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Organic Chemistry.

Derivatives of Acetylene. By A. SABANEJEFF (Annalen der Chemie, clxxviii, 109—128).

THE best method for preparing acetylene is that devised by Miasnikoff and Sawitsh. Ethene dibromide is added drop by drop to alcoholic potash, which is heated on a water-bath. The gases which are evolved pass through a reversed condenser into another flask containing hot alcoholic potash, and from these again through another reversed condenser. After being washed with water, the acetylene is absorbed by passing it through several bottles containing a solution of cuprous chloride in ammonia. The precipitate thus obtained is then decom-

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posed by hydrochloric acid, and the gas is washed with water and caustic potash

When acetylene is passed into bromine which is covered with water, the tetrabromide is formed, which can be distilled with steam. It is a heavy, colourless, aromatic oil, having at 21·5° the sp. gr. 2·848. Acetylene tetrabromide dissolves in alcohol, ether, chloroform, carbon sulphide, acetic acid, and aniline. On heating it to 190°, it is resolved into hydrobromic acid and tribromethene, which is also produced by the action of alcoholic ammonia and by heating the tetrabromide with potassium acetate and acetic acid. It is a liquid boiling at 162°—163°, fuming in the air, being decomposed by moisture. A solid polymeride of tribromethene is formed, but in small quantity only in the preparation of the tetrabromide. It crystallises in colourless plates, which are sparingly soluble in alcohol and in the tetrabromide, more freely in ether and chloroform. It does not volatilise with steam, melts at 175°, and decomposes at a higher temperature.

When the tetrabromide is heated with alcoholic potash in varying proportions, only acetylene and bromacetylene are formed, while by the action of silver acetate, potassium cyanide, and silver cyanide, no definite products could be obtained. On heating the tetrabromide with alcoholic potassium or ammonium sulphide, it is converted into a strong-smelling sulphur-compound, crystallising in transparent plates. When an alcoholic solution of four molecules of potash is gradually added to a mixture of one molecule of the tetrabromide and two of aniline, the chief product consists of acetylenetriphenyltriamine:—

$$\begin{array}{l} HCBr_2 \\ | \\ HCBr_2 \end{array} + 3(H_2NC_6H_5) + 4HKO = \begin{array}{l} HC{-}HNC_6H_5 \\ | \quad\ \ NC_6H_5 \\ HC{-}HNC_6H_5 \end{array} + 4KBr + 4H_2O.$$

This triamine forms soft, silky needles, melting at 190°, and decomposing when more strongly heated. It dissolves sparingly in cold alcohol, more freely in hot alcohol, and in aniline, carbon sulphide, ether, and chloroform. The hydrochloride $C_{20}H_{19}N_3HCl$ is readily soluble in water, but insoluble in hydrochloric acid. This salt, as well as others, decompose slowly when their aqueous solution is left standing, and quickly when heated, aniline being formed. $(C_{20}H_{19}N_3ClH)_2 + PtCl_4$, and $(C_{20}H_{19}N_3HCl)_4 + 3HgCl_2$, are insoluble amorphous precipitates. The bye-products obtained in preparing the triamine consist of acetylene, bromacetylene, glycollic acid, and a compound having the smell of the isonitrils.

When sodium is added to a solution of the tetrabromide in ether, no dibromide is formed, but tribromethene and bromacetylene; while by heating the solution with silver-dust or mercury to 180° some dibromide is formed. The latter is also produced, together with a large quantity of tetrabromide, by passing acetylene into a cold solution of 1 pt. of bromine in 5 pts. of chloroform. Pure acetylene dibromide can only be obtained by saturating absolute alcohol with acetylene, of which it dissolves about six volumes, and then adding the calculated quantity of bromine. By repeating the same operation several times,

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and then adding water, the dibromide is precipitated, and separated from lower-boiling bye-products by heating the liquid in a salt-bath to 115°. Acetylene dibromide is a colourless, mobile liquid, which distils with decomposition.

Acetylene di-iodide is best prepared by passing acetylene through a number of flasks containing iodine, which is moistened with absolute alcohol, and keeping the flask in motion all the time. It is soluble in alcohol, ether, chloroform, carbon sulphide, methyl iodide, and aniline. It crystallises in long colourless flexible needles, having a strong and characteristic odour. Its sp. gr. at 21° is 3·303. It melts at 73°, solidifies again at 70°; volatilises at the common temperature, and sublimes without decomposition. It is a very stable body, acquiring a brown colour only when exposed to sunshine. Hot aqueous potash acts but little on it, but alcoholic potash decomposes it, a gas smelling like bromacetylene being given off, which is absorbed by ammoniacal cuprous chloride, with formation of copper-acetylene.

The mother-liquors of the solid iodide contain a non-volatile liquid isomeride, which is easily decomposed by light and by heat. It solidifies a few degrees below 0°, and has at 21° the specific gravity 2·942. Another product which was observed was a very volatile iodide, possessing an agreeable smell, which was formed in very small quantity only. C. S.

Action of Fuming Nitric Acid on Dichlorallylene.

By A. PINNER (Deut. Chem. Ges. Ber., viii, 959—963).

WHEN dichlorallylene is slowly dropped into well-cooled nitric acid, a vigorous action takes place, a clear solution being formed, from which a greenish oil deposits on dilution with water: a portion of the dichlorallylene is wholly destroyed, much hydrochloric acid being found in the liquid. The oily mass distils between 120° and 200°, with partial decomposition; after treatment with tin and strong hydrochloric acid, however, it does not decompose on heating; by fractional distillation the greater part is found to pass over between 130° and 140°, and at 190° to 195°; the more volatile portion is *trichloropropylene*, $C_3H_3Cl_3$, boiling at 120°, after treatment with caustic potash. The higher-boiling substance solidifies on cooling to a camphor-like mass, possessing an odour like that of chloropicrin; it is very soluble in alcohol, and on analysis gives numbers agreeing with the formulæ $C_3H_4Cl_3NO_2$, or $C_3H_2Cl_3NO_2$, better with the latter, whence apparently the body is *trichloronitropropylene:* on treatment with caustic soda, it furnishes common salt and a body having the composition of *dichloronitroallylene*, formed from trichloronitropropylene by loss of the elements of hydrochloric acid, and boiling at 162°. As this dichloronitroallylene appears to be formed by the action of soda on the crude greenish oil first obtained (before treatment with tin and hydrochloric acid), it seems probable that the first action of nitric acid consists in adding on the elements of nitric peroxide to dichlorallylene, forming dinitro-dichloropropylene, thus:—

$$CCl_2\overset{CH}{\diagup\!\!\!\!\diagdown}CH + 2NO_2 = CCl_2\overset{CH(NO_2)}{\diagup\!\!\!\!\diagdown}CH(NO_2),$$

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and that the product becomes converted into trichloronitropropylene by the action of the chlorine set free by the total decomposition of a part of the dichlorallylene used.

The reducing action of the tin converts a portion of the trichloronitropropylene into *trichloramidopropylene*, $C_3H_2Cl_3(NH_2)$; this is an oily base, slightly soluble in water, and forming a hydrochloride excessively soluble in water, and readily soluble in alcohol; at 100° this salt decomposes into its components; it forms a platinum salt, readily soluble in water and alcohol, crystallising in yellow prisms.

C. R. A. W.

Chlorobromated Ethene Chloride. By E. Bourgoin (Bull. Soc. Chim. [2], xxiv, 114).

By the action of chlorine on acetylene perbromide the author obtained a crystalline body which he proposes to call chlorobromated ethene chloride. It is isomeric with perchlorated ethylene bromide, but possesses different properties.

H. J. H.

Ethidene Oxychloride.

By A. Lieben (Annalen der Chemie, clxxviii, 43—48).

The author attributes the failure of Geuther and Cartmell in attempting to prepare ethidene oxychloride to the fact that they allowed the crude product to remain for a long time in contact with calcium chloride and lead oxide before purifying it by distillation.

The author prefers to just dry the product with calcium chloride before distillation, and not to distil from the calcium chloride.

In order to ascertain if Kessel's difficulties in preparing ethidene oxychloride were due to a faulty description in the original paper, the author caused Roth to prepare some of the substance, and very good results were obtained. Perhaps Kessel did not thoroughly separate the two layers of liquid.

T. B.

Direct Union of Propene with the Hydracids.

By M. Berthelot (Bull. Soc. Chim. [2], xxiv, 106).

If a flask filled with pure and dry propene be placed over a flask of equal size filled with hydriodic acid gas, and communication be established, small drops of isopropylhydriodic ether will soon be observed to form on the sides of the flask of propylene, and collect at the bottom. In about half an hour the quantity of ether formed will be found to correspond with a nearly complete combination of the two gases.

H. J. H.

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Two Isomeric Butenes obtained by the action of Zinc Chloride on Butylic Alcohol from Fermentation. By M. NEVOLE (Bull. Soc. Chim. [2], xxiv, 122).

THE author believes that by the action of zinc chloride on butylic alcohol two isomeric butenes are formed, one giving with bromine a dibromide boiling at 158°—159°, and the other giving a dibromide boiling at 147°—148°.

H. J. H.

Synthesis of Alcohols by means of Chlorinated Ethers. By A. LIEBEN (Annalen der Chemie, clxxviii, 1—42).

THE preparation of diethylic ethyl oxide, $(C_2H_5)_2C_2H_3.C_2H_5O$, presents many practical difficulties, and the author now prepares it by digesting chlorethylic ethyl oxide, $C_2H_5.O.C_2H_3(C_2H_5.Cl)$, with rather less than the theoretical quantity of zinc-ethyl in a copper vessel in which a pressure of about one extra atmosphere is maintained. Among the products were alcohol, hexene, zinc ethylate, and ethane. The reactions may be represented as follows:—

$$(1.)\ 2C_2H_3\left\{\begin{matrix}Cl\\C_2H_5\\OC_2H_5\end{matrix}\right. + Zn\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right. = ZnCl_2 + 2C_2H_3\left\{\begin{matrix}C_2H_5\\C_2H_5\\OC_2H_5\end{matrix}\right..$$

$$(2.)\ 2C_2H_3\left\{\begin{matrix}CH_5\\CH_5\\OC_2H_5\end{matrix}\right. = 2C_6H_{12} + 2C_2H_5HO.$$

$$(3.)\ 2C_2H_5OH + Zn(C_2H_5)_2 = Zn(OC_2H_5)_2 + 2C_2H_6.$$

Besides the above mentioned substances, two viscous products were obtained, one of which boiled at about 200°, while the other boiled above 300°. The former of these gave numbers corresponding with the formula $C_{12}H_{24}O_2$, and is probably formed by the elimination of 2HCl from 2 molecules of chlorethylic ethyl oxide; while the latter, which contained $C_{22}H_{36}O$ was perhaps derived from 5 molecules of chlorethylic ethyl oxide, with elimination of 5HCl and $4C_2H_6O$.

The crude diethylic ethyl oxide obtained as above described boiled at 125°—150°, and contained about 6 per cent. of chlorine, this being clearly due to the presence of unaltered chlorethylic ethyl oxide; and prolonged digestion with zinc-ethyl, or with sodium and ethyl iodide, did not entirely convert this into diethylic ethyl oxide, while its separation by fractional distillation was found to be impracticable. The last traces of chlorethylic ethyl oxide were, however, removed by the long continued action of metallic sodium at 140°, and fractionation now yielded pure diethylic ethyl oxide. It boils at 131·1°, and its specific gravity is 0·7865 at 0°, 0·7702 at 20°, and 0·7574 at 40°. The sodium employed in the above process becomes converted into a yellowish product, which contains sodium ethylate, and the sodium salt of some organic acid or acids. Details of slightly modified processes for preparing diethylic ethyl oxide are given, and it can be

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obtained by the action of zinc on a mixture of chlorethyle thyl oxide and ethyl iodide.

The conversion of diethylic ethyl oxide into ethyl iodide and hexyl iodide by hydriodic acid is most conveniently performed by means of an acid having a specific gravity of 1·95, the mixture being heated to 120°—140° for 20—30 hours. When the hexyl iodide thus obtained is treated with silver acetate and glacial acetic acid, a hexylene boiling at 67°—68° was obtained, together with hexyl acetate boiling at 154°—157°. The hexyl alcohol obtained by the saponification of this acetate forms an aromatic oil, boiling at 138°, and its oxidation by dilute chromic acid mixture leads to the formation of butyric acid, acetic acid, and perhaps a trace of propionic acid, or rather to the ethers of these acids.

The hexene referred to as being formed by the action of silver acetate on hexyl iodide, is reconverted into an iodide by the action of strong hydriodic acid, but the alcohol obtained from this iodide was not thoroughly examined. Its oxidation, or the oxidation of the hexylene, yielded butyric acid and acetic acid.

The above results, more especially the reaction of diethylic ethyl oxide with hydriodic acid, and the subsequent oxidation of the hexene compounds, indicate that diethylic ethyl oxide is a hexyl ether, having the constitution—

$$\begin{array}{l} CH_3 \\ CH_2 \\ CH_2 \\ CH\,.\,OC_2H_5 \\ CH \\ CH_3 \end{array} \quad \text{or} \quad \begin{array}{l} CH_3 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2.OC_2H_5 \end{array} \quad ; \text{ and the formula, } \begin{array}{l} CH_3 \\ CCl\,.\,OC_2H_5, \\ CH_2 \\ CH_3 \end{array}$$

appears, on the whole, the most probable one for chlorethylic ethyl oxide; but this requires further consideration.

T. B.

Reducing action of Hydriodic Acid at Low Temperatures on Ethers and Mixed Ethers. By R. D. SILVA (Compt. rend., lxxxi, 323—325).

THE experiments were conducted by passing dry hydriodic acid gas into the anhydrous liquid, the latter being kept between 0° and 4°.

Alcohols.—Methyl alcohol is entirely converted into iodide. Alcohols containing a larger number of atoms of carbon in their molecule form very little iodide.

Ethers.—Methyl oxide is converted into iodide without any formation of methyl alcohol, but ethyl oxide yields iodide and alcohol at the same time. The quantity of ether which is acted on diminishes as the number of atoms of carbon increases.

Mixed Ethers.—The action was similar to that observed in the case of the simple ethers. It was noticed that the iodine attached itself to the molecule containing less carbon, while the hydroxyl united with the molecule richest in carbon. In the case of propyl-isopropyl oxide, the isopropyl group was the one which was converted into iodide.

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When one of the radicles of a mixed ether is methyl, the ether is converted with such neatness into methyl iodide and the corresponding alcohol, that the author proposes to use this reaction as a means of preparing alcohols, which otherwise are difficult to obtain. The hydrocarbon is to be converted into the chloride, and the chloride into the mixed ether $C_nH_{2n+1}—O—CH_3$, the latter then treated with hydriodic acid gas will give at once the desired alcohol.

J. W.

Glycin Derivatives.

By K. Kraut (Annalen der Chemie, clxxvii, 267—271).

By heating glycin with alcohol and ethyl or methyl iodide, G. v. Schilling obtained compounds which he regarded as the hydriodides of ethylamidacetic acid and dimethylamidacetic acid, $\begin{array}{l} CH_2(NH.C_2H_5) \\ | \\ CO.OH \end{array}$ and $\begin{array}{l} CH_2N(CH_3)_2 \\ | \\ CO.OH \end{array}$ respectively. The author and Hartmann, however, found that silver oxide gives rise to ethylic or methylic alcohol and glycin when boiled with these compounds, and hence regarded them as the hydriodide of $\begin{array}{l} CH_2.NH_2 \\ | \\ CO.O.C_2H_5 \end{array}$ and the methyliodide of $\begin{array}{l} CH_2.NH_2 \\ | \\ CO.O.CH_3 \end{array}$ respectively. The author now finds that the product is in each case the same, viz., the *hydriodide of glycin-ether* $\begin{array}{l} CH_2.NH_2 \\ | \\ CO.O.C_2H_5 \end{array}$; when methyl iodide is employed, it reacts on the ethylic alcohol present, forming methylic alcohol and ethyl iodide, so that the end-result is the same as though ethyl iodide had been originally employed. The identity of the products was proved by analysis, and by the fact that the same melting point, 137°, was exhibited by the hydrochloride obtained in each case from the hydriodide by shaking with silver chloride; moreover the liquid obtained by boiling the product from methyl iodide with silver oxide and water, gave most readily the iodoform reaction. In each case small quantities of bye-products are formed, possibly diethyl glycin, methyl-glycin, &c.

C. R. A. W.

Advantageous Method of Preparing Epichlorhydrin.

By E. W. Prévost (J. pr. Chem. [2], xii, 160).

To avoid the loss of material, owing to the epichlorhydrin forming a pasty mass with the potassium chloride, during the preparation of the above from potash and dichlorhydrin, the two substances are made to act on one another in a retort, the heat generated being sufficient to drive over a great part of the liquid. The remainder may be distilled off in the ordinary way, but the temperature should not be allowed to exceed 130°, else decomposition sets in.

E. W. P.

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Examination of Gums and Mucilages. By M. GIRAUD (Compt. rend., lxxx, 477—480).

ALTHOUGH presenting certain physical resemblances, gummy bodies exhibit great chemical differences. Three classes are distinguishable. In the first is gum tragacanth, characterised by yielding pectinous bodies. In the second are mucilages, characterised by their freedom from pectin and their precipitation by dilute acids. The third class comprises mucilages, also free from pectinous substances, but convertible by acids and warmth into a body comparable with dextrin and a saccharine substance. They possess in common the property of being converted into galactoses by dilute acids and heat, and the last two classes differ entirely from gum arabic.

Gum Tragacanth.—This gum is transformed by digesting with water into pectin, not into arabin. It contains more than half its weight of pectose, from which pectic acid may be prepared by precipitating with baryta and decomposing with hydrochloric or acetic acid. The analyses of pectic acid gave—

C	40·52	40·70	40·82
H	5·30	5·409	5·33
O	54·18	53·891	53·85
	100·00	100·00	100·00

The pectate of lead contained 31 per cent. of base, and the barium salts 23·48 per cent. of baryta.

The composition of gum tragacanth is,

Water	20	per cent.
Pectose	60	,,
Soluble gum	8 to 10	,,
Cellulose	3	,,
Starch	2 to 3	,,
Ash	3	,,
Albuminoïds	traces.	

M. L.

The Sweet Principle of Liquorice Root. By Z. ROUSSIN (J. Pharm. Chim. [4], xxii, 6—15).

THE author shows that the sweetness of liquorice-root is due—not to glycyrrhizin, but to a combination of that substance with ammonia. Glycyrrrhizin itself is nearly insoluble in cold water, and is in reality insipid, the slight savour it possesses being merely the result of its combination with the alkali naturally contained in the saliva. In its combinations with alkalis, glycyrrhizin plays the part of an acid, for it forms true salts. There are two glycyrrhizates of ammonia; a basic salt, which gives its solution a deep yellow colour, and another containing less ammonia, and imparting to the liquid merely an amber tint. The residue left on evaporation of the solution with excess of ammonia is, when dried, a yellowish, scaly, shining, brittle substance,

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quite unchangeable in the air, from which it attracts no moisture. It is immediately and completely soluble in cold water, to which it imparts an excessively sweet taste and a pale yellow colour. The addition of a few drops of ammonia to this solution develops a deep yellow colour, owing to the formation of the basic compound. The pale yellow solution has precisely the taste of the liquorice-root, which in reality owes its savour to ammoniacal glycyrrhizin; and the method of obtaining this in a state of purity is described at length by the author, who also indicates some interesting medical, pharmaceutical, and industrial applications of the substance. He suggests that by reason of its intense sweetness, its remarkable stability in solution, and the ease with which it may be prepared, it may even economically replace sugar for alimentary purposes.

R. R.

Some Double Metallic Sulphocarbonates. By A. MERMET (Compt. rend., lxxxi, 344).

THE deliquescence of the alkaline sulphocarbonates interferes with the determination of their crystallographic relations. In order to obviate it, the author has prepared a double salt containing potassium and nickel.

A solution of the alkaline sulphocarbonate is poured into a solution of a salt of nickel until the precipitate which is at first produced is redissolved; the liquid is then allowed to remain in a vacuum for a few days, or until the new salt has crystallised. The crystals are large and well defined.

An ammoniacal solution of a nickel salt is recommended as a test for the presence of a sulphocarbonate (*ibid.*, 344).

The alkaline solution of nickel is diluted with water until it is practically colourless, and to this liquid some drops of the solution to be examined are added; if it contains a trace of sulphocarbonate, a characteristic cherry-red tint is produced, even with a dilution of $\frac{1}{60,000}$.

The colour is quite distinct from that caused by an alkaline mono- or polysulphide.

J. W.

Ammonium Acetates. By M. BERTHELOT (Bull. Soc. Chim. [2], xxiv, 107).

WHEN commercial ammonium acetate is dissolved in its own weight of crystallisable acetic acid, an acid ammonium acetate is obtained which crystallises in long brilliant needles, having the composition $3C_2H_4O_2.2(NH_4C_2H_3O_2).H_2O$.

H. J. H.

Conversion of Acrylic Acid into Lactic Acid. By E. LINNEMANN (Deut. Chem. Ges. Ber., viii, 1095—1097).

WHEN sodium acrylate is heated with aqueous soda to 100°, it is converted into a mixture of sodium *hydracrylate* and *ethenelactate*, which

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can be easily separated by alcohol of 98 per cent., in which the lactate dissolves freely in the cold, while the hydrocylate is freely soluble only in boiling alcohol. The formation of ethenelactic acid and its isomeride hydracrylic acid is a further proof that acrylic acid does not contain the methyl-group.

C. S.

Oxidation-products of Acrolein Bromide. By E. LINNEMANN and C. PENL (Deut. Chem. Ges. Ber., viii, 1097—1100).

HENRY has found that the liquid acrolein bromide is changed into a solid modification when left in contact with nitric acid. The same body is formed when the liquid is kept under water, and more slowly when the dry liquid compound is allowed to stand. Both modifications are readily oxidised by nitric acid of 1·42 specific gravity, yielding a dibromopropionic acid, crystallising from water, ether, or carbon sulphide in monoclinic plates. The pure acid unites with water in all proportions, but if traces of salts or acids be present it does not, but forms a hydrate which is a heavy oil and solidifies at $-5°$. The acid melts at 63°—64°; but changes at the same time into another modification melting at 51°, which may be converted again into the first modification by keeping it at 53°—55° until it becomes solid. This acid is identical with that obtained from allyl alcohol.

C. S.

Production of Malonic Acid from Chloracrylic Ether. By A. PINNER (Deut. Chem. Ges. Ber., viii, 963—967).

BY acting on trichlorolactic acid with zinc and hydrochloric acid, the author obtained, not as was to be expected, the ether of monochlorolactic acid, but that of its derivative, *chloracrylic acid*, formed therefrom by removal of the elements of hydrochloric acid; under different conditions, however, mono- and dichlorolactic acids can thus be formed, as already announced by Rudneff, who was unable to verify the production of chloracrylic acid in this manner. From five pounds of chloral hydrate (by conversion into cyanhydrate and thence into chlorinated lactic acid ether), the author obtained about one pound of nearly pure chloracrylic ether, by acting on the alcoholic solution of the lactic ether with granulated zinc, hydrochloric acid being passed in from time to time, so as to keep the mixture warm; the product thus obtained gave numbers represented by the formula $C_3H_2ClO_2(C_2H_5)$.

Chloracrylic ether is partially decomposed by distillation with steam, an acid solution being formed containing *chloracrylic acid*, $C_3H_3ClO_2$. This acid is a syrup, which cannot be distilled; its salts are very soluble, and readily decompose on heating their aqueous solutions, forming metallic chlorides. On boiling the ether with baryta-water (an inverted condenser being attached), for a long time, a difficultly soluble barium salt is formed, together with small quantities of a more soluble one (probably chloracrylate or acryl-lactate); by means of sulphuric acid and ether the acid of the difficultly soluble salt can be extracted; it crystallises in flat prisms, melting at about 138°, and is

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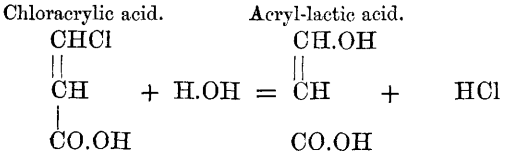
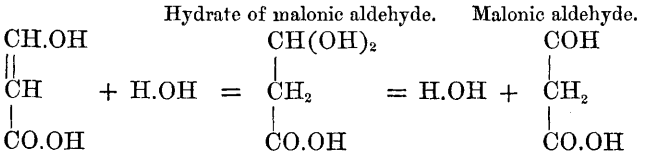
identical with *malonic acid* (m.p. 132°, Heintzel; 140°, Dessaignes); the silver salt gave numbers agreeing with $C_3H_2Ag_2O_4$, and exploded on heating; the barium salt contains $2H_2O$, of which half is lost at 100°, the other half only at 150°, thus agreeing with malonic acid from cyanacetic acid.

The author regards this malonic acid as formed by the following train of reactions from the chloracrylic acid and produced by the saponification:—





The malonic aldehyde, or homologue of glyoxylic acid thus formed, being excessively oxidisable, immediately oxidises to malonic acid.

Chloracrylic ether, heated in a sealed tube with water, gives no malonic acid, much gas only being formed, and scarcely any residue being left on evaporation of the resulting solution.

Bromine acts energetically on malonic acid; in presence of water, it forms tribromacetic acid and carbon dioxide; but if water be absent, *monobromomalonic* acid results; this is not crystallisable. When treated with baryta-water, it apparently forms *oxymalonic acid*, $C_3H_4O_5$, together with barium bromide, as an insoluble barium salt is thus produced, containing 53·91 per cent. of barium, whilst oxymalonate requires 53·72. The author proposes to study this lower homologue of malic acid, and the corresponding asparagin, &c.

Dichlorolactic acid is a liquid boiling at 219°—221°, with slight decomposition; it is formed in small quantity only by the short-continued action of zinc on trichlorolactic acid, and is difficult to separate completely from that portion of the latter acid which remains undecomposed.

C. R. A. W.

Oxidation of Tartaric Acid by Silver Oxide in Ammoniacal Solution. By AD. CLAUS (Deut. Chem. Ges. Ber., viii, 950—952).

IT might be supposed, theoretically, that tartaric acid would give rise,

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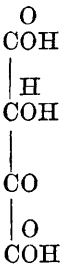
by simple oxidation, to an alcohol-acetone-dicarbonic acid, of the following structure :—



which, on further oxidation, might be converted into tartronic acid, with separation of carbonic acid. Bothe supposed that he had obtained a new organic acid, which he named oxytartaric acid, by precipitating nitrate of silver with sodium-potassium tartrate, extracting the precipitate with boiling water, and allowing the solution to cool after separation of the reduced silver. The author prepared this acid, thinking that it might be the compound mentioned above, but found it to consist only of crystallised silver tartrate.

In order to investigate the decomposition of tartaric acid by silver oxide on boiling, silver carbonate in ammoniacal solution was made to react on the acid in different proportions—one, two, and three molecules of the silver salt to one of tartaric acid. In all cases, oxalic acid was formed. An attempt to convert all the carbon into oxalic acid, according to the equation—

$$C_4H_6O_6 + 3O = 2(C_2H_2O_4) + H_2O$$

was not successful. Whether carbonic acid is formed or not in these decompositions has not been determined; but, without doubt, an organic acid is always produced in small quantities, which, on evaporation of its ethereal solution, remains as a thick syrup, gradually passing into the crystalline form on standing, and giving a calcium salt easily soluble in water. This acid is formed in largest quantity when two molecules of silver carbonate react on one of tartaric acid.

The author is investigating the action of ammoniacal solution of silver carbonate on other acids.

When one molecule of silver carbonate and one of malic acid are boiled together, a strong smell of decomposing aldehyde-ammonia is produced; whereas, if the proportions are two of the silver salt to one of malic acid, not the least trace of this odour is perceptible.

G. T. A.

Pyroracemic Acid. By C. Böttinger (Deut. Chem. Ges. Ber., viii, 957—958).

The author described some experiments on the decomposition of pyroracemic acid in a former paper (see this *Journal* [2], xii, 1158). Since then, he has begun his researches anew.

The products of decomposition of pyroracemic acid were found to be—

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(*a*.) In acid solution:

Uric acid, pyrotartaric acid, carbonic acid, to which were added, as bye-products, acetic acid, and two bodies which could not be accurately estimated on account of their small quantity.

(*b*.) In alkaline solution:

Uvitic acid, uvitonic acid (?), oxalic acid; and, as bye-products, carbonic acid, acetic acid.

The object of the new experiments was to investigate the bye-products more thoroughly, and especially to determine more accurately the characteristics of uvic acid. A third object was to ascertain the products of decomposition of neutral solutions of barium pyroracemate.

On heating a dilute aqueous solution of exactly neutral barium pyroracemate, using a vertical condenser, carbonic acid gas was given off. After a short time the evolution of gas ceased, and flocculi separated out from the liquid. The boiling was stopped at the end of two hours, and the precipitate which separated on cooling, as well as the liquid, was examined. The precipitate consisted of barium carbonate. The crystalline mass obtained from the liquid on evaporation, after removal of the barium, seemed to be pyrotartaric acid. But, besides this, a syrupy part remained, which has not been accurately examined, but probably consists of the same acid. It is to be remarked that on evaporation of the aqueous solution of the acid, the unpleasant penetrating odour (aldehydic (?)) was produced, which makes the preparation of pyroracemic acid so disagreeable an operation.

The author believes more strongly than ever that the body described by him (*Berichte*, v, 956; *Chem. Soc. J.* [2], vi, 297), as hydruvic acid, is really the acid obtained by Berzelius, which affords amorphous salts, but that the acid described in the same place as decarbohydruvic acid, is nothing else than altered hydruvic acid, from which, by separation of CO_2, pyrotartaric acid is formed. He thinks, also, that his uvitonic acid consists of impure pyrotartaric acid.

G. T. A.

Dinitro-compounds of the Fatty Group.

By E. TER MEER (Deut. Chem. Ges. Ber., viii, 1080—1088).

DINITROETHANE is best obtained by dissolving 21 grams of monobromonitroethane in twice its weight of alcohol, and adding first a solution of 12 grams potassium nitrite in the same weight of water, and then gradually 45 parts of alcoholic potash (1 : 5). After standing for one to two hours, the crystals which have separated out are first washed with alcohol and ether, and then with water to remove the potassium bromide. On adding a dilute acid to the potassium compound, dinitroethane separates out as a colourless, very refractive liquid, having a peculiar, sweet taste, and a faint alcoholic smell. It boils at 185°—186° (corrected), and has, at 23·5°, the specific gravity 1·3503. It is a tolerably strong acid, which even decomposes carbonates, but not readily. The potassium salts form yellow glistening monoclinic crystals, $a : b : c = 0{\cdot}58124 : 1 : 0{\cdot}99016$. (The measurements of the different angles are given in the original.) It is sparingly soluble

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in cold water, readily in hot water, and insoluble in absolute alcohol; when exposed to light it acquires an orange colour. The sodium compound is a very similar body, but dissolves more freely in water and alcohol. The barium salt crystallises in yellow needles or small plates, and the very explosive silver salt forms small yellow plates having a metallic lustre and dissolving but sparingly in water.

The aqueous solution of the potassium salts is not precipitated by calcium, barium, strontium, aluminium, cobalt, and ferrous salts. Ferric chloride forms a reddish-brown precipitate; lead acetate gives a pure yellow, crystalline, and basic lead acetate a bulky yellow precipitate, while that produced by copper sulphate is pale blue, and by mercuric chloride, light brown. Mercurous nitrate produces a greyish-black precipitate, changing soon into colourless crystals.

When bromine-water is added to an aqueous solution of the potassium salt, *monobromodinitroethane* separates in the form of a colourless heavy oil, having a very pungent smell. It decomposes on distillation, but volatilises with steam. Potash and even potassium carbonate decompose it, with formation of potassium dinitroethane—

$$CH_3—C(NO_2)_2Br + 2KOH = CH_3—C(NO_2)_2K + KBr + H_2O + O.$$

When dinitroethane is reduced with tin and hydrochloric acid, it ought to yield aldehyde and hydroxylamine, for Meyer has shown that dinitropropane produces, by reduction, acetone and hydroxylamine. But only a trace of aldehyde was observed, the products being acetic acid, ammonia, and hydroxylamine. This is easily explained by assuming that the aldehyde in the nascent state is oxidised by hydroxylamine, and this was confirmed by experiment. On passing the vapour of aldehyde mixed with carbon dioxide into a boiling solution of pure hydroxylamine hydrochloride, containing a little freshly prepared spongy platinum the hydroxylamine was soon reduced to ammonia. Therefore, on reducing dinitroethane, the following reactions take place:—

$$(1.)\ CH_3.C(NO_2)_2H + 4H_2 = CH_3.COH + 2NH_2OH + H_2O.$$
$$(2.)\ CH_3.COH + NH_2OH = CH_3.COOH + NH_3.$$

To obtain normal or *α-dinitropropane*, the corresponding monobromonitro-compound was treated in the same way as the ethane-compound. The potassium dinitropropane thus obtained has the greatest resemblance to potassium dinitroethane, and gives very similar reactions. The silver-salt crystallises in greenish-yellow plates, with a steel-blue lustre. α-dinitropropane, $CH_3.CH_2.C(NO_2)_2H$, is a colourless oil, boiling at 189°, and having the specific gravity 1·258 at 22·5°.

C. S.

Potassium Cyanate and Urea. By C. A. Bell (Chem. News, xxxii, 99).

The following modification of Liebig's well-known process for the preparation of potassium cyanate is suggested. Four parts of perfectly dried and finely powdered potassium ferrocyanide are intimately

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mixed with three parts of dry and pulverised potassium bichromate. A small quantity of this mixture is placed in a porcelain or iron dish, the temperature of which is then raised until a tinder-like combustion takes place, and the mixture blackens, which happens considerably below a red heat. The rest of the mixture is then thrown in by small quantities at a time, each successive portion being allowed to blacken completely before it is covered by the next. This is necessary, for if air be excluded during the combustion, a considerable quantity of potassium cyanide will be found unoxidised.

When all the mixture has been added the dish is allowed to cool. The result of the reaction is a porous friable mass, from which the cyanate may be extracted with boiling alcohol. To diminish as much as possible the loss from conversion of the cyanate into carbonate during boiling, and also to economise alcohol, it is advisable to add to the latter at each boiling only about as much of the mixture as can be thoroughly exhausted by it. The crystallisation of the cyanate may be hastened by immersing the vessel containing the alcoholic solution in cold water. In a favourable experiment the resulting cyanate, equal to about 42 per cent. of the dried ferrocyanide, contained less than 1 per cent. of impurity.

To obtain the insoluble cyanates, lead, silver, &c., it is only necessary to exhaust the black mass with very cold water, remove the chromate and unaltered ferrocyanide with barium nitrate, and finally to precipitate with a nitrate of the metal.

From the above aqueous solution urea may obviously be prepared by the addition to it of $4\frac{1}{4}$ parts of ammonium sulphate, evaporation to dryness, extraction with boiling alcohol, &c. For the purification of urea on the small scale, amylic alcohol is a much more convenient crystallising medium than ordinary alcohol.

H. J. H.

Synthetic Researches on the Uric Acid Group.

By E. Grimaux (Compt. rend., lxxxi, 325).

In a previous communication, some ureic derivatives of asparagin were noticed, among them *malylureic acid* and its corresponding *amide:* the action of bromine in presence of water on this acid has now been studied.

Three compounds have been formed—

(1.) $C_9H_6Br_6N_4O_6$. (2.) $C_9H_2Br_2N_4O_4.H_2O_2$. (3.) $C_8H_7BrN_4O_4$.

(1.) *Hexbromo-lactomaluryl* crystallises in nacreous scales, soluble in 35 parts of boiling water. Treated with an alkali, even in the cold, it gives bromoform, an oxalate, and a bromide.

Boiled with ammonia, it yields a yellow amorphous powder, which, under the influence of a few drops of nitric acid, is converted into a crystalline substance presenting the reactions of dialuric acid, but rather more soluble in water. The latter warmed with ammonia is directly converted into murexide.

(3.) The substance having the third formula given above is con-

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verted by the joint action of water and bromine at 100° into *hydrodibromo-malonylurea*, $C_4H_4Br_2N_2O_3$, a body which can also be formed directly by the action of dry bromine on malylureic acid. This dibromo-compound differs from dialuric acid by containing 2 atoms of bromine in place of 1 atom of oxygen; its relationship is further proved by the fact that when heated gently with silver oxide, it yields silver bromide and a solution presenting the characters of dialuric acid.

When warmed in dilute solution with ammonia it absorbs oxygen from the air, and is converted into murexide.

Another body, $C_9H_6Br_2N_4O_5$, is also produced by the action of dry bromine on malylureic acid; the further action of bromine and water upon it converts it into hexbromo-lactomaluryl. The above experiments are being continued in the hope of arriving at the constitution of the derivatives of uric acid.

J. W.

Reduction of Aromatic Compounds by Hydriodic Acid and Phosphorus. By C. GRAEBE (Deut. Chem. Ges. Ber., viii, 1054—1056)

IT has been previously shown (see p. 457 of last vol.) that the aromatic ketones are reduced by hydriodic acid and phosphorus. The author has now extended the reaction to other compounds.

Benzoylbenzoic acid is reduced very easily and completely to benzylbenzoic acid by heating it to 160°—170° for six or eight hours with hydriodic acid and phosphorus. This is, indeed, the best method of preparing benzylbenzoic acid.

Diphtalyl, $C_{16}H_8O_4$, similarly treated, yields a small quantity of a hydrocarbon, the chief product being a dibasic acid having the formula $C_{16}H_{14}O_4$, which when heated with soda-lime yields a hydrocarbon of as yet unknown constitution.

Bitter almond oil, as shown by Berthelot, is reduced to toluene by heating it with fuming hydriodic acid to 280°. The same reaction takes place at 130°—140° with hydriodic acid boiling at 127°, in presence of phosphorus.

Benzyl alcohol yields, at 140°, chiefly toluene, with small quantities of compounds of higher boiling-points.

Benzopinacone is less easily reduced. When heated for 6 or 8 hours, however, it is converted into *tetraphenylethane*, $(C_6H_5)_2CH-CH(C_6H_5)_2$. This body is readily separated from any unaltered benzopinacone by treatment with alcohol, in which it is only sparingly soluble. It dissolves sparingly in ether and cold glacial acetic acid, more freely in boiling acetic acid, and abundantly in warm benzene and toluene. It crystallises in large prisms melting at 206°, and sublimes in broad needles or laminæ. With bromine and nitric acid it yields substitution-products.

Phenanthrene, at 200°—210°, yields a hydrocarbon which is liquid at ordinary temperatures, boils about 310°, and solidifies below 0°. Its sp. gr. at 10·2° is 1·067. It contains 92·29 p.c. carbon, and 7·73

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hydrogen, and has, therefore, the composition of *tetrahydride of phenanthrene.*

J. R.

Formation of Bromine Substitution-products. By F. KRAFFT (Deut. Chem. Ges. Ber., viii, 1044).

IODIC acid acting, either alone or in presence of free iodine, upon hydrocarbons or their derivatives yields, as is well known, iodine substitution-compounds. Chloric acid, under certain conditions, acts in an analogous manner. The author finds that bromic acid may likewise be employed with advantage to effect the substitution of bromine for hydrogen.

When powdered potassium bromate (50 grams) and benzene (25—30 grams) are introduced into a flask half filled with sulphuric acid diluted with twice its weight of water, and the flask is agitated, the bromate gradually dissolves, and the mixture becomes warm. After some time, provided the temperature is not allowed to rise above 30°, the benzene is converted into a dense, colourless, oily body which, when dried over calcium chloride and rectified, distils for the most part at 155°, and has the composition and properties of monobromobenzene. A little dibromobenzene is almost always formed at the same time, especially if the temperature rises too high, or excess of bromate is employed. With only slightly diluted sulphuric acid the products are entirely different.

In this reaction it is evident that the oxygen of the bromate plays the part of one-half of the bromine in the process usually employed. To render available the oxygen present in the bromate in excess of that so acting, it is only necessary to add bromine and a corresponding quantity of benzene, in about the proportion shown by the equation:—

$$HBrO_3 + 2Br_2 + 5C_6H_6 = 5C_6H_5Br + 3H_2O.$$

Practically it is better to use rather less bromine and more bromate than are thus indicated. The yield is 70—80 per cent. of the theoretical amount.

J. R.

Metabromotoluene. By E. A. GRETE (Liebig's Annalen, clxxvii, 231—267).

WROBLEWSKY has found that by treating metabromotoluene with fuming sulphuric acid, three different bromotoluene-sulphonic acids result (two in small proportion only), differing from one another in the amounts of water of crystallisation possessed by their barium salts, the amount in the most abundant isomeride being H_2O, and the quantities in the other two modifications being $1\frac{1}{2}H_2O$ and $2H_2O$ respectively. The author, however, attributes the formation of the latter two sulphonic acids to the presence of other bromotoluenes in the metabromotoluene used, inasmuch as he finds that perfectly pure

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metabromotoluene yields but one sulphonic acid, the barium salt of which crystallises always with H_2O. The pure metabromotoluene was prepared by Griess's method from the product of the bromination of paracetoluidine, this product (metabromoparacetoluidine) melting at 117·5° after several crystallisations; the paracetoluidine was frequently recrystallised from water and alcohol, and melted constantly at 146°, solidifying instantly on cooling. In order to brominate it, a slight excess of bromine was added and the whole warmed; in this way a little dibromoacetoluidine was produced, but this was readily separated from the crude product of saponification with caustic soda (metabromotoluidine), as its transformation-product (dibromotoluidine) does not dissolve in acids forming a salt, and remains insoluble on crystallisation from water. Finally the product of the decomposition of metabromotoluidine by Griess's reaction was treated with tin and hydrochloric acid to remove nitro-compounds; the metabromotoluene thus obtained boiled constantly at 183·5° (mercury column wholly in vapour).

By fractional crystallisation various barium salts were isolated from the product of the action of fuming sulphuric acid on this pure substance; but in every instance the salt contained about 2·7 per cent. of water, corresponding with the formula $Ba(C_6H_3Br.CH_3SO_3)_2 . H_2O$; this result was confirmed in several ways. In order to expel the water of crystallisation, a temperature of 220°—230° is necessary, whilst decomposition is brought about at 240°—250°. Wroblewsky's barium salts containing $1\frac{1}{2}$ and 2 molecules of water lost their water at 140°.

The metabromotoluene sulphonates of strontium, calcium, magnesium, copper, lead and potassium are indicated by the formulæ—

$Sr(C_6H_3.Br.CH_3.SO_3)_2.H_2O$, $Ca(C_6H_3.Br.CH_3.SO_3)_2.2H_2O$,
$Mg(C_6H_3.Br.CH_3.SO_3)_2.6H_2O$, $Cu(C_6H_3.Br.CH_3.SO_3)_2.4H_2O$,
$Pb(C_6H_3.Br.CH_3.SO_3)_2.3H_2O$, and $K(C_6H_3.Br.CH_3.SO_3)$

respectively; the first two salts, when rendered anhydrous, are excessively hygroscopic. On fusing the last salt with caustic potash, an acid giving with ferric chloride the violet colour of salicylic acid is formed, whence probably the sulphonic acid is metabromotoluene-orthosulphonic acid.

Boiling fuming nitric acid acts on metabromotoluene, forming a dinitro-derivative melting at 103°—104° after crystallisation from alcohol; weaker acid gives in the cold *mononitrometabromotoluene*, melting at 54°—55° after the same treatment, the crude oil obtained in each case by dilution with water being solidified in a freezing mixture and well pressed in blotting paper before recrystallisation. A liquid nitro-derivative solidifying at 15° is contained in the paper thus used for pressing; the author considers that this is not (as supposed by Wroblewsky) an isomeric mononitro-metabromotoluene, but only the solid mononitro-compound mixed with a little of some fluid substance of different character, *e.g.*, unaltered bromotoluene, or some decomposition-product. By reducing the solid and liquid mononitro-derivatives, the same bromoamidotoluene is produced in each case, the product from the solid nitro-compound melting at 57·5°—58°, and

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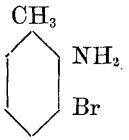
that from the liquid body at 56°. The salts also (sulphate, hydrochloride, nitrate and oxalate) are exactly alike, and the bromoacetoluidines obtained from each melt at the same temperature, viz., 156°. The formation of a second mononitrobromotoluene is thus, if not absolutely excluded, at least rendered highly improbable.

On reduction with tin and hydrochloric acid of the dinitro-derivative, the corresponding diamidobromotoluene is obtained, melting at 107°. It is noteworthy that the difference between the melting points of the mono-nitro- and mono-amido-derivatives is exactly the same as that between the dinitro- and di-amido-derivatives, thus—

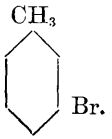
Mononitrometabromotoluene	54—55
Monoamidometabromotoluene	57—58
Difference about..	3°
Dinitrometabromotoluene	103—104
Diamidometabromotoluene ..	107
Difference about	3°

or otherwise, the dinitro-derivative melts about 49° above the mononitro body, as also does the diamido-derivative above the monoamido-body.

Wroblewsky has shown that the bromo-orthoacetoluidine obtained by brominating orthoacetoluidine melts at 156°, and yields on saponification a bromorthotoluidine melting at 57°. Hence the bromotoluidine obtained by reducing the nitrobromotoluene produced by nitrating metabromotoluene is identical with that prepared by brominating and saponifying orthoacetoluidine, *i.e.*, each body is—



The following table shows the relationship of metabromotoluene to various substances with which it is intimately connected—

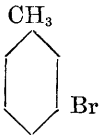
Metabromotoluene 

b.-p. 183·5°.

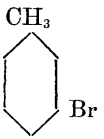
Para-series.

m.-p. 46°. Paratoluidine.

m.-p. 146°. Paracetoluidine.



m.-p. 117·5°. Metabromoparacetoluidine.



Fluid. Metabromoparanitrotoluene.

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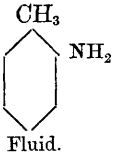
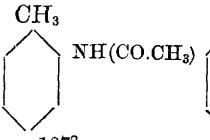
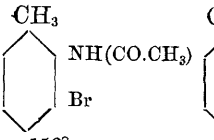
Ortho-series.



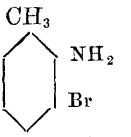
Fluid. Orthotoluidine.



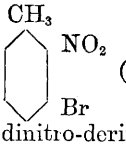
m.-p. 107°. Orthoaceto-luidine.

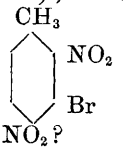


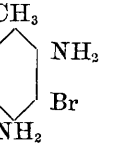
m.-p. 156°. Metabrom-ortho-acetoluidine.



m.-p. 57°—58°. Metabrom-ortho-toluidine.

The solid mononitro-compound then is 

(m.-p. 54°—55°: metabrom-orthonitrotoluene); whilst the dinitro-derivative is represented by the author as 

(m.-p. 103° — 104°: metabrom-orthonitroparanitrotoluene), its diamido-derivative being 

(m.-p. 170°: metabrom-orthoamido-paramidotoluene).

Whether, therefore, one start from paratoluidine or orthotoluidine, the same metabromotoluene is ultimately arrived at by converting into acetoluidine, brominating, and destroying the NH_2 group by Griess's process, the bromine in each case taking up the meta position with reference to the CH_3 group. By nitrating or sulphonating metabromotoluene, only *one* mononitro-derivative and *one* sulphonic acid are formed; in each case the newly-entering radical takes the ortho position with reference to the CH_3 group.

It is noticeable that by brominating paracetoluidine the melting point is *lowered* 28°, whilst by brominating ortho-acetoluidine the melting point is *raised* 49°.

C. R. A. W.

Constituents of Wood-tar Creasote. By FERD. TIEMANN and BENNO MENDELSOHN (Deut. Chem. Ges. Ber., viii, 1136—1139).

THE portion of Rhenish wood-tar creasote boiling at 200°—230°, was dissolved in ether and the solution agitated with potash. The aqueous liquid, after separation from the ether, was acidified, and the oil thereby liberated was separated by fractional distillation into two portions boiling at 195°—212° and 217°—226° respectively. The latter consisted of phlorol and creosol.

Methylcreosol (*Dimethylhomopyrocatechin*).—This body was obtained thus:—The foregoing mixture of phlorol and creosol, dissolved in

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alcohol and mixed with a slight excess of potash, was evaporated till it began to crystallise, and the crude creosol-potassium-salt thereby formed was dissolved in methyl alcohol and boiled with excess of methyl iodide. The product was a dense oily body, distilling for the most part at 214°—218°.

Methylcreosol is a transparent heavy liquid, of not unpleasant odour when pure, insoluble in water and dilute alkalis, but easily soluble in alcohol and ether.

Dimethylprotocatechuic acid.—Methylcreosol was oxidised by heating it with a dilute solution of potassium permanganate. The product was an acid, crystallising in long prisms, dissolving sparingly in water and freely in alcohol and ether, melting at 174°, and having the composition of dimethoxybenzoic acid. By gentle fusion with potassium hydrate it was converted into pyrocatechuic acid. This decomposition and its melting point characterise the body as dimethylprotocatechuic acid.

Creosol is therefore a derivative of protocatechuic acid, and must be regarded as methylated methylpyrocatechin or homoguaiacol.

Indifferent Oils of Wood-tar Creasote.—The ethereal solution above mentioned contained an oil boiling at 214°—218°, which was separated by fractional distillation. This body yielded by oxidation dimethylpyrocatechuic acid, and therefore consisted of methylcreosol or dimethylhomopyrocatechin. Other oils present in the ethereal solution are being examined by the authors.

J. R.

On a mode of Synthesis of Vanillin, and on Hydrovanilloin and Vanillyl Alcohol. By FERD. TIEMANN (Deut. Chem. Ges. Ber., viii, 1123—1127).

WHEN an intimate mixture of vanillate and formate of calcium is submitted to dry distillation in small portions, the product is an oily distillate containing a small quantity of vanillin, but consisting for the most part of guaiacol. The vanillin may be separated by shaking an ethereal solution of the distillate with a strong solution of acid sodium sulphite, decomposing this solution with sulphuric acid, and again shaking with ether, which takes up the vanillin and leaves it in crystals when evaporated.

Action of Nascent Hydrogen on Vanillin.—Vanillin under water or weak spirit quickly dissolves therein on addition of sodium-amalgam. After repeated additions of fresh portions of the amalgam and frequent agitation, vanillin can no longer be detected in the liquid. The pale-yellow solution, when carefully neutralised with sulphuric acid, deposits white prismatic crystals, which are insoluble in ether and cold water, sparingly soluble in warm water and boiling alcohol, but easily in dilute caustic alkalis and ammonia, from which they are deposited unaltered when the solutions are neutralised with acids.

The pure compound melts at 222°—225°, undergoing decomposition. Its composition, deduced from analysis, is represented by the formula $C_{16}H_{18}O_6$, according to which it is formed by the union of 2 atoms of hydrogen with 2 molecules of vanillin, and stands in the same relation

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to vanillin as hydrobenzoin to benzaldehyde. Hence the author calls it *hydrovanilloïn*. In contact with strong sulphuric acid it acquires a brilliant green colour and dissolves to a reddish-violet liquid.

The neutral liquid filtered from hydrovanilloïn, when shaken repeatedly with ether, gives up thereto a body which is left on evaporation of the ether as a pale-yellow oil easily soluble in ether, alcohol, and warm water. On long standing over sulphuric acid it solidifies in a crystalline mass. This body, which is still under investigation, is *vanillyl alcohol*.

The foregoing bodies both possess a characteristic odour, different from but recalling that of vanillin, into which they are readily reconverted by the action of oxidising agents.

J. R.

On Ethylvanillin, Methylvanillin, and Coniferyl Alcohol. By FERD. TIEMANN (Deut. Chem. Ges. Ber., viii, 1127—1136).

Ethylvanillin.—This substance is obtained by heating the potassium-salt of vanillin with excess of ethyl iodide. When pure it forms colourless prismatic crystals, which are easily soluble in ether and alcohol, but very sparingly soluble in water. It melts at 64°—65°, and sublimes without decomposition. The numbers furnished by analysis agree with the formula $C_6H_3\overset{OCH_3}{\underset{COH}{}}OC_2H_5$.

Ethylvanillin is converted by oxidising agents into ethylvanillic acid, a body melting at 193°—194°, and apparently identical with Graebe and Borgmann's ethylmethylprotocatechuic acid obtained by the oxidation of ethyleugenol. It does not dissolve in weak potash- or soda-ley more readily than in water. Its solutions in water or weak spirit are not affected by mineral acids. Strong sulphuric acid dissolves it without decomposition, forming a pale-yellow solution. Strong nitric acid readily forms substitution-products.

Methylvanillin, $C_6H_3\overset{OCH_3}{\underset{COH}{}}OCH_3$ (*dimethylprotocatechuic aldehyde*), is obtained in the same manner as the ethyl-compound. In the pure state it forms at the ordinary temperature a thick heavy pale-yellow oil. It boils without decomposition at 285°, and in a freezing mixture solidifies in needles which melt at 15°—20°. With nitric acid it yields nitro-substitution-products. Oxidising agents readily convert it into pure dimethylprotocatechuic acid (dimethoxybenzoic acid).

Ethylvanillin and methylvanillin both possess a distinct odour of vanilla. Like vanillin itself they are taken up from ethereal solution by acid sodium sulphite.

Coniferyl Alcohol.—Coniferin, $C_{16}H_{22}O_8$, is broken up by the action of emulsin into glucose and a crystalline compound, the formula of which, as deduced from analysis, is $C_{10}H_{12}O_3$. This compound is converted by oxidation into vanillin, protocatechuic acid, and acetic acid. Under the action of fuming hydriodic acid it yields methyl and ethyl iodides. Now, if this last product were derived from pre-existing

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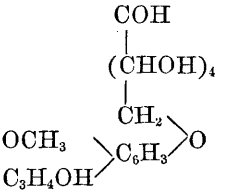
ethoxyl, the constitution of the body could be represented only by the formula $C_6H_3\begin{matrix}OCH_3\\COH\end{matrix}OC_2H_5$, which is that of ethyl-vanillin. The physical and chemical properties of the compound, however, are totally different from those of ethylvanillin. It melts at 74°—75°, and crystallises with difficulty. From its solution in water or weak spirit, mineral acids throw down a white amorphous body, softening like a resin at 150°—160°, which is also formed when an aqueous solution of coniferin is boiled with dilute acids. In its crystalline state the compound dissolves easily in dilute alkalis, and is thrown down by acids in an amorphous condition. Strong sulphuric acid turns it red and then dissolves it, forming a reddish-violet solution. Nitric acid acts upon it in such a way as either to decompose it completely or to convert it into picric acid, according to the conditions of its action. Oxidising agents convert it in acid or alkaline solution into vanillin, though slowly and imperfectly: in no case has the formation of vanillic acid been observed. From the properties of the body, together with various theoretical considerations, the author concludes that its constitution is expressed by the formula $C_6H_3\begin{matrix}OCH_3\\OH\\C_3H_4OH\end{matrix}$, which is that of an alcohol: having regard to its source, he calls it *coniferyl alcohol.*

J. R.

On the action of Acetic Anhydride on Coniferin and some of its Derivatives. By FERD. TIEMANN and NAGAJOSI NAGAI (Deut. Chem. Ges. Ber., viii, 1140—1144).

CONIFERIN is a glucoside and may be regarded as being formed by the union of glucose and coniferyl alcohol, with elimination of water. Since coniferyl alcohol, as shown by Tiemann, has the formula $C_6H_3\begin{matrix}OCH_3\\OH\\C_3H_4OH\end{matrix}$; and since, moreover, coniferin yields by oxidation a second glucoside which bears the same relation to coniferin that vanillic acid bears to coniferyl alcohol, the constitution of coniferin can be expressed only by the formula—



Tetracetoconiferin.—A body constituted as above can, by analogy, exchange only the hydrogen contained in the four hydroxyl-atoms of the sugar-residue for acetyl. The correctness of this view is borne out by experiment.

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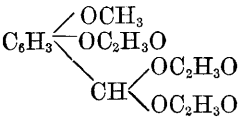
When coniferin dried at 100° is heated with excess of acetic anhydride, a body is formed which, when pure, is white and crystalline, softens at 97°, and melts at 125°—126° to a clear liquid which remains transparent after cooling. Analysis of the body agrees with the formula $C_{16}H_{18}(C_2H_3O)_4O_8$.

Tetracetosaccharovanillic Acid.—Saccharovanillic acid when heated with acetic anhydride yields a body which crystallises in delicate white needles melting at 181°—182°. The crystals dissolve easily in alcohol and ether, and sparingly in water. The formula deduced from analysis is $C_{14}H_{14}(C_2H_3O)_4O_9$.

Acetovanillic Acid. — Vanillic acid, $C_6H_3\begin{matrix}OCH_3\\OH\\COOH\end{matrix}$, likewise exchanges an atom of hydrogen for acetyl. The product forms delicate colourless needles melting at 142° and dissolving easily in alcohol and ether, but sparingly in water. When boiled with potash it is resolved into vanillate and acetate.

Acetovanillin Acetate.—When a solution of vanillin in acetic anhydride is heated over the water-bath for 5 or 6 hours, and after cooling mixed with water, a reddish-yellow oil is thrown down. If this oil be dissolved in ether and the solution agitated with acid sodium sulphite, the acetovanillin formed, together with any unaltered vanillin, is taken up thereby, whilst the ether retains a compound which crystallises on evaporation in six-sided tables melting at 88°—89°. Analysis of the body leads to the formula $C_{14}H_{16}O_7$. As this formula contains the elements of acetovanillin and acetic anhydride, the body is formed by the union of the two molecules. Its constitution is explained by the formula—



J. R.

On Arbutin. By H. Hlasiwetz and J. Habermann (Annalen der Chemie, clxxvii, 339—343).

Kawalier obtained from the leaves of *Arctostaphylos Uva Ursi* a bitter principle, which he regarded as the glucoside of a body, "Arctuvin," indicated by the formula $C_{20}H_{10}O_7$; subsequently Strecker identified arctuvin with hydroquinone, and regarded the bitter principle, *arbutin*, as a hydroquinone glucoside, $C_{12}H_6O_7$, splitting up in contact with emulsin into glucose and hydroquinone, taking up in so doing the elements of water. The authors find that, in addition to hydroquinone, *methyl-hydroquinone* is formed during this reaction, and regard the change as ensuing in accordance with the equation—

Arbutin.			Hydroquinone.		Methyl-hydroquinone.		Sugar.
$C_{25}H_{34}O_{14}$	+	$2H_2O$ =	$C_6H_6O_2$	+	$C_7H_8O_2$	+	$2C_6H_{12}O_6$.

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The arbutin employed (purchased from Trommsdorff of Erfurt), was treated with dilute sulphuric acid, and the product exhausted with ether; after evaporation of the ether, a residue was obtained, evidently consisting of at least two distinct bodies, one much more readily fusible than the other. The best way to separate these was found to be the addition of benzene to the residue freed as far as possible from ether, digestion at a gentle heat, and finally filtration; the hydroquinone is only sparingly dissolved and is thus left on the filter, whilst the methyl-hydroquinone is readily soluble in slightly warm benzene; an almost quantitative separation is thus effected. In this way it was found that 100 parts of arbutin furnished the following quantities of products, the glucose being estimated by Fehling's method:—

	Calculated for above equation.	Found.
Hydroquinone	19·7	18·2
Methyl-hydroquinone	22·5	20·6
Glucose	64·7	64·1 (mean of three estimations.)

The hydroquinone thus obtained melted constantly at 169° (not corrected), whether crystallised from water or sublimed, and whether in fine thin needles or in large individual crystals: Hesse has given 177·5° (uncorrected?), and later 172·5° (observed), as the melting point.

The methyl-hydroquinone was obtained in the pure state by evaporating off the benzene and distilling the residue; at about 243°, it passes over as a clear white oil, solidifying to a crystalline mass more or less rapidly according to the purity; it melts at 53° (not corrected), and has a burning taste with sweetish aftertaste: its crystals belong to the prismatic system, according to measurements by Ditschauer—

$$a : b : c = 1 : 0{\cdot}1601 : 0{\cdot}1379$$

When fused with caustic potash it forms hydroquinone, melting at 169°, after extraction by ether from the acidified solution of the product and purification by sublimation: hence it is veritably a methylic ether of hydroquinone, $C_6H_4\left\{\begin{matrix}O.CH_3\\O.H\end{matrix}\right.$. That this is so is proved by the circumstance that it can be synthesized from hydroquinone by treatment with methylsulphate of potassium and caustic potash; simultaneously, however, dimethyl-hydroquinone is formed. On heating to 170° for six hours a sealed tube containing 11 grams hydroquinone, 15 methylsulphate of potassium, and 6 of caustic potash, acidulating the product, and extracting with ether, a mixture of hydroquinone and the two methylic ethers is obtained; by treatment with benzene the hydroquinone is left behind, and on distilling with water the residue left after evaporation of the benzene, the dimethylic ether passes over, whilst the monomethylic ether remains behind: after recrystallisation from water, this ether exhibited exactly the same properties and melting point as the product from arbutin, which was also found to be non-volatile with steam. The dimethylic ether has a burning taste,

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resembles the monomethylic ether in its solubilities, and melts at 55° to 56°; neither ether gives with ferric chloride the green product obtained with hydroquinone; both reduce silver nitrate on warming, evolving the odour of quinone.

The *nitroarbutin* described by Strecker was found by the authors to give numbers agreeing with the formula $C_{25}H_{30}(NO_2)_4O_{14} + 3\frac{1}{2}H_2O$, with which, indeed, Strecker's own values agree very fairly.

C. R. A. W.

Solid Benzoyl Chloride. By A. LIEBEN (Liebig's Annalen, clxx, viii, 43).

A SAMPLE of benzoyl chloride which solidified during the late winter, was found to melt at −1°.

T. B.

Nitrobenzyl Chloride. By C. WACHENDORFF (Deut. Chem. Ges. Ber., viii, 1101—1102).

WHEN orthonitrotoluene is treated with chlorine at 150°—200°, it is converted into *orthonitrobenzyl chloride*, a thick, aromatic oil, which produces a burning sensation on the skin, and changes, on standing, into fine needles. Bromine acts at 150° to 200° on orthonitrotoluene. The bromide thus formed is a very unstable compound, which is decomposed by alcoholic silver nitrate even in the cold.

C. S.

On Phenyloxycrotonic Acid. By KAETA UKIMORI MATAMOTO (Deut. Chem. Ges. Ber., viii, 1144—1147).

IT has long been known that an aldehyde, when heated with hydrochloric acid in presence of hydrocyanic acid, yields the oxyacid of the next higher term of the series to which the aldehyde belongs. The reaction is a general one, and the author has applied it successfully to cinnamic aldehyde.

Cinnamic aldehyde (obtained from commercial oil of cinnamon by treating it with acid sodium sulphite in the usual manner), was boiled for 50—60 hours with hydrochloric and hydrocyanic acids. The product was an acid having the formula $C_{10}H_{10}O_3$, which is that of phenyloxycrotonic acid. The yield of this body was very small, amounting to not more than 4 or 5 per cent. of the aldehyde employed.

Phenyloxycrotonic acid forms colourless transparent crystals, melting at 115°, and dissolving freely in ether and alcohol, and sparingly in water. It is diatomic and monobasic, and forms well-characterised salts. Those of the alkalis were obtained only in deliquescent crystalline masses. The silver-salt, obtained by precipitation, is white and flocculent, and speedily blackens. The barium-salt, obtained by boiling the acid with barium carbonate, forms fine crystals. The lead-salt, obtained from the nitrate by precipitation, crystallises from hot water in needles

J. R.

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The Constitution of the Benzene-sulphonic Acids.

By E. NÖLTING (Deut. Chem. Ges. Ber., viii, 1091—1095).

BY heating equal molecules of chlorobenzenesulphonic chloride and phosphorus pentachloride to 200°—220°, *paradichlorobenzene*, melting at 53°, and boiling at 172°—174°, is formed. This observation, in connection with the results of the researches of Limpricht, Körner, and others, show that the sulphonic acids of benzene belong to the following groups:—

Ortho-series.	Meta-series.	Para-series.
γ Nitrobenzenesulphonic acid.	α Nitrobenzenesulphonic.	β Nitrobenzenesulphonic.
γ Amidobenzenesulphonic acid.	α Amidobenzenesulphonic.	Sulphanilic.
So-called phenolmetasulphonic acid.	—	Phenolparasulphonic.
γ Bromobenzenesulphonic acid.	α Bromobenzenesulphonic.	β Bromobenzenesulphonic.
	—	Chlorobenzenesulphonic (from sulphanilic).
	Benzenemetadisulphonic.	Benzeneparadisulphonic.

C S.

Amidobenzenesulphonic Acids and Derivatives.

By H. LIMPRICHT (Deut. Chem. Ges. Ber., viii, 1065—1073).

THE bromobenzenesulphonic acid obtained from bromobenzene is identical with that from β-amidobenzenesulphonic acid (sulphanilic acid). On distilling their potassium-salts with potassium ferrocyanide, the nitril of terephthalic acid is obtained.

α-amidobenzenesulphonic acid yields, by the same reactions, the nitril of isophthalic acid.

When in dibromosulphanilic acid the amido-group is replaced by hydrogen, *α-dibromobenzenesulphonic acid* is formed, which is crystalline and very soluble in water. Its salts crystallise well, and are partly sparingly soluble. The following were examined:—$C_6H_3Br_2SO_3NH_4$; $C_6H_3Br_2SO_3K$; $(C_6H_3Br_2SO_3)_2Ba + 3\frac{1}{2}H_2O$; $(C_6H_3Br_2SO_3)_2Ca + 3\frac{1}{2}H_2O$; $(C_6H_3Br_2SO_3)_2Pb + 1\frac{1}{2}H_2O$. The chloride of the acid forms large crystals melting at 57·5°, and the amide crystallises in snow-white needles, melting at 201·5°.

Nitrodibromobenzene-sulphonic acid, $C_6H_2(NO_2)Br_2SO_3H + xH_2O$, is readily soluble in water and crystallises in six-sided plates. Its concentrated solution is precipitated by potassium and barium salts, and a dilute solution by lead salts. $C_6H_2(NO_2)Br_2SO_3NH_4 + H_2O$; $C_6H_2(NO_2)Br_2SO_3K + H_2O$; $(C_6H_2(NO_2)Br_2SO_3)_2Ba + 1\frac{1}{2}H_2O$ and $4H_2O$; $(C_6H_2(NO_2)Br_2SO_3)_2Ca + 3H_2O$; $(C_6H_2(NO_2)Br_2SO_3)_2Pb + 5H_2O$. The chloride forms small plates, melting at 121°, and the amide is a crystalline powder, which blackens at 300° without melting.

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When the diazo-compound of dibromosulphanilic acid is treated with hydrobromic acid, a *tribromobenzenesulphonic acid* is obtained, which forms a very soluble, crystalline mass. Most of its salts are but sparingly soluble. $C_6H_2Br_3SO_3NH_4$; $C_6H_2Br_3SO_3K$; $(C_6H_2Br_3SO_3)_2Ba + 3H_2O$; $(C_6H_2Br_3SO_3)_2Ca + 2\frac{1}{2}H_2O$; $(C_6H_2Br_3SO_3)_2Pb + 3\frac{1}{2}H_2O$. The chloride forms a yellow crystalline mass or colourless needles, melting at 195°, and the amide is a crystalline powder, melting at 210°.

Nitrotribromobenzenesulphonic acid forms soluble plates. The following salts have been examined: — $C_6H(NO_2)Br_3SO_3NH_4 + H_2O$; $C_6H(NO_2)Br_3SO_3K + H_2O$; $(C_6H(NO_2)Br_3SO_3)_2Ba + 4H_2O$; $(C_6H(NO_2)Br_3SO_3)_2Ca + 3H_2O$; $(C_6H(NO_2)Br_3SO_3)_2Pb + xH_2O$. The chloride forms microscopic crystals, melting at 116°, and the amide is a crystalline powder, melting at 202°. By reduction of the nitro-acid, an *amidotribromobenzenesulphonic acid* is obtained, which is readily soluble, and crystallises in small needles. Its solution is precipitated by barium chloride, and its diazo-compound crystallises from alcohol in colourless needles.

α- or *Metamidobenzenesulphonic acid* yields, with bromine, a dibromo- and a tribromo-acid. The former was converted by the diazo-reaction into a *dibromobenzenesulphonic acid*, which forms a syrup. The salts $(C_6H_3Br_2SO_3)_2Ba + 2H_2O$ and $2\frac{1}{2}H_2O$; $(C_6H_3Br_2SO_3)_2Ca + 4_2H_2O$ and $2\frac{1}{2}H_2O$ have been prepared. The chloride forms large transparent prisms, melting at 84°, and the amide slender white needles, melting at 188°—189°.

To convert metamidodibromobenzenesulphonic acid into a *tribromo* benzenesulphonic acid, it was dissolved in hydrobromic acid, the solution treated with nitrous acid, and the diazo-compound decomposed by absolute alcohol.

The acid is a crystalline mass, forming the following salts:— $C_6H_2Br_3SO_3NH_4 + H_2O$; $C_6H_2Br_3SO_3K + H_2O$; $(C_6H_2Br_3SO_3)_2Ba + 4H_2O$?$(C_6H_2BrSO_3)_2Ca + 7H_2O$; $(C_6H_2Br_3SO_3)_2Pb + 9H_2O$. The chloride forms large plates, melting at 51°, and the amide is a powder which does not melt at 260°.

Metachlorobenzenesulphonic acid, obtained from the metamido-acid, crystallises in deliquescent plates and forms the following salts: $C_6H_4ClSO_3K$; $(C_6H_4ClSO_3)_2Ba + 2H_2O$; $(C_6H_4ClSO_3)_2Ca$; $(C_6H_4ClSO_3)_2Cu + 5H_2O$; $C_6H_4ClSO_3 + xH_2O$. The lead salt is deliquescent, the chloride an oil, and the amide crystallises in large plates melting at 148°.

γ- or Orthamidobenzenesulphonic acid, yields a *chlorobenzenesulphonic acid*, forming an oily chloride (?) and an amide crystallising in needles or plates, and melting at 182·5°.

Paradibromobenzenesulphonic acid (from paradibromobenzene), was purified by heating the chloride with water to 120°. It forms colourless needles, containing 2 mols. of water, and melting at about 100°; the anhydrous acid melts at 128°.

The following salts have been prepared:—$C_6H_3Br_2SO_3NH_4$; $C_6H_3Br_2SO_3K + H_2O$; $(C_6H_3Br_2SO_3)_2Ba + H_2O$; $(C_6H_3Br_2SO_3)_2Ca + 10H_2O$; $(C_6H_3Br_2SO_3)_2Pb + 3H_2O$. The chloride forms well-defined plates, melting at 70·5°, and the amide small silky needles, melting at 192°.

The acid was converted into $C_6H_2(NO_2)Br_2SO_3H + H_2O$, which forms very soluble salts. $C_6H_2(NO_2)Br_2SO_3NH_4 + 3H_2O$;

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$C_6H_2(NO_2)Br_2SO_3K + 3H_2O$; $(C_6H_2(NO_2)Br_2SO_3)_2Pb + 1\frac{1}{2}H_2O$. The chloride solidifies at 0°.

When metabromoacetanilide is treated with fuming sulphuric acid, it yields a bromamidobenzenesulphonic acid, crystallising from hot water in white needles. $(C_6H_3(NH_2)BrSO_3)_2Ba + H_2O$ forms pearly plates.

C. S.

Derivatives of Diphenylamine. By R. GNEHM (Deut. Chem. Ges. Ber., viii, 925—930).

HOFMANN'S tetrabromodiphenylamine was prepared; it melts at 182°.

Hexbromodiphenylamine, $N\left\{\begin{array}{l}C_6H_2Br_3\\C_6H_2Br_3\\H\end{array}\right.$, was obtained, together with tetrabromodiphenylamine, by adding bromine to a solution of diphenylamine in acetic acid. It melts at 218°, is insoluble in water, almost insoluble in alcohol, and moderately soluble in benzene, from which it separates in colourless prismatic crystals.

When bromine is added to a solution of methyldiphenylamine in acetic acid, the mixture becomes hot, evolves hydrobromic acid, and finally solidifies to a crystalline mass. Fractional crystallisation separates this product into three portions, the least soluble being *tribromomethyldiphenylamine*, which forms colourless needles melting at 98°, and dissolving readily in benzene.

The fraction having an intermediate solubility in alcohol proved to consist of *tetrabromomethyldiphenylamine*, and it forms needles and prisms which melt at 129°, and dissolve readily in benzene. The third, or least soluble fraction was found to be tetrabromodiphenylamine, and its formation may probably be represented as follows:—

$$N\left\{\begin{array}{l}C_6H_3Br_2\\C_6H_3Br_2\\CH_3\end{array}\right. + HBr = CH_3Br + N\left\{\begin{array}{l}C_6H_3Br_2\\C_6H_3Br_2.\\H\end{array}\right.$$

The methyl may be removed from either of the above described methylated bromodiphenylamines by digestion with glacial acetic acid and bromine, either tetrabromodiphenylamine or hexbromodiphenylamine being formed.

Methyldiphenylamine is not acted on by acetyl chloride, but when tetrabromodiphenylamine is heated with acetyl chloride an *acetyl tetrabromodiphenylamine* is formed, and it was found to melt at 158°. The brominated methyldiphenylamines did not yield acetyl derivatives.

Sodium-amalgam has no action on an alcoholic solution of methyldiphenylamine, but it removes the bromine from the above described bromine-compounds, diphenylamine or methyldiphenylamine being formed.

Tribromomethyldiphenylamine is readily attacked by hot nitric acid, a resinous product being formed, and the continued action of fuming nitric acid on this compound leads to the formation of *tetranitrodibromodiphenylamine*.

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It separates from glacial acetic acid in beautiful yellow leaflets, which melt and decompose at 235°—242°, and dissolve readily in alkalis.

The remainder of the above described brominated bodies yield small proportions of nitro-compounds, which are perhaps identical with that just described.

T. B.

Constitution of Tetraphenylmelamine. By WEITH and EBERT (Deut. Chem. Ges. Ber., viii, 912—917).

WHEN cyanogen chloride is passed into cold aniline, the melaniline of the author and Schröder is produced, but Hofmann has since proved this base to be diphenylguanidine. The authors now find that when cyanogen chloride is passed into hot aniline, different results are obtained, Hofmann's tetraphenylmelamine being formed. When tetraphenylmelamine is heated to 280° with strong hydrochloric acid, ammonia, carbonic acid, and aniline are formed, but no diphenylamine was found among the products. As diphenylamine is not decomposed when heated to 280° with hydrochloric acid, it cannot have been produced and subsequently destroyed. This experiment tends to prove that Hofmann's tetraphenylmelamine does not contain the group $N.(C_6H_5)_2$, and this view is confirmed by the fact that it yields sulphanilide and not a sulpho acid of diphenylamine when it is heated with sulphuric acid.

When Hofmann's tetraphenylmelamine is distilled either alone or with potash, ammonia, aniline and diphenylamine are formed, and in the former case hydrocyanic acid is also produced.

The above results induce the authors to regard Hofmann's tetraphenylmelamine as a derivative of triple carbodiimide $[C(NH_2)_2]_3$, and they represent it by the following formula:—

$$C_3 \left\{ \begin{matrix} (N.C_6H_5)_4 \\ (NH)_2 \end{matrix} \right. .$$

It is probably formed by the resolution of diphenyl-guanidine into carbodiphenylimide and ammonia on the one hand, and into carbophenylimide and aniline on the other hand: the nascent carbodiphenylimide and the carbomonophenylimide then uniting to form tetraphenyltricarbodiimide (Hofmann's tetraphenylmelamine).

T. B.

Mixed Azo-compounds. By V. MEYER and G. AMBÜHL (Deut. Chem. Ges. Ber., viii, 1073—1078).

WHEN aniline is dissolved in exactly two equivalents of nitric acid, and an aqueous solution of one equivalent of potassium nitrite is added to the strongly diluted solution, diazobenzene nitrate is obtained—

$$C_6H_5NH_2 + 2HNO_3 + KNO_2 = C_6H_5N_2.NO_3 + 2H_2O + KNO_3.$$

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The solution thus obtained may be used for almost all diazo-reactions.*

Thus on adding it to a freshly prepared solution of nitroethane in one equivalent of aqueous potash, *azonitroethylphenyl* $C_6H_5.N_2.C_2H_4NO_2$ is precipitated either as an oil, which soon solidifies, or if the solution be more diluted, in yellow flakes, crystallising from hot alcohol in golden-yellow plates.

By using pseudonitropropane the corresponding pseudopropyl-compound $(CH_3)_2C(NO_2)N_2C_6H_5$ is obtained as a heavy yellow oil, which is *quite insoluble* in alkalis, while the ethyl-compound is a strong *bibasic acid;* but as the constitution of the latter is undoubtedly—

$$CH_3—CH(NO_2)—N_2C_6H_5,$$

it ought to contain only one atom of hydrogen replaceable by metals, and therefore its metallic compounds must be regarded as basic salts. Of these the following were prepared:—

$C_8H_8N_3O_2K + KOH + 3H_2O$ is obtained by mixing the acid with alcoholic potash and washing with alcohol and ether. It forms an orange-coloured crystalline mass, which decomposes a little above 100°. $C_8H_8N_3O_2Na + NaOH + 6H_2O$ crystallises in orange-coloured plates. $C_8H_8N_3O_2.ZnOH + 2H_2O$ is a chrome-yellow precipitate. $C_8H_8N_3O_2.PbOH + PbO + 1\frac{1}{2}H_2O$ is a brownish yellow or brick-red precipitate. The silver salt is a brown precipitate which soon blackens. All the salts are decomposed by hydrochloric acid, with separation of the original compound. On boiling it with fuming hydrochloric acid, it loses about one-third of its nitrogen, and a colourless base is formed, whose hydrochloride seems to be $C_6H_{10}N_2O_2Cl_2$.

C. S.

Mixed Azo-compounds. By P. Friese (Deut. Chem. Ges. Ber., viii, 1078—1080).

Azonitromethylphenyl, $C_6H_5.N_2.CH_2NO_2$, is obtained like the ethyl-compound, but to avoid the formation of resinous bodies, the solutions must be very dilute. The compound separates as a cherry-red oil, which soon solidifies. It crystallises from alcohol in fine red needles having a brilliant silky lustre, and from carbon sulphide in prisms resembling chromic trioxide. At 153° it melts and decomposes, and when more strongly heated it deflagrates. In concentrated sulphuric acid it dissolves with an intense purple colour; water precipitates again the unaltered compound.

C. S.

* To convert amido-compounds into phenols, sulphuric acid must be used instead of nitric. Diazoamidobenzene is also readily obtained by dissolving 2 mols. of aniline in ether, adding 1 mol. of amyl nitrite, and allowing the solution to evaporate over sulphuric acid:

$$2C_6H_5NH_2 + C_5H_{11}ONO = C_6H_5N_3H.C_6H_5 + C_5H_{11}OH + H_2O$$

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Dry Distillation of Caoutchouc. By G. BOUCHARDAT (Bull. Soc. Chim. [2], xxiv, 108).

FIVE kilograms of new caoutchouc yielded 250 grams of isoprene, C_5H_8; 2000 grams of caoutchin, $C_{10}H_{16}$, volatile at 176°—180°; and 600 grams of heveene, $C_{15}H_{24}$, volatile at 255°—265°. There remained other less volatile products, less and less fluid, some distilling below 360°, among which is probably the carbide, $C_{40}H_{32}$, and others which decompose by heat and produce the preceding carbides. It may then be said that caoutchouc is a certain carbide $n(C_5H_8)$ which is decomposable by heat into a series of polymerides of the carbide C_5H_8.

Caoutchin, washed with slightly acidulated water and rectified repeatedly from sodium, is a volatile liquid distilling at 177°—179°. Its density is ·855 at 0° and ·842 at 20°. In odour and many other properties it bears a strong resemblance to turpentine, especially in absorbing and combining with hydrochloric acid. Concentrated sulphuric acid modifies it, and produces a certain quantity of cymene, $C_{10}H_{14}$, but the larger part is converted into polymeric carbides, $C_{15}H_{24}$ and $C_{20}H_{32}$, and the latter by dry distillation reproduces a carbide, $C_{10}H_{16}$. No terebene appears to be formed by the action of sulphuric acid, as the most volatile of the products does not boil below 173°.

H. J. H.

Retene. By A. G. EKSTRAND (Bull. Soc. Chim. [2], xxiv, 55).

AMONG the products obtained in the dry distillation of wood is an oily body very rich in retene. On expression of this body, a greyish, soapy product is obtained having the odour of creosote, and melting at 84°—85°. This is washed with ether, dissolved in boiling alcohol, decolorised with animal charcoal, and on cooling the filtered solution, the retene is obtained pure; and in white, crystalline plates. It melts at 98·5° and has the percentage composition C 92·30, H 7·70. Its density is about 1·13 in crystals, and 1·08, after being melted and cooled. At the ordinary temperature it combines with chlorine and bromine, forming addition-products, which at a higher temperature are decomposed into products of substitution. Chromic acid forms with it several products, the chief of which is *dioxyretistene*, $C_{16}H_{14}O_2$. Fuming sulphuric acid gives with it a sulphoconjugated acid which forms well-defined salts with the alkalis, alkaline earths, and metallic oxides.

H. J. H.

Astringent Principle of Mahogany.
By MM. LATOUR and CAZENEUVE (Bull. Soc. Chim. [2], xxiv, 118).

THE astringency of mahogany is due to principles identical with those from catechu, the chief of which is catechin, $C_{20}H_{20}O_9$. Its percentage composition is C 59·43, H 5·00, O 35·57.

H. J. H.