insoluble in hot alcohol. The picrate, $C_{11}H_{11}NO \cdot C_6H_3N_3O_7$, crystallises in large prisms, melts at 225° with decomposition, is very sparingly soluble in most ordinary solvents and almost insoluble in water. The dichromate is not easily obtained in crystals.

F. S. K.

β -Naphthaquinaldine. By F. SEITZ (*Ber.*, **22**, 254—266).— β -Naphthaquinaldine crystallises in rhombic plates, melts at 82°, and distils with difficulty with steam. The hydrochloride, with 2 mols H_2O , crystallises in slender, lustrous needles, sparingly soluble in cold water; the nitrate, with 1 mol. H_2O , forms slender needles which become pale rose-coloured when exposed to air; the sulphate, $C_{14}H_{11}N \cdot H_2SO_4 + 2H_2O$ crystallises in very slender needles, very readily soluble in hot water; the picrate forms microscopic needles, melts at 220—221° with decomposition, dissolves very sparingly in boiling water, readily in glacial acetic acid; the methiodide crystallises in straw-coloured needles, melts at 241—247° with decomposition, and dissolves readily in boiling water, sparingly in alcohol.

By the action of a mixture of fuming nitric and strong sulphuric acids on β -naphthaquinaldine, four nitro-compounds are formed, two of which are soluble and two insoluble in alcohol.

Dinitro- β -naphthalquinaldine, $C_{14}H_9N(NO_2)_2$, is obtained by crystallising that portion of the product which is soluble in alcohol from

glacial acetic acid, and melts at 226—227°. The other soluble compound melts at 250°; it was not further examined.

A second *dinitro-derivative* crystallising in long, yellowish needles, melting at 230°, and the *tetrานitro-compound*, $C_{14}H_8N(NO_2)_4$, which crystallises in yellowish-brown, lustrous plates melting at 277°, are insoluble in alcohol, and are separated by crystallisation from glacial acetic acid.

A third *dinitro-derivative* is formed when dry β -naphthaquininaldine nitrate is added to strong sulphuric acid. It crystallises in colourless needles, melts at 205—212°, dissolves readily in benzene and is insoluble in light petroleum.

Carboxyphenylpicolinecarboxylic acid, $COOH \cdot C_6H_4 \cdot C_5NHMe \cdot COOH$ [$C_5N : COOH = 1 : 2$; $C_6H_4 : Me : COOH = 3 : 6 : 2$], is obtained by treating β -naphthaquininaldine (10 grams) suspended in water ($1\frac{1}{2}$ litre) with sulphuric acid (10 grams), and adding to the cold solution potassium permanganate (30 grams), dissolved in water (500 c.c.). Orthophthalic and naphthaquinolinecarboxylic acids are also formed. It crystallises in needles (anhydrous) or in prisms (with 1 mol. H_2O), melts at 201° with violent evolution of carbonic anhydride, and is very sparingly soluble in cold water. *Sodium carboxyphenylpicolinecarboxylate*, $C_{14}H_8Na_2NO_4 + 2H_2O$, forms slender needles, sparingly soluble in boiling alcohol, readily in water; the *potassium salt* is more readily soluble; the *zinc salt* (with $1\frac{1}{2}$ mol. H_2O) is almost insoluble in water; the *copper salt* (with $1\frac{1}{2}$ mol. H_2O) crystallises in microscopic, bluish-green plates. The formation of the acid from β -naphthaquininaldine is analogous to that of β -phenylpyridinedicarboxylic acid from β -naphthaquinoline (Skraup and Cobenzl, Abstr., 1883, 1011). Assuming the acid to have the constitution given above, β -naphthaquininaldine would have the constitution $C_{10}H_8 \begin{array}{c} N=CMe \\ | \\ CH:CH \end{array} [CH:N = 1:2]$.

β -Naphthaquinolinecarboxylic acid, $C_{10}H_6 \begin{array}{c} N=COOH \\ | \\ CH:CH \end{array} [CH:N = 1:2]$, is obtained as sodium salt by extracting the manganese dioxide formed in the above oxidation experiment with dilute aqueous soda. The acid crystallises from alcohol in very slender, matted needles, which melt with decomposition at 187°; when heated on platinum foil, it evolves irritating vapours. It is almost insoluble in water, sparingly soluble in alcohol and boiling glacial acetic acid. The *sodium salt*, $C_{14}H_8NaNO_2 + 2\frac{1}{2}H_2O$, crystallises in very lustrous scales or needles, sparingly soluble in cold water. The *barium salt* (with 4 mols. H_2O) separates as a flaky precipitate, which becomes crystalline by prolonged boiling; the *copper salt* (with $1\frac{1}{2}$ mol. H_2O) is insoluble in water. The *hydrochloride*, $C_{14}H_8NO_2 \cdot HCl$, crystallises in yellow, hair-like needles, and is readily decomposed by water and alcohol; the *platinochloride*, $(C_{14}H_8NO_2)_2 \cdot H_2PtCl_6 + 2H_2O$, forms yellow, matted needles, very sparingly soluble in hot dilute hydrochloric acid; water decomposes it readily. The production of the carboxylic acid in the oxidation of β -naphthaquininaldine corresponds with the formation of quinaldic acid from quinaldine (Döbner and v. Miller, Abstr., 1884, 185).

When β -naphthaquinolinecarboxylic acid is heated at 190—200°, β -naphthaquinoline is formed. The platinochloride crystallises with 2 mols. H₂O (not 1 mol. Compare Skraup and Cobenzl; *loc. cit.*, and Lellmann and Schmidt, *Ber.*, **20**, 3156).

Trichlorhydroxyethylidene- β -naphthaquininaldine, C₁₆H₁₀NCl₃ + H₂O, is prepared by v. Miller and Spady's method (*Abstr.*, 1886, 264), by the action of chloral on β -naphthaquininaldine (equal mols.). The reaction takes place with rise of temperature. The whole is then heated for five hours on a water-bath. It crystallises in rhombs, melts at 185°, is insoluble in water, almost insoluble in ether; the best solvent is boiling benzene.

N. H. M.

Oxidation of β -Naphthaquinolinesulphonic Acid. By C. IMMERHEISER (*Ber.*, **22**, 402—411).—The β -naphthaquinolinesulphonic acid was prepared by Skraup's method from pure β -naphthylamine- α -sulphonic acid (*Abstr.*, 1885, 561).

β -Phenylpyridinesulphodicarboxylic acid,



[C₅N : COOH : SO₃H = 1 : 2 : 6; C₆ : COOH = 3 : 2], is formed by oxidising a 1 per cent. solution of potassium β -naphthaquinolinesulphonate with the calculated quantity of potassium permanganate in $\frac{1}{2}$ per cent. solution. It crystallises from water in transparent, colourless, hard crystals, has an unpleasant, sour taste, and is readily soluble in hot, sparingly soluble in cold water, and almost insoluble in alcohol, ether, benzene, &c. The potassium, barium, silver, and lead salts were prepared, but could not be obtained in crystalline form.

β -Pyridinephenyleneketonesulphonic acid, SO₃H·C₆H₃<^{CO —}_{C₅NH₃}>, is prepared by oxidising a solution of potassium β -naphthaquinoline-sulphonate in 50 times its weight of 20 per cent. aqueous potash with the calculated quantity of potassium permanganate in $\frac{1}{2}$ per cent. solution. It crystallises from water in scales with 1 mol. H₂O, is readily soluble in hot, and sparingly soluble in cold water, and is almost insoluble in alcohol and ether. The potassium salt with 1 mol. H₂O crystallises in long, yellow needles, or in yellow, transparent, monoclinic prisms; the barium salt with 2 mols. H₂O crystallises in tufts of yellow needles; the silver salt with 1 mol. H₂O crystallises in slender, yellow, hair-like forms; the lead salt with 3 mols. H₂O crystallises in lustrous, yellow needles. The phenylhydrazone,



crystallises from acetic acid in small, red needles, decomposes at 295° without melting, and is insoluble in almost all solvents; the oxime, C₁₂H₇NSO₃NOH, forms yellowish, crystalline flocks, decomposes at 290° without melting, and is sparingly soluble in cold water.

W. P. W.

Condensation of Paranitrobenzaldehyde with Quinaldine. By W. BULACH (*Ber.*, **22**, 285—290).—When a dry ethereal solution

of paranitrobenzylidenequinaldine (Abstr., 1887, 976) is treated with bromine, the compound $C_{17}H_{12}N_2O_2Br_2$ is formed; this crystallises from alcohol in lustrous, gold-coloured, matted needles which become brown at 230° and melt at 276° .

Amidobenzylidenequinaldine, $C_{17}H_{14}N_2$, prepared by reducing the nitro-compound with tin and hydrochloric acid, crystallises from weak alcohol in long, gold-coloured needles melting at 172 — 173° . It is also formed when the base $C_{17}H_{14}N_2O_2$ (*loc. cit.*) is reduced with tin and hydrochloric acid. The *acetyl-derivative*, $C_{19}H_{16}N_2O$, prepared by heating the amido-base with acetic anhydride in a reflux apparatus, crystallises from alcohol in large, tabular, monoclinic crystals which melt at 194° and dissolve readily in alcohol and light petroleum.

Parahydroxybenzylidenequinaldine, $C_9NH_6\cdot CH\cdot CH\cdot C_6H_4\cdot OH$, is obtained by diazotising the amido-base and boiling the product with water; it forms brown crystals melting at 255° with decomposition. With β -naphtholdisulphonic acid, the *diazo-compound* yields a dye which colours silk copper-red.

Diquinolylethylene (ethylenediquinoline), $C_2H_2(C_9NH_6)_2$, [$CH = 2'$; $CH = 3$], is prepared by heating paramidobenzylidenequinaldine (20 grams) with glycerol (70 grams), sulphuric acid (30 grams), and orthonitrophenol (14 grams) in a reflux apparatus; the heating is discontinued as soon as gas is evolved, as the reaction becomes very violent; it is then heated for one or two hours. The product is diluted with water, saturated with potash and boiled; the resin is dissolved in benzene and boiled with animal charcoal. It crystallises in groups of needles, melts at 146 — 147° , is sparingly soluble in alcohol and benzene, readily in glacial acetic acid. The *hydriodide* crystallises in brick-red prisms; the *sulphate* in needles. The *dibromide*, $C_2H_2Br_2(C_9NH_6)_2$, crystallises in needles, becomes brown at 280° , and does not melt at 300° ; it is readily soluble in hot alcohol. When ethylenediquinoline is heated with hydriodic acid and amorphous phosphorus at 150° , the compound $C_{20}H_{16}N_2$ is formed; this crystallises in lustrous prisms melting at $106\cdot 5^\circ$.

Ethylenediquinolinequinaldine, $C_9NH_6\cdot CH\cdot CH\cdot C_9NH_6Me$ [$CH = 2'$; $CH : Me = 3 : 2'$], is prepared by adding a slight excess of paraaldehyde to paramidobenzylidenequinaldine (20 grams) and hydrochloric acid (70 grams) heated at 150° ; the reaction soon becomes violent. It is heated for five hours, diluted with water, filtered, and treated with aqueous soda; the resin is dried and repeatedly extracted with alcohol. It is purified by means of the picrate, and the free base crystallised from petroleum (b. p. 100 — 130°). It crystallises in lustrous, reddish plates, melts at $157\cdot 5^\circ$, and dissolves very easily in alcohol, ether, and chloroform, less readily in benzene. The salts are mostly sparingly soluble, gelatinous substances. N. H. M.

The Sulphur of Proteids. By A. KRÜGER (*Pflüger's Archiv*, **43**, 244—264).—Mulder (*Annalen*, **61**, 121) was the earliest to investigate the condition of the sulphur contained in proteids, and the fruit of his work was his “Protein Theory.” He observed that the sulphur is readily separated from the remainder of the proteid, and the sulphur-

free radicle protein was supposed to be combined with different amounts of sulphur, so producing different proteids.

Liebig and others, who showed the inaccuracy of Mulder's work and conclusions, pointed out that warming a proteid with potash not only removed sulphur but ammonia; and even though the residue gives no further colour with lead salts, it still retains some sulphur.

It is thus possible to speak of two forms of sulphur in proteid: that which is loosely and that which is firmly combined; and Danilewsky (*Zeit. physiol. Chem.*, 7, 440) further differentiated the loosely combined sulphur into four varieties according as to whether it was removable with a $\frac{1}{2}$, 2, 5, or 10 per cent. solution respectively of sodium hydroxide. The slowness of the alkali in removing all removable sulphur is analogous to what occurs in cystin (Goldmann and Baumann, *Abstr.*, 1888, 519). The total sulphur (S) and the loosely bound sulphur (L) were estimated in white of egg and fibrin. The results were as follows:—

	S.	L.	S : L.
White of egg	1·66	0·44	4 : 1·06
Fibrin	1·20	0·38	3 : 0·95

There appear to be certain native proteids which give no blackening with lead and alkali: these contain about 0·8 per cent. or less of sulphur, and seemingly all is in the firmly combined condition. Legumin (sulphur 0·4 per cent., Ritthausen), and casein (sulphur 0·8 per cent., Hainmarsten) are examples of these.

The proteid which had been treated with potassium hydroxide for the removal of the loosely combined sulphur was then examined: it was found to be an amorphous peptone-like substance which by saturation with ammonium sulphate was separated into two substances: one precipitable by the salt gave the reactions of an albumose, the other left in solution was a peptone (in Kühne's sense of the word). The percentage composition of these substances was as follows:—

	C.	H.	N.	S.	O.	Ash.
Egg albumin ...	52·98	7·09	15·70	1·6—1·8	22·41	—
Propeptone	55·76	6·93	14·46	1·28	21·57	(0·31)
Peptone	48·06	6·73	11·70	0·47	33·04	(2·88)
	C.	H.	N.	S.	O.	Ash.
Fibrin	52·50	6·95	16·57	1·22	22·76	—
Propeptone	55·26	6·75	15·46	0·79	21·74	(0·21)
Peptone	52·58	6·60	14·43	0·47	25·92	(0·85)

In the propeptone in both cases there is a fall in the percentage of nitrogen and sulphur, which is still more marked in the peptone. The sulphur in the propeptone is approximately equal to that in the mother substance which was in the firmly combined condition; and the composition of the two propeptones is nearly the same: thus a substance appears to be formed from different proteids which has the same composition and which contains all the firmly combined sulphur. The composition of the two peptones is, however, very different,

and they are probably produced from the propeptones by further hydrating action; the loss of sulphur is probably due to the formation of another sulphur-containing organic compound that escaped detection; sulphates are not formed.

The concluding portion of the paper is devoted to a theoretical consideration of the probable way in which the sulphur is actually present in the proteid. Tables are given of the chief sulphur-containing substances known, and as to whether or not they are blackened by lead and alkali. The number of those that are not blackened is much smaller than those that are. The firmly bound sulphur is compared to that in mercaptan, thioether, and sulphinic compounds, and the loosely combined sulphur to that in thio-acids, cystin, and compounds in which either the group :C:S or :C·S·S·C: is present.

W. D. H.

Myosin. By R. H. CHITTENDEN and G. W. CUMMINS (*Studies from Lab. Physiol. Chem., Yale Univ.*, **3**, 115—138).—Ammonium chloride solutions were found the most efficacious in extracting myosin from flesh. The salt was removed by dialysis, and the myosin obtained in a jelly-like condition. This appears to be, as pointed out by Halliburton, a genuine recoagulation rather than a simple precipitation (Abstr., 1887, 984). A large number of preparations were made from different animals, and the results of elementary analysis show a very close agreement. With regard to the temperature of heat-coagulation of this proteid, the results differ slightly in different animals, and also differ, to a slight extent, from those obtained by Halliburton: this is, no doubt, to be explained by the character of the saline solution used, Halliburton having used a magnesium or sodium sulphate solution. The general results justify the assumption that myosin as it occurs throughout the animal kingdom is a single chemical compound formed, as suggested by Halliburton, by the interaction of one or more myosinogens and a ferment.

W. D. H.

Caseoses, Casein Dyspeptone, and Casein-Peptone. By R. H. CHITTENDEN and others (*Studies from Lab. Physiol. Chem., Yale Univ.*, **8**, 66—105).—This paper gives fuller and further details than were before published (Abstr., 1888, 76) of the properties and elementary composition of the peptone formed from casein, of the intermediate products (caseoses), and of an insoluble bye-product formed during the earlier stages of the digestive process (casein-dyspeptone).

W. D. H.

Reduced Hæmoglobin. By L. HERMANN (*Pflüger's Archiv*, **43**, 235).—The spectrum of reduced hæmoglobin is generally described as showing only one absorption-band. But if this band be examined carefully (whether the reduction has been produced by Stokes' reagent, ammonium sulphide, or a stream of hydrogen), it will be seen to consist of two: a wide dominant band, and, separated from it by a less brightly illuminated narrow space, a narrow band almost coincident with the D line.

W. D. H.

Reducing Action of Indigo-white on Oxyhæmoglobin. By E. LAMBLING (*Compt. rend. Soc. Biol.*, [2], **5**, 394—396).—Schützen-

berger (*Bull. Soc. Chim.*, 1873, 150) used indigo-white to remove the oxygen from oxyhaemoglobin, and obtained by that method a result higher by 4—5 c.c. of oxygen per 100 c.c. of blood than by the method of extracting the gas by the mercurial air-pump. This difference increases with the length of time employed in the extraction of the gas by the air-pump, and it is easily explicable on the theory that the loss of the oxygen is due to its combination with the still living tissue elements in the blood, especially as the temperature at which the operation is performed is 40—50°, and, perhaps, also to the formation of methaemoglobin. Hoppe-Seyler (*Physiol. Chem.*, 451), however, considers that the reduction of oxyhaemoglobin does not stop at haemoglobin, but goes on to haemochromogen when indigo-white is employed: the experiments on which this opinion is based are, however, not stated. In the present research, spectroscopic observations were made on the effect of the prolonged action of a stream of hydrogen and of indigo-white respectively on solutions of oxyhaemoglobin obtained by diluting blood with water. In neither case did the bands of haemochromogen appear, but the reduction always stopped when haemoglobin was formed.

W. D. H.

Pigments of the Urine. By C. A. MACMUNN (*J. Physiol.*, **10**, 71—121).—A full account, with plates of absorption-spectra and measurement of bands, of experiments of which an account has already appeared (*Abstr.*, 1888, 614).

W. D. H.