# Organic Chemistry.

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**A New General Synthetical Method of Producing Hydrocarbons, &c.** By C. FRIEDEL and J. M. CRAFTS (*Compt. rend.*, lxxxiv, 1392—1395).—When to amyl chloride small quantities of anhydrous aluminium chloride are added, there occurs a brisk disengagement of hydrochloric acid gas, accompanied by hydrocarbons which are not absorbed by bromine. The liquid divides into two layers, and, on the completion of the reaction one of these is found to contain an extremely varied series of hydrocarbons, ranging from highly volatile bodies to products having a boiling point above that of mercury. The lower members of the series belong to the hydrocarbons $C_nH_{2n+2}$, while the higher members are richer in carbon. When the above reaction was made to take place in presence of a hydrocarbon, it was easy to obtain a combination of the radicle of the organic chloride with the hydrocarbon, less the hydrogen replaced. Thus, the authors mixed amyl chloride with a considerable excess of benzene, and having added aluminium chloride by small quantities at a time, they obtained, by fractional distillation of the products, a liquid boiling at 185—190°, and having the composition and properties of amyl-benzene, $C_6H_5.C_5H_{11}$. By using ethyl iodide instead of amyl chloride, ethyl-benzene was obtained, together with many compounds having a high boiling point. Similarly, by operating under proper conditions with benzene and methyl bromide or chloride, toluene and other higher derivatives of benzene were obtained. The other halogen salts of aluminium gave reactions analogous to those of the chloride. R. R.

**An Absorbent of Carbon Monoxide.** By C. BÖTTINGER (*Deut. Chem. Ges. Ber.*, x, 1122—1123).—On passing pure carbonic oxide into pure anhydrous hydrocyanic acid, carefully cooled, it was found to be rapidly absorbed. The product was not miscible with concentrated hydrochloric acid, but on removing it from the freezing mixture carbonic oxide was evolved in a regular stream. On gently warming, the gas is given off more rapidly, and ultimately the liquids mix, when the evolution of gas becomes stormy. The author was in hopes of obtaining glyoxylic acid, but none could be detected. C. E. G.

**On Partial Decomposition and the Formation of Ethers.** By JULIUS THOMSEN (*Deut. Chem. Ges. Ber.*, x, 1023—1026).—In a paper on the formation of ethers (p. 418 of this volume), van't Hoff has described the partial decomposition of the alcohols by the acids; and in a paper on Berthollet's theory of affinity (*Pogg. Annalen*, cxxxviii, 65) the author has treated of the partial decomposition of salts by acids. Both have arrived at exactly the same formula for expressing the amount of decomposition, and the constants of the two formulæ agree. The formation of ethers and the partial decomposition of salts by acids in aqueous solution follow the same laws. G. T. A.

**Reactions of certain Fatty Bodies under Energetic Chlorination.** By F. KRAFFT (*Deut. Chem. Ges. Ber.*, x, 801—806).—It is already known that hexyl iodide can be readily converted into perchlorobenzene. This is interesting, on account of the striking proof which it furnishes that the energetic action of chlorine on hydrocarbons not only leads to a splitting up of the carbon nucleus, but that if excess of chlorine be avoided, a closer and firmer binding together of the carbon-atoms results. In the first place the prominently interesting circumstance is pointed out that on perchlorination the most stable decomposition-products appear together, such as perchloromethane, perchlorethylene, perchlorethene, perchlorobenzene, and the long known condensation-series of perchloromethane. This appears to be the actual result of experiences gained in the field of perchlorination. The conversion already mentioned, of hexyl iodide into perchlorobenzene, finds its most probable expression in the final equation:—

$$\text{(I.)}\quad C_6H_{13}I + 10Cl_2 = C_6Cl_6 + 13HCl + ClI.$$

Of course this equation, like all of the kind, merely exhibits the ingredients on one side, and the final products on the other, but does not touch upon the mechanism of the process with its series of associations and dissociations. The inverse reaction, viz., the conversion of perchlorobenzene into hexane has already been realised by Berthelot. It thus becomes probable from the outset that the above process takes place without intermediate splitting up, and that we have here to do with an alternation of additions of chlorine on the one side, and separations of hydrogen chloride on the other. The author has lately made the observation that perchlorobenzene is never the exclusive product of the reaction. With the bye-products, when only in small quantity, perchloromethane was mostly found, and a little of a body not yet investigated, having a peculiar odour. In another preparation of perchlorobenzene, a somewhat greater quantity of hexyl iodide was employed, and a shorter time allowed for the heating in the tube. A smaller yield of perchlorobenzene was the result. The oil, formed now in greatest quantity, was purified by distillation. First perchloromethane passed over in considerable quantity; perchlorethane could not be detected; the remainder almost all distilled over from 270° to 290°. This last product on standing yielded crystals; and when strongly cooled solidified for the most part to a crystalline mass, fusing again at the heat of the hand. In this case the condensation had evidently not proceeded to the formation of perchlorobenzene, but only to that of perchloromethane and another hydrocarbon chloride. About the same time it was observed that by perchlorinating such bodies as oenanthol, oenanthylic acid, and oenanthyl chloride, there was always formed, besides perchlorobenzene, more or less of the hydrocarbon chloride boiling at 280°, with varying quantities of perchloromethane.

To obtain this new hydrocarbon chloride, hexyl iodide in portions of 10 grams at a time was heated in sealed tubes with addition of nearly equal quantities of iodine, in such a manner that the action of the iodine chloride was exhausted first at 100—120°, and then the temperature was allowed to mount gradually to about 240°, till the iodine trichloride which was continually regenerated appeared to be no more acted upon.

Under these conditions no perchlorobenzene is formed, a further very remarkable complication setting in. The new chloride was now purified by fractional distillation, passing over below 290°. To separate it from still adhering perchlorethane, the original mixture of chlorides is placed in a tubulated retort, and gradually heated in the paraffin-bath to 200—223°. The perchlorethane then escapes completely but slowly; in fact, some hours must be allowed for it. At length the heating is stopped, and the retort left to cool. The substance then solidifies after some time. Just before this solidification takes place, the perchlorethane which covers the neck of the retort may be easily removed with a pipette. The above distillation or heating must be repeated to remove the last traces of perchlorethane, the purity of the product being tested by inserting a glass rod, which should no longer become covered over with little stellate crystals of a camphor-like odour, but with slowly solidifying oily drops, or drops which do not solidify. The product is a quite colourless crystalline body, forming in flat vessels twin-crystalline plates. It may be freed from impurities by pressure. This body has the composition $C_4H_6$, and may be called provisionally* *perchloromesol*, because of its genetic relations to perchlorethane and perchlorobenzene, holding a kind of mid-position between them. In water this body is not soluble, but it crystallises from alcohol, on standing and cooling the solution, in thin shining prisms often of considerable length. When the crystallisation is hastened by dropping in the fragment of a crystal, the whole suddenly solidifies to a pasty mass, consisting of fine needles. Melting point = 39°. Perchloromesol distils over, with very slight decomposition and evolution of chlorine, between 283—284° (bar. ·733 mm.). Under the same conditions perchlorobenzene distils at 310° (uncorrected). Perchloromesol is far less volatile than perchlorethane, and does not sensibly diminish on exposure in the air. Its odour is much fainter than that of perchlorethane, and resembles that of turpentine more than that of camphor. At a very high temperature, like all lower hydrocarbon chlorides, it forms perchlorobenzene. It appears to be as little affected by iodine trichloride as perchlorethane or perchlorobenzene.

Investigations carried out with a series of fatty bodies, have shown that the formation of perchloromesol by perchlorination under special conditions, is almost as general as that of perchlorethane or perchlorobenzene. These conditions refer to the necessity of raising the temperature finally for further action of the chlorine, especially with molecules richer in carbon.

These results give increased importance to the fact that crotonylene,

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* *Note by Abstractor.*—As the author further on remarks that crotonylene, $C_4H_6$, is the hydrocarbon which is in all probability analogous to perchloromesol, it seems a pity that this idea did not suggest to him a more appropriate and scientifically consistent name than perchloro*mesol.* Why did he not call it perchlorocrotonylene? The name "perchloromesol" suggests the idea that the body in question is in some way related to the mesitylene-group, with which, however, it has nothing in common.—W. S.

the hydrocarbon which corresponds in all probability with perchloromesol, occurs in coal gas, together with pyrogenic hydrocarbons like methane, ethene, acetylene and benzene, and is formed by the condensation of ethene and of acetylene. From all this it appears that perchloromesol plays the same part in the condensation series of the hydrocarbon chlorides, as for example perchloromethane. The decomposition of the hexyl iodide to form perchloromesol, takes place (at least in its last phases) by processes quite independent of those giving rise to perchlorobenzene;

$$\text{(II.)}\quad C_6H_{13}I + 14Cl_2 = C_4Cl_6 + 2CCl_4 + 13HCl + ClI.$$

It has been already mentioned that perchlorethane often appears, besides perchloromesol, as a decomposition product. Perchlorethane, however, is often quite missing when perchloromesol is present. This fact indicates that the formation of perchlorethane from hexyl iodide is quite independent of that of perchlormesol, and a further equation is necessary, in which *à priori* only the proportional quantities of perchlorethane and perchloromethane remain doubtful:

$$\text{(III.)}\quad C_6H_{13}I + 17Cl_2 = 2C_2Cl_6 + 2CCl_4 + 13HCl + ClI.$$

That the process can go on in this manner is shown by the fact that normal butyl iodide heated with excess of iodine chloride to 250°, is easily converted into perchlorethane—

$$C_4H_9I + 11Cl_2 = 2C_2Cl_6 + 9HCl + ClI.$$

W. S.

**Reduction of Organic Haloïd Compounds by Zinc and Zinc-dust.** By A. SABANEJEFF (*Bull. Soc. Chim.*, xxvii, 446).—At ordinary temperatures the product of the reaction of granulated zinc on an alcoholic solution of tetrabromated acetylene is dibromacetylene, whilst at higher temperatures the reduction is complete and acetylene is formed. Zinc acts in an analogous manner on ethylene bromide and propylene bromide, but it is without action on trimethylene bromide. In presence of water, zinc decomposes chloroform with liberation of marsh-gas, thus:—

$$2CHCl_3 + 3H_2O + 3Zn_2 = 2CH_4 + 3ZnCl_2$$

and ethyl iodide is easily reduced to ethane. R. R.

**Normal Propylene.** By E. REBOUL and E. BOURGOIN (*Compt. rend.*, lxxxiv, 1395—1398).—As succinic acid in alkaline solution splits up, under the influence of an electric current, into ethylene and carbonic acid, the authors hoped, by the electrolysis of potassium pyrotartrate, the superior homologue of the succinate, to obtain carbonic acid and trimethylene. The products collected at the positive pole were, however, found to be only a mixture of oxygen, carbonic acid, and carbonic oxide gases. Trimethylene bromide also failed to yield trimethylene, by treatment either with sodium or with nascent hydrogen. R. R.

**The Inability of Propylene to Combine with Water.** By E. LINNEMANN (*Deut. Chem. Ges. Ber.*, x, 1111—1121).—Siersch, on decomposing normal propylamine nitrite by boiling it with water, found that, besides nitrogen and nitrosodipropylamine, a mixture of alcohols was formed: this, when submitted to distillation, yielded a fraction boiling at 89—96°, and another boiling at 81—85°, which he considered to be pseudopropyl alcohol. Meyer and Foster have recently repeated this experiment and obtained, besides nitrogen and nitrosodipropylamine, propyl alcohol, pseudopropyl alcohol, and propylene; moreover, butylamine nitrite is decomposed in a manner precisely similar. Meyer lays great stress on the formation of propylene and butylene in these reactions, and considers that the formation of the secondary alcohol is due to the union of the olefine with water. It seemed to the author, therefore, a point of the greatest importance to obtain some evidence of the behaviour of propylene with water under various circumstances, especially as if the two did unite, they might form either pseudopropyl or normalpropyl alcohol.

In the first series of experiments the action of water at 100° on nascent propylene was tried by heating pure propylene bromide with zinc and water; propylene and hydrogen were evolved in abundance, but no propane. The hydrogen is formed by the action of zinc bromide on the metallic zinc in presence of water, zinc oxide being separated; in this way a comparatively small quantity of zinc bromide will yield a large quantity of hydrogen. If the zinc is not free from arsenic, the propylene evolved in this reaction will be contaminated with arseniuretted hydrogen, and lead to an error in the determination of the amount of propylene evolved from a given weight of propylene bromide. Two experiments were made with every precaution, in both of which the quantity of propylene evolved was found to be only 5 per cent. less than that required by theory. A large quantity of propylene bromide (430 grams) was then decomposed in a similar manner, and the evolved gases were carefully washed, but neither in the retort nor in the wash-water could any trace of an alcohol be detected.

In the second series of experiments, propylene bromide was heated at 100° with zinc and a solution of potassic hydrate, the reaction being:—

$$C_3H_6Br_2 + Zn + 4KHO = C_3H_6 + 2H_2O + 2KBr + Zn(KO)_2.$$

In this case the nascent propylene is brought in contact with nascent water, at 100°. The analytical results showed that the propylene evolved fell short of the theoretical amount indicated in the above equation by about 12 to 16 per cent., but not a trace of any alcohol could be discovered. These experiments prove conclusively that at 100°, nascent propylene does not combine with water, even if the latter be nascent. The author has not yet succeeded in ascertaining what is the cause of the amount of propylene given off being less than that indicated by theory.

The latter part of the paper is occupied by a discussion of alleged misstatements on the part of Meyer and Foster, and of Meyer, Barbieri, and Forster, with regard to the results obtained by the author in the decomposition of normal propylamine nitrite and normal butylamine nitrite. C. E. G.

**Preparation of Allyl Iodide and of Acetic Anhydride.** By SAYTZEFF and KANONNIKOFF (*Bull. Soc. Chim.*, xxvii, 433).—Allyl iodide was prepared from 1,000 grams of iodine, 3,000 of glycerin, and 300 of phosphorus. The phosphorus was added to the mixture of glycerin and iodine, in small quantities at a time. The distillation was carried on in a current of dry carbonic acid gas, in order to prevent any explosion. The quantity of $C_3H_5I$ obtained about 1150 grams, whilst Claus and Oppenheim's method would yield only 700 grams.

Acetic anhydride was prepared by the action of acetyl chloride on crystallisable acetic acid. Half the theoretical quantity, in a perfectly pure state, was thus obtained. R. R.

**Retarding Action of Glycerin.**—By DUNN (*Chem. News*, xxxvi, 88).—The action of a glycerin solution of iodine on iron was tried. Four cylinders were taken, and into each was put 25 c.c. of a solution of iodine in iodide of potassium. They were then made up to 50 c.c., two with water and two with glycerin. A piece of iron wire was then placed in each; in two, the iron wire was suspended near the surface of the fluid, and in the others, it was placed at the bottom.

The water solutions were found, after a week, to have been acted on much more rapidly than the glycerin solutions, the difference being most marked in the case of those in which the wire was at the surface. In all the cylinders, however, the wire became covered with bubbles of gas, so that the protective action of the film of gas is not eliminated by using iodine. By using bromine instead of iodine, the iron was rapidly attacked in the water cylinders, but the action in the glycerin solution appeared to be complicated by other reactions; the bromine in one cylinder was completely decolorised save at the bottom, and in the other, the colour was paler than originally. In this case, also, bubbles of gas were observed, larger and fewer in the water solutions than in the glycerin solutions. D. B.

**Crystallised Grape-sugar.** By HALSE and STEINER (*Chem. News*, xxxvi, 87—88).—In 1875, a cargo of starch-sugar was returned from Australia and offered for sale in England, when it was found to be partially crystallised and to resemble cane-sugar, and it actually was taken as such. The authors for this reason obtained samples, which were analysed. The samples were of three different sorts—amorphous, amorphous with superficial crystallisation, and others completely crystallised. The amorphous substance, similar to starch-sugar, is greyish-white with stripes of brown passing through it. It feels dry, is hard, and slightly hygroscopical. The second sample consisted of amorphous dark-brown lumps of a very pasty nature, with completely developed crystalline groups (rosettes) imbedded in them, and a yellow, very well crystallised thin crust on some parts of the surface. The rosettes are of the size of a bean up to that of a chestnut, and have a clear amber or pale-yellow colour, with a fatty glance. To free the rosettes from the adhering amorphous substance, they were first immersed in dilute alcohol, then dipped in absolute alcohol, and subsequently dried with filter paper. The third kind of sample was in completely crystallised compact pieces, remaining dry in the air, and being very hard. By treatment with alcohol, a part of the mass was dissolved out and a network of the larger warty crystals of an amber-yellow colour was obtained, while the pieces of the very fine crystallisation are of very much darker colour, and soluble in alcohol. The following are the results of the analyses:—

*Crystals.*

| | Rosettes. | Nodules of the size of a bean. | Nodules smaller. | $C_6H_{12}O_6 + H_2O$ corresponding to. |
|---|---|---|---|---|
| Ash...... | trace | trace | trace | — |
| Water.... | 9·45 | 9·26 | 9·45 | 9·09 |
| Glucose .. | 90·35 | 90·45 | 90·20 | 90·91 |
| Dextrin .. | 0·20 | 0·29 | 0·35 | — |
| | 100·00 | 100·00 | 100·00 | 100·00 |

*Samples.*

| | Amorph. with rosettes. | Amorph. without rosettes. | Fine crystallised. | Warty, small. | Warty, larger. | Amorphous. |
|---|---|---|---|---|---|---|
| Ash ...... | 0·36 | 0·37 | 0·33 | 0·29 | 0·15 | 0·45 |
| Water .... | 12·00 | 12·20 | 11·80 | 11·20 | 10·50 | 8·60 |
| Glucose ... | 80·10 | 78·60 | 81·40 | 84·60 | 85·00 | 83·90 |
| Dextrin ... | 1·74 | 1·90 | 1·53 | 0·79 | 0·68 | 1·54 |
| Optic inact. subst. .. | 5·80 | 6·93 | 4·94 | 3·12 | 3·67 | 5·51 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

In considering the results of the analyses of the samples with the warty crystals, the author mentions that only an increase of sugar takes place with the growth of the crytallisation, and it may also be assumed that if the adherent amorphous mass could be completely separated from the crystals, the latter would represent pure grape-sugar. The darkening of the amorphous mass may have been effected by the combined action on partly caramelised products, of moisture, lime, and of the ammonia liberated by the putrefaction of the albuminous matter (gluten) present. A long voyage in a tropical climate furnished not only the necessary conditions for the melting of the substance and for the development of ammonia, but was also favourable to such a slow crystallisation as grape-sugar requires. Once the crystallisation introduced, a continual growth took place.

D. B.

**Optically Inactive Sugar.** By W. E. HALSE and E. STEINES (*Chem. News*, xxxvi, 107).—A sample of molasses, the drainings of molasses into a ship's hold, and consequently mixed with bilge-water, had the following composition: organic matter, 42·50 p. c.; water, 51·75 p. c.; ash, 5·75 p. c. After clarification with subacetate of lead, it reduced copper solution to an amount equal to 27·70 p. c. of glucose. It was optically inactive. To decide whether it was a mixture of levulose with dextrose or saccharose, it was partially fermented, and even then remained without action on polarised light. Even after treatment with caustic soda to destroy levulose, it remained inactive. The only possible conclusion accordingly is that the sugar was an inactive modification. W. R.

**Action of Acid Chlorides on Organo-Zinc Compounds.** By D. PAWLOW (*Liebig's Annalen*, clxxxvii, 104—143).—*Formation of Ketones.*—The author has made quantitative experiments on the production of acetone by the reaction of acetic chloride with zinc methide. He finds that with 2 mols. of the chloride to 1 mol. of zinc methide, the yield of acetone is about 80 per cent. of the theoretical amount, and that the yield is not greatly increased by employing larger proportions of zinc methide. The reaction of 2 mol. R'COCl with 1 mol. $ZnR'_2$ may serve for the synthesis of ketones in general, but for the preparation of the pinacolins (of which tertiary butyl-methyl ketone is the simplest) it is advantageous to employ 1½ or 2 mol. of the zinc-compound to 1 mol. of acid chloride, on account of the greater cost of the latter.

*Synthesis of Tertiary Alcohols containing three Different Radicles.*—The first known representatives of this class of bodies, *methyl-ethyl-propyl carbinol* and *methyl-ethyl-isopropyl carbinol*, have been obtained by the author by the reaction of butyric chloride or isobutyric chloride on a mixture of zinc methide and zinc ethide, and subsequent decomposition of the product with water.

Methyl-ethyl-propyl carbinol is a colourless liquid, having a faint camphor-like odour, and boiling at 135-138°. It forms with gaseous hydrogen iodide a compound which, by treatment with alcoholic potash, yields the corresponding heptylene. The latter is a colourless liquid, smelling like amylene and boiling between 90° and 95°; it combines with bromine to form the compound $C_7H_{14}Br_2$.

Methyl-ethyl-isopropyl carbinol boils at 124—127°. It forms with hydrogen iodide a compound which is decomposed by alcoholic potash, yielding a heptylene boiling at 75—80°, and combining with two atoms of bromine.

*By-products in the Preparation of Ketones.*—In the reactions of acid chlorides with organo-zinc compounds, there are formed, besides ketones and tertiary alcohols, certain products of high boiling-point, the nature of which has not hitherto been made out. These substances the author finds to be condensation-products of ketones, formed by the direct action of the zinc-compounds. Thus, for instance, zinc ethide or methide acting on acetone produces mesityl oxide:

$$2C_3H_6O + ZnR_2' = C_6H_{10}O + 2R'H + ZnO.$$

Mesityl oxide, however, is not the only product thus formed from acetone. It seems probable that further condensation takes place, owing to the elimination of more water, higher products being thus formed.

*Some Bodies analogous to Mesityl Oxide.*—1. A substance having the formula $C_8H_{14}O$ is formed, together with methyl-ethyl-ketone, by the reaction of equal numbers of molecules of propionic chloride and zinc methide. It is a colourless liquid, insoluble in water, boiling at 167—168°. Sp. gr. 0·877 at 0°; 0·862 at 18°. Its formation from methyl-ethyl-ketone may be represented by the equation:—

$$2C_4H_8O - H_2O = C_8H_{14}O.$$

This substance forms with hydrogen iodide a heavy dark-coloured oil, represented by the formula $C_8H_{15}IO$.

2. Similarly, the compound $C_{10}H_{18}O$ is formed as by-product in the reaction between isobutyric chloride and zinc methide. It is a colourless liquid of peculiar odour, insoluble in water, boiling at 189—191°. Sp. gr. 0·87 at 0°; 0·855 at 20°. It combines with hydrogen chloride to form a yellowish oily body ($C_{10}H_{19}ClO$) having the odour of turpentine; and with hydrogen iodide to form a dark-coloured crystalline body.

3. A by-product having the formula $C_{12}H_{22}O$ is formed in the preparation of dimethyl-isobutyl carbinol. It is a colourless liquid, insoluble in water, boiling at 217—219°. Sp. gr. 0·864 at 0°; 0·849 at 20°. Like the two preceding bodies, it combines with hydrogen chloride and iodide.

All these compounds combine with bromine, and may, therefore, be regarded as non-saturated ketones. Their chemical structure has yet to be made out. J. R.

**Constitution of Cyanamide.** By M. FILETI and R. SCHIFF (*Gazetta chimica italiana*, vii, 204—209).—It has long been a question as to whether the formula, $CN.NH_2$ or $HN{=}C{=}NH$, represents the constitution of cyanamide. The first, however adapts itself most readily to the explanation of the formation of cyanamide by the action of ammonia on cyanogen chloride: $CN.Cl + NH_3 = CN.NH_2 + HCl$, and also by the desulphuration of sulphurea, $S{=}C(NH_2)_2 = CN.NH_2 + H_2S$, whilst Mulder urges that the existence of the silver derivativo of cyanamide, $CN_2Ag_2$, requires cyanamide to have the formula, $HN{=}C{=}NH$, as only in imides can the hydrogen be displaced by metals. This argument, however, is not conclusive, as several amines and amides containing metals exist, such as the sodio-amides and anilines, and argento-acetamide. Moreover, aldehyde, as Knop has shown, acts on cyanamide, giving a derivative of melamine, which cannot be explained with the imide formula. Again, amides unite with chloral, forming substitution-products of chloral-ammonia, whilst no compound of chloral with an imide is known. This reaction takes place with cyanamide, affording strong evidence that it is an amide of the formula $CN.NH_2$. Cyanamide dissolves in chloral with development of heat, and the syrupy product, after being allowed to stand for 24 hours, and then heated at 100°, solidifies, and at the same time swells up to about 20 times its bulk. It is soluble in alcohol, ether, and chloroform, but separates as a resin. The authors consider the syrupy product as a simple product of addition, $CN.NH.CH(OH).CCl_3$, whilst the solid has probably triple that formula, and is a product of the addition of melamine.

When the diargentic compound of cyanimide is heated with ethyl iodide, silver iodide is formed, and a red liquid which, from the results of analysis and its boiling point, was proved to be diethylcyanamide. Heated for some time with hydrochloric acid, the crude product yielded a mixture of ammonium chloride and diethylamine hydrochloride.

These results prove that the only possible formula for cyanamide is $CN.NH_2$.
C. E. G.

**Absence of Rotatory Power in Iodide of Triethyl-methyl-stibine.** By J. A. LE BEL (*Bull. Soc. Chem.*, xxvii, 444, 445).—The dextrogyratory power attributed to iodide of triethyl-methyl-stibine, was indeed found to exist in a sample prepared by the author, but to be extremely small. As, however, its presence contradicts the law which asserts that optically active compounds cannot be formed without some optically active constituent, the author sought for such a constituent among the substances used in the preparations. He found it in the commercial alcohol, which is contaminated with more or less amylic alcohol, an optically active substance. On submitting the alcohol used in the preparation of the ethyl iodide to a process by which the optical power of the contained amylic alcohol was obviated, the author was able to prepare iodide of triethyl-methyl-stibine in which no rotatory power could be detected.
R. R.

**Formation of Sulphinic Acids of the Fatty Group from the Chloranhydrides of the Sulphonic Acids.** By C. PAULY (*Deut. Chem. Ges. Ber.*, x, 941—943).—Schiller and Otto having shown that the chloranhydrides of the aromatic sulphonic acids (benzene-sulphonic and paratoluene-sulphonic acids) could easily be converted into the zinc salts of the sulphinic acids by the action of zinc dust, it was thought interesting to determine whether this method could be applied to the preparation of sulphinic acids of the fatty group. Accordingly the author has studied the behaviour of the ethyl- and isobutyl-sulphochlorides towards zinc-dust, and found his expectations realised, the sulphinic zinc salts being formed just as readily as those in the aromatic series.

I. *Ethyl-sulphinic Acid*, $C_2H_6SO_2$.—Ethyl sulphochloride and zinc dust were allowed to react under water, which took up the sulphinic zinc salt formed. This salt was purified by evaporation of the solution, out of which it crystallised, and then it was recrystallised from alcohol. It possessed the composition and properties of the zinc ethylsulphinate, described by Wischin as prepared by the action of sulphur dioxide on zinc-ethyl. Analysis yielded numbers agreeing with the formula, $(C_2H_5SO_2)_2Zn + H_2O$.

The barium and sodium salts were prepared from this zinc salt, analysed and identified. Both salts crystallised with difficulty. The sodium salt was deliquescent.

II. *Isobutylsulphinic Acid*, $C_4H_{10}SO_2$.—The isobutyl sulphochloride was prepared by the action of phosphorus pentachloride on potassium isobutylsulphonate, the sulphonic acid by oxidation of the mercaptan with nitric acid. The sulphochloride is a colourless, tolerably mobile liquid, heavier than water, and not decomposed by the latter in the cold. By taking small quantities at a time, it may be distilled without decomposition (between 189° and 191°, uncorrected). Its vapours have a penetrating odour, and strongly irritate the mucous membrane. Analysis confirmed the formula, $C_4H_9SO_2.Cl$.

It was converted into zinc sulphinate by treatment with zinc-dust under water, like the ethyl sulpho-chloride. This salt was extracted from the frothy mass by boiling water, and recrystallised from alcohol.

*Zinc isobutylsulphinate* forms white and tolerably large plates, with a mother-of-pearl lustre, freely soluble in hot water and alcohol, sparingly in cold. The salt obtained from alcohol is anhydrous, but from water it appears to separate with water of crystallisation. Analysis confirmed the formula, $(C_4H_9SO_2)_2Zn$, (crystallised from alcohol).

The *sodium salt* crystallises with difficulty, and is easily soluble in water and alcohol. It forms thin hygroscopic plates. The *isobutylsulphinic acid* prepared from this salt by addition of sulphuric acid, shaking with ether, &c., forms a faint yellow syrup, strongly acid, bleaching litmus paper, and easily soluble in water. After long standing in the exsiccator it showed no disposition to crystallise. The *barium salt*, prepared from the free acid, is very soluble in water, like the sodium salt, also in alcohol, and crystallises with difficultly. Nascent hydrogen easily converts the isobutylsulphinic acid into the corresponding mercaptan. W. S.

**Behaviour of Sodium Acrylate with Fused Potash.** By E. LINNEMANN (*Deut. Chem. Ges. Ber.*, x, 1121—1122).—In 1873 the author stated that Redtenbacher's observation that sodium acrylate gave acetic and formic acids when fused with potassium hydrate, was incorrect, since he found that this salt was carbonised when added to the fused alkali. As, however, acrylic acid when heated with a solution of sodium hydrate yields ethylenelactic acid and hydracrylic acid, and the latter is decomposed by fusion with potash, giving rise to acetic and formic acids, it is evident that if Redtenbacher had evaporated a solution of potassium hydrate to which he had added the sodium acrylate, and subsequently fused the mixture; or if the potash had contained so much water that it fused below the temperature at which sodium acrylate is decomposed, a hydracrylate would have been formed and subsequently converted into acetate and formate. From Redtenbacher's description, however, it does not appear in what way he conducted the experiment. C. E. G.

**On the Non-saturated Acids.** By RUDOLPH FITTIG. Part I. (*Liebig's Annalen*, clxxxvii, 42—104).—1. *The Crotonic Acid from Citraconic and Mesaconic Acids.*—Citraconic anhydride, when heated to

100° with hydrochloric acid saturated at 0°, is partially converted into citrachloropyrotartaric acid, which is resolved by boiling with strong soda-ley into an acid having the composition of crotonic acid, $C_4H_6O_2$, but differing in properties from any of the three known varieties of that body. The product crystallises from water, in which it is easily soluble, in long, colourless prisms, which melt at 16°. It has a strong but not unpleasant odour, dissolves in all proportions of alcohol and ether, and boils constantly at 160·5°.

The *calcium salt* $(C_4H_5O_2)_2Ca$, crystallises in tufts of long colourless needles, easily soluble in water.

The *silver salt*, $C_4H_5O_2Ag$, precipitated by silver nitrate from the calcium salt, crystallises from boiling water in long needles or in small compact crystals, which are scarcely affected by light. It dissolves sparingly in cold, and more freely in hot water. The dry salt does not lose weight at 70°, but about 100° a sudden decomposition takes place throughout the mass, the odour of the acid being evolved.

The acid is completely decomposed by melting potash at a comparatively low temperature, being resolved into propionic acid and carbon dioxide only.

Mesaconic acid heated to 140° with strong hydrochloric acid, is converted into mesachloropyrotartaric acid; and the latter, by boiling with soda-ley, yields a crotonic acid identical with that obtained from citraconic acid.

2. *Methacrylic Acid.*—The author has compared the crotonic acid obtained as above with methacrylic acid, and finds that the two are identical in their properties and in the characters of their salts.

Methacrylic acid is completely converted into isobutyric acid by the action of sodium-amalgam at the ordinary temperature. This fact agrees with the observation of Gromont and Swarts, that Kekulé's monobromocrotonic acid obtained from citradibromopyrotartaric acid is converted by the action of sodium amalgam into isobutyric acid.

Methacrylic acid dissolves in concentrated hydriodic acid at the ordinary temperature, forming a clear solution. When the hydriodic acid is in large excess, the solution deposits, after some time, tufts of long prisms consisting of *iodisobutyric acid*, $C_4H_7IO_2$ This body dissolves easily in carbon bisulphide, and crystallises therefrom in brilliant tablets. It melts at 36°.

3. *Xeronic Acid, a new derivative of Citraconic Acid.*—Xeronic acid is the name given by the author to an acid, the anhydride of which is formed, together with citraconic anhydride, in the distillation of citric acid. Xeronic anhydride is formed whenever citraconic anhydride is distilled. Citraconic anhydride begins to boil at 212°, and the greater part of it distils about that temperature; but at the same time a constant evolution of carbon dioxide takes place, and the temperature gradually rises until, at 250°, there passes over a yellow oil consisting chiefly of a mixture of citraconic and xeronic anhydrides. The decomposition of citraconic anhydride goes on even below its boiling point, direct experiment having shown that carbon dioxide is slowly and regularly evolved at 160°.

*Xeronic Anhydride*, $C_8H_{10}O_3$, is a colourless liquid of peculiar odour, boiling at 242° (mercury entirely in vapour), and remaining liquid at

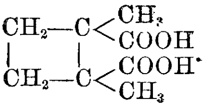
− 18°. It distils readily with water, in which it sinks, dissolving sparingly. In alcohol and ether it dissolves easily. The corresponding acid appears not to exist in the free state, but to break up, like carbonic, sulphurous, and arsenious acids, into the anhydride and water. Hence the name (from ξηρός, dry). The anhydride does not combine with water. A dilute solution of the sodium salt, when acidified with hydrochloric acid, is clear at first, but after a time becomes turbid and deposits the anhydride.

The *silver salt* $C_8H_{10}O_4Ag_2$, thrown down by silver nitrate from a solution of the anhydride in ammonia, is a heavy, white, pulverulent precipitate, very sparingly soluble in boiling water, and not affected by light.

The *calcium salt*, $C_8H_{10}O_4Ca + H_2O$, is the most characteristic of the salts of xeronic acid, and serves admirably for the detection of the acid, and for the separation of this from other acids. It is easily obtained by dissolving xeronic anhydride in ammonia, driving off excess of ammonia by boiling, and adding calcium chloride. At ordinary temperatures the solution remains clear, even after long standing; but when gently heated, it becomes turbid, and on boiling for a short time, the whole of the calcium salt is deposited in the form of a flocculent precipitate, which afterwards turns crystalline. The salt thus obtained is soluble only in a very large quantity of water. It gives off half a molecule of water at 130—140°, and the rest at 170°.

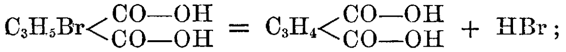
The *barium salt*, $C_8H_{10}O_4Ba + \frac{1}{2}H_2O$, is obtained in the same manner as the calcium salt, which it resembles in every respect. It loses its water at 140°.

Xeronic acid is shown by the composition of its salts to be a dibasic acid of the formula $C_8H_{12}O_4 = C_6H_{10}{<}\begin{smallmatrix}COOH\\COOH\end{smallmatrix}$, breaking up, however, when set free, into water and the anhydride, $C_6H_{10}{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}O$. It is homologous with citraconic acid, but behaves in an entirely different manner. It combines neither with nascent hydrogen nor with bromine, and therefore does not belong to the so-called non-saturated acids. Seeing that xeronic acid is polymeric with methacrylic acid, and that citraconic acid is resolved, in certain circumstances, into carbon dioxide and methacrylic acid, whilst xeronic anhydride is likewise produced from citraconic anhydride by elimination of carbon dioxide, it seems very probable that xeronic acid is formed by the union of two molecules of methacrylic acid, and is constituted in accordance with the formula—



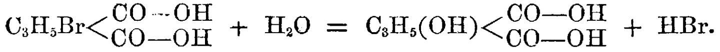
4. *Addition-products of Itaconic, Citraconic, and Mesaconic Acids.*—Itaconic acid, in fine powder, is converted by contact for a few days with fuming hydrobromic acid (in which it does not dissolve) into small hard crystals of itabromopyrotartaric acid, melting at 137°.

This product, when heated with water, is completely resolved into itaconic and itamalic acids and hydrogen bromide:



$$C_3H_5Br{<}\begin{array}{l}CO{-}OH\\ CO{-}OH\end{array} = C_3H_4{<}\begin{array}{l}CO{-}OH\\ CO{-}OH\end{array} + HBr;$$

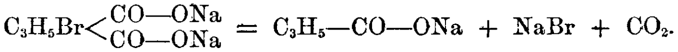
Itaconic acid.



$$C_3H_5Br{<}\begin{array}{l}CO{-}OH\\ CO{-}OH\end{array} + H_2O = C_3H_5(OH){<}\begin{array}{l}CO{-}OH\\ CO{-}OH\end{array} + HBr.$$

Itamalic acid.

Citraconic acid and its anhydride dissolve readily in fuming hydrobromic acid, and in the course of a few days are converted into hard, shining crystals of citrabromopyrotartaric acid melting at 148°. On prolonged boiling of its aqueous solution, this substance gives off the whole of its bromine as hydrogen bromide, and is resolved into methacrylic and mesaconic acids: in alkaline solution, it is decomposed much more rapidly on warming, yielding almost exclusively methacrylic acid:



$$C_3H_5Br{<}\begin{array}{l}CO{-}ONa\\ CO{-}ONa\end{array} = C_3H_5{-}CO{-}ONa + NaBr + CO_2.$$

This decomposition of citrabromopyrotartaric acid affords the best means of preparing methacrylic acid, which may thus be easily obtained in large quantity.

Mesaconic acid is converted by heating to 140° with concentrated hydrobromic acid into citrabromopyrotartaric acid, identical with that formed by the action of hydrobromic acid on citraconic acid in the cold.

*Dibromopyrotartaric Acids from Citraconic and Mesaconic Acids.*—Bromine combines very readily with citraconic acid in the cold; with mesaconic acid only on warming. Both the products ($C_5H_6O_4Br_2$) crystallise easily: that obtained from citraconic acid melts at 150°; that from mesaconic acid, at 170°. By prolonged boiling with water, they are resolved into carbon dioxide, hydrogen bromide, and bromomethacrylic acid.

5. *Behaviour of Fumaric and Maleic Acids with fuming Hydrobromic Acid.*—Fumaric acid, when heated with concentrated hydrobromic acid in sealed tubes is converted into monobromosuccinic acid, apparently identical with that formed by the action of bromine on succinic acid. When boiled with water the brominated acid is almost entirely re-converted into fumaric acid.

Maleic acid, in fine powder, dissolves quickly in cold fuming hydrobromic acid, and is almost immediately converted into fumaric and monobromosuccinic acids in equal numbers of molecules.

Maleic anhydride behaves in the same manner.

6. *Constitution of the Non-saturated Dibasic Acids.*—The author's conclusions as to the constitution of these acids, based upon the foregoing facts, coincide with those given in a previous paper, of which an abstract appears in this volume (p. 429). J. R.

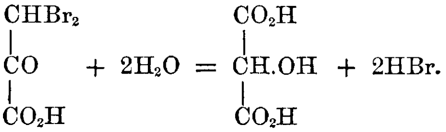
**Diallyl-oxalic Acid.** By M. Saytzeff (*Bull. Soc. Chim.*, xxvii, 446).—By acting on oxalic ether with zinc and allyl iodide, the author obtained diallyloxalic ether, which he heated with barium hydrate, and having removed the excess of the latter by means of carbonic acid, decomposed by sulphuric acid the barium salt which had been formed, and extracted the diallyloxalic acid with ether. The acid presents itself in minute crystals, soluble in ether and alcohol, but not readily soluble in water. These crystals melt at 48·5°, but the acid cannot be distilled without decomposition. By oxidation this acid gives rise to a resinous substance which has not yet been examined. R. R.

**Glutamic Acid from the Juice of Vetch-germs.** By GORUP-BESANEZ (*Deut. Chem. Ges. Ber*, x, 780—782).—It has been shown by the author and also by Cossa, that during the germination of the vetch, leucine is always formed, together with asparagin. It is, therefore, reasonable to suspect, also, the presence of tyrosine and glutamic acid in the juice of the vetch-germs. This latter acid has been already found by Scheibler in beet-root molasses. Evidently during the germination of the vetch a splitting-up of the albuminous body of the reserve-substance of the seed takes place, chemically coinciding with that which occurs during the renewal of substance in the animal economy, and likewise externally to the living organism by the action of known chemical agents. Attempts to obtain glutamic acid from the above-mentioned source were, however, unsuccessful, until a research by E. Schulze and Barbieri on the occurrence of an amide of glutamic acid in gourd-germs, suggested the proper course to be taken. The mother-liquors of the separated leucine were boiled for some hours with hydrochloric acid in a vessel with inverted condenser, and then precipitated with lead acetate in excess. The filtrate, evaporated to a small bulk, was treated with a large excess of alcohol. The precipitate of lead salts, completely separated out after twenty-four hours' standing, was thrown on a filter, washed, and then suspended in water, and a stream of sulphuretted hydrogen passed through. The hydrochloric acid in the filtrate was removed by oxide of silver, and the filtrate evaporated to a small bulk. White crystalline crusts separated gradually, having a strongly acid reaction, and reducing Fehling's solution on warming. The aqueous solution of the acid was neutralised by boiling with copper carbonate, and filtering hot. From the deep-blue filtrate the characteristic, shining, bright-blue needles of glutamate of copper separated out. These crystals contain water of crystallisation, which they lose at 140°. The formula found to coincide best with the results of analysis was $C_5H_7CuNO_4 + 2\frac{1}{2}H_2O$. The author hopes soon to obtain further results with a fresh quantity of material just prepared. There appears to be no longer any doubt as to the existence of a very soluble glutamine. Hitherto tyrosine has not been obtained in more than traces from the source afore-named. It was easily detected by L. Meyer's delicate reaction with mercuric nitrate and nitrous acid. W. S.

**Action of Potassium Cyanide on Chloromaleic Ether.** By A. CLAUS (*Deut. Chem. Ges. Ber.*, x, 928—930).—Continuing his researches on the action of potassium cyanide on halogenised organic compounds, the author, in conjunction with Franck, has studied the behaviour of chloromaleic ether. To prepare this ether it is recommended to take choromaleic chloride, directly prepared by heating together tartaric acid and phosphorus pentachloride, and to decompose it with absolute alcohol. After repeated distillation, the ether is then obtained as an almost colourless liquid, distilling without decomposition. Boiling point at 735 mm. bar. = 243—245° (uncorrected). Spec. grav. at 20° = 1·178. 1 mol. of the ether is treated with 3 mols. potassium cyanide dissolved in double its weight of water, and to this mixture so much alcohol is added that a clear solution is obtained. After some five minutes the liquid becomes hot and potassium chloride crystallises out, whilst the solution assumes an intensely brown colour. After several hours' standing the reaction appears to be at an end, no more chloromaleic ether separating out on addition of water. Efforts were made to isolate the cyanised products which were at first formed, but without success. Mixtures were always obtained, the separation of which could not be effected, the products when operated upon suffering a further partial conversion. Continued boiling with potash or hydrochloric acid effects the complete conversion of the originally formed or partially decomposed cyanogen-compounds, succinic acid being formed. Considering the final result in itself, the reaction with potassium cyanide is a reduction, the conversion of chloromaleic acid into succinic acid being effected by substitution of hydrogen for chlorine, and at the same time addition of hydrogen taking place. This reaction is quite analogous to that which Böttinger obtained by treating pyroracemic acid with hydrocyanic and hydrochloric acids, whereby lactic acid was produced. The simplest explanation of the foregoing accords well with an earlier assumption of the author, that at first a dicyanosuccinic acid arises, in consequence of simultaneous substitution of chlorine by cyanogen and addition of hydrocyanic acid. This dicyanosuccinic acid, on the decomposition of its cyanogen-residue, retains in the molecule, not two carboxyl groups, but simply two hydrogen-atoms, carbonic acid being given off. The study of the behaviour of monobromosuccinic and dibromosuccinic acid to potassium cyanide, which is in progress, may be expected to yield similar results.

W. S.

**Tartronic Acid.** By E. GRIMAUX (*Bull. Soc. Chim.*, xxvii, 440—442).—When baryta water is added to a solution of dibromated pyruvic acid, a barium salt is precipitated, which by decomposition with sulphuric acid yields a crystalline substance identical with tartronic acid, $C_3H_4O_5$. Their action may be represented by this equation :—



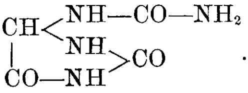
$$\begin{array}{l} CHBr_2 \\ | \\ CO \\ | \\ CO_2H \end{array} + 2H_2O = \begin{array}{l} CO_2H \\ | \\ CH.OH \\ | \\ CO_2H \end{array} + 2HBr.$$

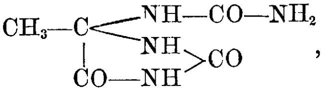
R. R.

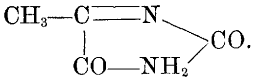
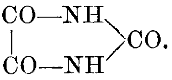
**Synthetic Researches on the Uric Acid Group.** By E. GRIMAUX (*Ann. Chim. Phys.*, 356—432).—The contents of this paper have been published in the *Comptes rendus*, and abstracts of the work have appeared in vols. xxvii—xxix of this *Journal*.

The following are the most important results of this investigation :—

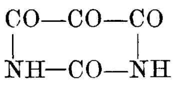
The action of aldehydic and acetonic acids on urea gives rise to compounds analogous in their properties and constitution to the true uric derivatives.

Glyoxylic diureide is identical with allantoïn,  $\begin{array}{l}\mathrm{CH}<\begin{array}{l}\mathrm{NH{-}CO{-}NH_2}\\ \mathrm{NH}\end{array}\!\!>\mathrm{CO}\\ |\\ \mathrm{CO{-}NH}\end{array}$ .

Pyvuvil,  $\begin{array}{l}\mathrm{CH_3{-}C}<\begin{array}{l}\mathrm{NH{-}CO{-}NH_2}\\ \mathrm{NH}\end{array}\!\!>\mathrm{CO}\\ \quad|\\ \quad\mathrm{CO{-}NH}\end{array}$ , is a homologue of this body.

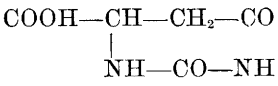
Monopyruvic ureide is represented thus:  $\begin{array}{l}\mathrm{CH_3{-}C{=}N}\\ \quad|\\ \quad\mathrm{CO{-}NH_2}\end{array}\!\!>\mathrm{CO}$. The pyruvic ureides are intimately connected with the uric series by their decomposition into parabanic acid,  $\begin{array}{l}\mathrm{CO{-}NH}\\ |\\ \mathrm{CO{-}NH}\end{array}\!\!>\mathrm{CO}$. The constitution of the malic ureides is similar to that of the uric derivatives.

The malic ureides are connected with the alloxanic compounds by their decomposition into iso-alloxanates—



$$\begin{array}{l}\mathrm{CO{-}CO{-}CO}\\ |\qquad\quad\ |\\ \mathrm{NH{-}CO{-}NH}\end{array}$$

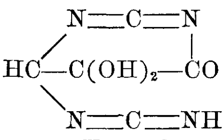
Alloxan.



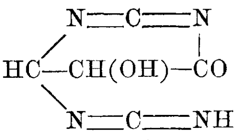
$$\begin{array}{l}\mathrm{COOH{-}CH{-}CH_2{-}CO}\\ \qquad\quad\ \ |\\ \qquad\quad\ \mathrm{NH{-}CO{-}NH}\end{array}$$

Malyluric acid.

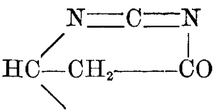
The decomposition of uric acid (1) into urea and alloxan, and (2) into allantoïn and carbon dioxide, and the reduction of the acid by nascent hydrogen to xanthine and sarcine, show that uric acid, xanthine, sarcine, and guanine have the following constitution :—



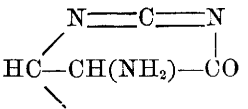
Uric acid.



Xanthine.

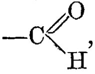
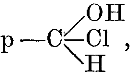


Sarcine (hypoxanthine).

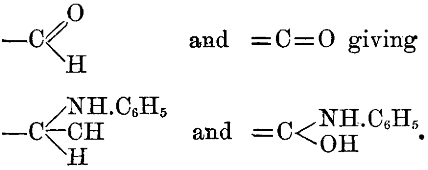


Guanine (amidosarcine).

W. C. W.

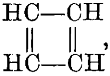
**Reaction of Urea with Furfurol.** By HUGO SCHIFF (*Deut. Chem. Ges. Ber.*, x, 773—776).—Whereas most aldehydes easily react on aqueous or alcoholic solutions of urea, forming condensed ureas, furfurol appears to have no action upon such solutions. It acts, however, in a peculiar manner on solutions of urea nitrate, a violet colour being produced, which gradually disappears, with deposition of a black substance. The colour is not occasioned by the nitric acid. Aqueous solutions of furfurol are not coloured by dilute mineral acids, except after the furfurol has begun to decompose, when they certainly have this effect. Now although neither acid nor urea alone colours pure furfurol, yet a very characteristic change occurs when the two substances react together. If a solution of urea in about three parts of concentrated furfurol solution be treated with a few drops of concentrated hydrochloric acid, the liquid becomes warm, and then gradually of a splendid purple-violet colour, and finally solidifies to a solid brownish-black mass. This phenomenon takes place in alcoholic solutions. Aqueous furfurol solutions after some days, even if kept in the dark, acquire the property of becoming coloured by mineral acids. If hydrochloric acid of spec. grav. 1·10 be employed, a pale-red colour appears in about ten minutes, but if a small crystal of urea be dissolved in this solution, a deep violet colour is formed in a few minutes, slowly changing to brown and depositing a black substance. The reaction is very delicate, especially when conducted under the same conditions as a comparative test. The reaction was obtained with the slightly soluble polyureïds of the aldehydes. Urine gives the reaction. With many amides, as acetamide, benzamide, oxamide, sulpho-urea, mono- and diphenylthiocarbamide, taurine, glycocine, creatine, cyanuric acid, uric acid, alloxan, oxaluric acid, parabanic acid, the reaction is not obtainable; but it is obtained with allantoïn, though perhaps somewhat more tardily and less intensely than with urea. Setting out with the view that urea, a very soluble body, might favour the separation of water, and thus the formation of condensation-products, several very soluble salts were added to the furfurol solution, but no violet colour was occasioned. The hydrochloric acid acts in such a manner that the aldehyde group,  $—C\begin{smallmatrix}\nearrow O \\ \searrow H\end{smallmatrix}$, changes into the group  $—C\begin{smallmatrix}\nearrow OH \\ \leftarrow Cl \\ \searrow H\end{smallmatrix}$, which, having but little stability, acts easily on the amide-groups of the urea, water being separated, and hydrochloric acid re-produced, just as is the case in aldehyde-condensations effected by small quantities of hydrochloric acid, as formerly observed by the author. A result testifying in favour of such a primary reaction is observed when rather more hydrochloric acid is used, and the experiment is conducted as follows:—(The experiment is thus capable of the greatest delicacy.) A very small crystal of urea in a small dish is covered with a drop of highly concentrated aqueous furfurol solution, and a drop of hydrochloric acid of spec. grav. 1·10 is at once added. A change of colour occurs very rapidly through yellow, green, and blue into violet, the latter in a few minutes passing into a splendid purple-violet. This change of colour is quite different from that which altered furfurol-water would undergo without the addition of urea. The tint becomes so intense that in ten minutes the solution may be diluted with 50 to 80 times its bulk of water, and yet maintain its colour most definitely. The black substance separating in this latter case is amorphous, like carbon, and insoluble in ordinary solvents. Washed with water and dried at 110° it contains hydrogen and nitrogen. It is suspected to be a humus-like body, which has carried down some urea with it, to which it obstinately adheres. From the foregoing it is observed that furfurol behaves quite differently with urea and amides to what other aldehydes do. The difference of behaviour is observable in the case of basic amines. According to earlier researches by the author, aldehydes react with aniline and toluidine in such a manner that water separates and the diatomic aldehyde residue takes the place of the hydrogen of the $NH_2$— group: $C_6H_5-NH_2 + C_nH_mO = H_2O + C_6H_5-N{=}C_nH_m$, whilst, according to Stenhouse, two molecules of aniline or toluidine unite directly and without separation of water, with one molecule of furfurol to form basic bodies.

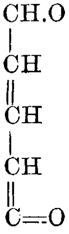
These compounds, likewise arising only on co-operation of acids, point to the presence of a second doubly combined oxygen-atom, so that two molecules of aniline could form two groups without water being taken up—

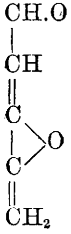


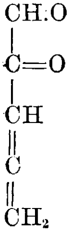
$-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup \mathrm{O}}{\diagdown \mathrm{H}}$ and $=\mathrm{C}=\mathrm{O}$ giving

$-\mathrm{C}\genfrac{}{}{0pt}{}{\diagup \mathrm{NH.C_6H_5}}{\genfrac{}{}{0pt}{}{-\mathrm{CH}}{\diagdown \mathrm{H}}}$ and $=\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{NH.C_6H_5}}{\mathrm{OH}}$.

Nearly ten years ago the author sought to establish constitutional formulæ for the pyromucic acid group, just as Limpricht more recently has done in almost exactly the same manner, these compounds being regarded as derivatives of a diacetylene, , just as the salicylic compounds are derived from benzene. This view is supported by the fact that furfurol resembles salicyl-aldehyde in many respects. The author is nevertheless of opinion that setting out from mucic acid and the polyanhydrides of glucose, it is possible to develop formulæ for furfurol, consisting of open chains, thus:—







W. S.

**Furfurol.** By ADOLF BAEYER (*Deut. Chem. Ges. Ber.*, x, 695—698 and 1358—1365).—In a previous communication (*Berichte*, x, 325: *Chem. Soc. Journ.*, 1877, 444) the author has shown that furfuracrylic acid on treatment with nascent hydrogen passes into furfuropropionic acid, the furfurol nucleus remaining unchanged. This nucleus does not however resist the action of oxidising agents, since according to Limpricht (*Liebig's Annalen*, clxv, 284) pyromucic acid, subjected to the regulated action of bromine, loses $CO_2$ and yields a body $C_4H_4O_3$, which by excess of bromine is changed into the mucobromic acid of Schmelz and Beilstein, $C_4H_2Br_2O_3$.

The author has now attempted, by the action of bromine in excess upon an aqueous solution of furfuropropionic acid, to obtain a body analogous to this mucobromic acid, but without success. He has therefore attempted a more limited oxidation of it.

Contrasting the formulæ of pyromucic and furfuropropionic acids, $C_4H_3O.CO_2H$ and $C_4H_3O.CH_2.CH_2.CO_2H$, it appeared probable that, if the development of $CO_2$ by the action of bromine upon the former acid depended on the destruction of the carboxyl group, the oxidation of the latter would take place without separation of $CO_2$. Experiment has confirmed this expectation, and also demonstrated that the evolution of $CO_2$ in the first case is really due to oxidation of the point of attachment in the molecule of the $CO_2H$ group; for in this reaction four atoms of bromine are used, whereas *two* only are required for the oxidation of furfuropropionic acid.

When furfuropropionic acid in cold aqueous solution is treated with exactly one molecule of bromine, and the solution extracted with ether, a body is obtained which in all probability is the analogue of Limpricht's $C_4H_4O_3$. On account of its instability, the author did not attempt its purification, but at once treated the bromine mixture with 3 molecules of silver oxide, whereby a reaction was obtained corresponding with the equation—

$$C_7H_8O_3 + Br_2 + H_2O + 3Ag_2O = C_7H_6Ag_2O_5 + 2AgBr + 2H_2O + Ag_2.$$

When the reaction was terminated, a sufficiency of hydrochloric acid was added, and by shaking with ether the resulting mass, a bibasic acid, *furonic acid*, $C_7H_8O_5$, was obtained in colourless needles, melting at 180°. These are sparingly soluble in cold water and in ether.

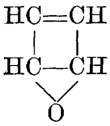
By the action of sodium amalgam in the cold, or by heating with hydriodic acid and amorphous phosphorus to 160°, furonic acid passes into *hydrofuronic acid*, $C_7H_{10}O_5$. This acid, which is very soluble in water, crystallises in colourless needles fusing at 112°.

Heated with hydriodic acid and red phosphorus to 200—205°, furonic acid yields, in addition to an oily body which is probably caproic acid, crystals of a bibasic acid having the composition $C_7H_{12}O_4$. The identity of this acid with $\alpha$-pimelic acid obtained by Schorlemmer and Dale (*Deut. Chem. Ges. Ber.*, vii, 808) from suberone, was established by a careful comparison of their properties. From this it follows that furonic acid belongs to the normal series.

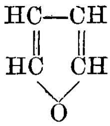
On boiling with baryta-water, furonic acid gives a yellow precipitate, possessing all the properties of the baryta-compound of fumaric aldehyde described by Limpricht.

*Constitution of the Furfurol-group.*—The author proposes for the group $C_4H_4O$ (Limpricht's *Tetraphenol*) the name "furfuran." Since this furfuran is not affected by sodium or sodium-amalgam, it cannot have the constitution of an aldehyde, ketone, alcohol, or ordinary ether. Of known types, then, it can belong only to that of ethylene oxide. Possibly it might be represented on the type of the unknown vinyl-ether, $CH_2=CH.OCH=CH_2$]. The first hypothesis leads to formula (1), the second to (2) or (3).

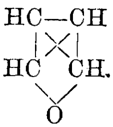
(1.)



(2.)



(3.)



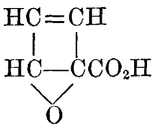
All three formulæ are in harmony with Malaguti's observation that pyromucic ether unites directly with 4 atoms of chlorine.

Limpricht has lately observed that pyromucic acid when acted upon by 4 atoms of bromine yields $CO_2$ and $C_4H_4O_3$:

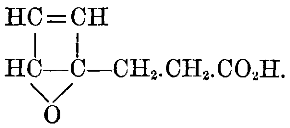
$$C_5H_4O_3 + 4Br + 2H_2O = CO_2 + C_4H_4O_3 + 4HBr.$$

Inasmuch as this body yields by oxidation fumaric acid, Limpricht regards it as the aldehyde of that acid. Omitting its separation, the author, by treating the product of the above reaction with silver oxide, has also obtained fumaric acid, but in such small quantity as to show that the reaction is by no means so simple as it at first sight appears; and he remarks that if the body $C_4H_4O_3$ is really the aldehyde of fumaric acid, analogy would lead us to expect the formation from it, by the action of bromine in excess, of an aldehyde of dibromosuccinic acid; whereas it yields a substitution product, namely, mucobromic acid.

Independently of these considerations, if it be admitted that the splitting of the chain of nuclear carbon atoms on oxidation of pyromucic acid, takes place at the locus of the oxygen, formula (1) most easily explains the formation of fumaric acid. The position of the side-chain in pyromucic acid and in the furfuro-propionic acid formed from its aldehyde, is then determined by the oxidation of the latter, which yields α-pimelic acid, a *normal* compound. Hence these acids must have the constitution—



and



For the formation of furonic aldehyde one additional atom of oxygen is necessary, the one already present forming with one of the parted carbon atoms an aldehyde-group, while that which enters unites with the other to form a ketone group, which remains joined with the side-chain—

$$COH.CH{=}CH.CO.CH_2.CH_2.CO_2H.$$

The aldehyde, by oxidation, changes into furonic acid,

$$CO_2H.CH{=}CH.CO.CH_2.CH_2.CO_2H,$$

and this by reduction yields, as a final product, normal pimelic acid—

$$CO_2H.CH_2.CH_2.CH_2.CH_2.CH_2.CO_2H.$$

The intermediate products have not yet been investigated. On the other hand, when pyromucic acid is oxidised to fumaric aldehyde, 2 atoms of oxygen (= 4 atoms bromine) are necessary, since not only is $CO_2$ split off, but the carbon atom to which it was united is oxidised to a carboxyl group, giving an aldehyde of fumaric acid,

$$COH.CH{=}CH.CO_2H.$$ Ch. B.

**Furfurangelic Acid and Furfurobutylene.** By Adolf Baeyer and P. Tönnies (*Deut. Chem. Ges. Ber.*, x, 1364—1365).—When furfurol, normal butyric anhydride and sodium butyrate are heated gradually for 12 hours from 100° to 180°, and the resulting mass is dissolved in soda-solution, and treated with sulphuric acid, a considerable quantity of *furfurangelic acid*, $C_4H_3O.CH{=}CH.CH_2.CH_2.CO_2H$, is separated. The acid crystallises from hot water in colourless silky needles, which melt at 87—88°. Sodium amalgam reduces it easily to normal *furfurovaleric acid*, $C_4H_3O.CH_2.CH_2.CH_2.CH_2.CO_2H$, a colourless oil, which gives a crystalline acid on treatment with silver oxide.

Isobutyric anhydride, potassic isobutyrate and furfurol behave differently. The reaction, accompanied by copious evolution of $CO_2$, begins at 70°, is energetic at higher temperatures, and is complete after four hours at 150°. A very small quantity of a crystalline acid is obtained, the principal product being an oil insoluble in potash, which has the composition of *furfurobutylene*,

$$C_4H_3O.CH = CH.CH_2.CH_3.$$

It boils at 153°, and smells like *Carabus sycophanta.*

It is the second known hydrocarbon derivative of furfuran, the first being a body obtained by Cahours from thio-furfurol, and consisting, according to Schwanert's analyses, of the stilbene of furfuran,

$$C_4H_3O.CH{=}CH.C_4H_3O.$$

Both are under examination. Ch. B.

**Some Products of the Distillation of Wood at Low Temperatures.** By H. B. Heill (*Deut. Chem. Ges. Ber.*, x, 936—939).—The author paid a visit to a wood-vinegar factory in Brooklyn, in which the wood was distilled at a carefully maintained temperature below 200°. He observed that in the rectification of the crude products, a heavy oil but slightly soluble in water, went over with the steam. The oil freshly obtained, was reddish-yellow, and of peculiar odour. Dried over calcium chloride and distilled, it began to boil at 100°, the thermometer quickly rising to 160°, and remaining between 160° and 170°, when the greater part came over: it then quickly rose to 200°.

By repeatedly fractionating, 60 per cent. of an oil was at last obtained, distilling between 160—165°. Most of it passed over at 162°. The almost colourless, strongly refractive liquid, smelling of bitter almond oil, was easily recognised as furfurol.

The occurrence of furfurol amongst the products of the distillation of wood is not new. Völkel has found it in small quantities in crude wood-vinegar. The author is not in the position to give the quantity of furfurol formed at these low temperatures, but says it must be considerable in order to separate out spontaneously from the aqueous distillate, as it does.

The crude oil shaken with dilute soda solution, assumes a deep yellow colour, becomes turbid, and on standing for a long time, deposits a yellow precipitate, which crystallises from alcohol in beautiful needles. An attempt was made to separate this body by distillation, but without success, as this means is insufficient to separate it from the furfurol. It was found impossible also to separate the furfurol by means of sodium bisulphite solution, or other solvents.

To prepare this yellow body in the pure state, it was found best first to free the crude oil partially from the high-boiling portions. The distillate coming over under 175°, and consisting of nearly 85 per cent. of the oil employed, is shaken with soda-solution (1 : 4), and the whole cooled down. After a short time it is separated from the lye, washed with a little water, and distilled with steam. A red oil is left in the retort, which mostly solidifies on cooling. This residue treated with cold alcohol, gives up to this solvent the red oil arising from the decomposition of the furfurol, and crystals of the yellow body are left behind, which were re-crystallised from boiling alcohol. The properties of the body are as follows:—Long, orange-yellow needles, which melt at 162°, and volatilise, but not without decomposition at a higher temperature. Easily sublimed in a slow stream of air. Insoluble in potash. Soluble in sulphuric acid with splendid purple colour, in concentrated hydrochloric acid with purple-red, and in acetic acid with yellow colour. Soluble with some difficulty in ether and carbon bisulphide; insoluble in cold, easily soluble in hot alcohol. Apparently unaltered by reducing agents. There can scarcely be a doubt that this body is the pyroxanthine discovered by Scanlan, and more closely investigated by Gregory and Apjohn. A combustion gave results agreeing very nearly with those obtained by Gregory and Apjohn. In the soda-lye separated from the furfurol were found pyromucic acid, and a small quantity of an oil not yet investigated, and smelling strongly like smoke-dried fish. It distilled over easily with steam.

W. S.

**On Benzene Formulæ.** By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1154—1155).—This is a criticism on a notice by van't Hoff with regard to the prismatic formula, in which the author points out that the error which van't Hoff has fallen into of there being two ortho and two meta derivatives possible, is due to his considering the position of the atoms in space and not merely with reference to their mode of connection. C. E. G.

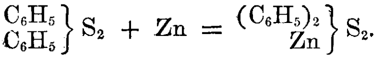
**The Oxychlorination of Benzene.** By F. KRAFFT (*Deut. Chem. Ges. Ber.*, x, 797—800).—Carius obtained trichlorophenomalic acid by the action of potassium chlorate and dilute sulphuric acid on benzene, and it is regarded as a substance homologous with malic acid. As this body with its reactions belongs to that part of organic chemistry which contains debateable ground, the author determined upon a revision of Carius' statements. This determination was in part carried out. Pure benzene was used for preparing the trichlorophenomalic acid. The deep shades of colour produced in the benzene by the action of very small quantities of potassium chlorate were very striking, but these shades quickly disappeared in the course of the reaction. The reaction runs to a great extent in the direction of forming trichlorophenomalic acid, but the presence of syrupy bodies occasions a considerable loss of substance. The yield of pure product does not amount to more than 3 to 4 per cent. of the benzene employed. A portion of this benzene itself is lost by evaporation.

The following physical properties of trichlorophenomalic acid were observed, and they agree with Carius' observations. This body dissolves with difficulty in cold water, but easily in boiling water, in which it usually melts to a colourless oil before dissolving. Incompletely saturated hot solutions show evidences of supersaturation on cooling. The solution when left at rest deposits crystals only after a long time, but on agitating or introducing a fragment of a crystal, it becomes a pasty mass of minute, colourless, shining plates or needles. The body is easily soluble in the cold in alcohol, ether, and benzene. Once or twice recrystallised from boiling water, in the vapour of which it is tolerably volatile, it had a melting point of 131—132°. (Carius.) At higher temperatures it volatilised without change. The author obtained 133—134° as the melting point. Heated in a fine capillary tube for some minutes to 200° the trichlorophenomalic acid acquired a brown colour and diffused the odour of chloranil. The product melting at 131—132°, whose properties agreed well with those given by Carius, was analysed. The chlorine determinations were made with a substance dried in the exsiccator, whereas Carius dried his substance at 100°, and hence lost crystallisation-water. There was thus a difference of about 8 per cent. in Carius' and the author's results as regards the chlorine. Altogether the total results were found to agree very well with the empirical composition of trichlorhydroquinone, ($C_6Cl_3H_3O_2$). The great difficulty in purifying the body is quite in accordance with the remarks of Graebe with respect to tetrachlorhydroquinone. In fact the description of trichlorophenomalic acid by Carius is an almost exact repetition of what was said a long time ago by Städeler, and more recently by Graebe, about trichlorhydroquinone. The trichlorophenomalic acid, in hot aqueous solution was now oxidised with nitric acid (fuming). Nitrogen escaped, and delicate yellow plates with the properties of trichloroquinone were obtained. Melting point 165—166°. According to a statement of

Carius, "The layer which floats on the acid solution of the trichlorophenomalic acid, during this preparation, contains a chlorine compound, scarcely soluble in water, and crystallising in delicate yellow plates." This benzene solution, forming the layer alluded to, was collected and evaporated on the water-bath. On cooling, golden-yellow crystals separated abundantly, mixed with a thick syrup. On addition of alcohol the syrup dissolved, leaving the crystals undissolved. These consisted of a mixture of small plates and thick prisms, the former of which easily dissolved in cold alcohol, whilst the prisms remained. Analysis showed a very near agreement with the numbers required for trichloroquinone, $C_6Cl_3(HO)_2$. The substance melted at 165—166°, and sublimed below this temperature without alteration. Dilute potash first coloured it green, and then dissolved it with reddish-brown colour, and the liquid on standing deposited the characteristic needles of potassium chloranilate. Sulphurous acid in aqueous solution, especially on warming, converted it into trichlorhydroquinone. The body which crystallised in thick prisms from the benzene solution forming the supernatant layer above alluded to, dissolves with great difficulty in cold, and by no means easily, in boiling alcohol. It is thus easily purified. According to analysis this body is dichloroquinone, and it appears to be isomeric with that of Faust. Its melting point (164°) does not differ greatly from that of trichloroquinone. The difference on the contrary is great between the dichlorhydroquinone, obtained from dichloroquinone by reduction with sulphurous acid and trichlorhydroquinone. On boiling the dichloroquinone with sulphurous acid it dissolves, giving a violet-black and then blood-red coloration, especially noticeable at first; with insufficient quantity of reducing agent, a colourless solution is finally obtained. This solution deposits slender shining needles soluble with difficulty in cold water. Melting point = 172°. Analysis proved it to be pure dichlorhydroquinone, $C_6Cl_2H_4O_2$. The direct formation of a phenol-like body (trichlorhydroquinone) from benzene by a process of oxidation running through different phases is deserving of notice from many points of view. First, as in the present case, there is proof that an immediate phenol-formation from aromatic hydrocarbons may, under certain conditions, take place, and especially where the previous entrance of electro-negative chlorine makes the supply of oxygen difficult. It is at the same time settled that the formation of trichloroquinone, as already hypothetically assumed by many chemists, precedes that of the trichlorohydroquinone; and it is not considered a too venturesome generalisation to assume that in other processes of oxidation also, the formation of quinones, ketones, and aldehydes precedes that of the corresponding hydro-compounds, which latter, under the conditions of the reaction, are mostly unstable, and can be isolated only in exceptional cases. W. S.

**Preparation of Benzene Hydrosulphide from Benzene-sulphinic Acid. New Method of converting Benzene Disulphide into Benzene Hydrosulphide.** By R. Otto (*Deut. Chem. Ges. Ber.*, x, 939—941).—Voigt's method for the preparation of benzene hydrosulphide by the reduction of the chloranhydrides of benzene sulphonic acid by means of zinc and dilute sulphuric acid gives only a moderate yield. It is not only the insolubility of the chloranhydride which stands in the way, thus making it difficult of access to the nascent hydrogen, but a portion of the undecomposed compound is withdrawn during the distillation from the reducing action, and converted into benzenesulphonic acid, which is not converted into hydrosulphide by nascent hydrogen.

The author and Schiller found that the chloranhydride of the benzenesulphonic acid could be easily converted into the zinc salt of the sulphinic acid (zinc benzenesulphite) by the action of zinc-dust. It was then proposed to prepare the hydrosulphide from this salt, or from the sodium salt prepared from it. The crude zinc salt (*i.e.*, the zinc benzenesulphinate) is to be added gradually to a mixture of zinc and hydrochloric acid which is gently giving off hydrogen, and the whole is cooled. The action is continued until all the sulphinic acid is converted into hydrosulphide and disulphide. A small quantity of the clear liquid taken out and examined will then redden blue litmus-paper, and when acted upon by a bit of zinc, will yield no more hydrosulphide (tested by the smell and action on a strip of lead-paper). As regards the formation of benzene disulphide, it is found that the hydrosulphide at ordinary temperatures has a great inclination, in presence of the sulphinic acid, to become changed to disulphide with liberation of water. This disulphide in neutral solution, treated with zinc in a finely divided state and gently warmed, is completely converted, after a short time, into the zinc salt of the hydrosulphide, thus:—



$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}S_2 + Zn = \left.\begin{matrix}(C_6H_5)_2\\Zn\end{matrix}\right\}S_2.$$

Zinc salt of hydrosulphide.

In the above-mentioned method of preparation, if care be not taken to cool the liquid, loss will result, part of the benzenesulphinic acid being split up into benzene disulphoxide and irreducible benzenesulphonic acid, thus:—

$$3C_6H_6SO_2 = C_{12}H_{10}S_2O_2 + C_6H_6SO_3 + H_2O.$$

(Benzene sulphinic acid is easily decomposed according to this equation by boiling with water.)

To the solution tested with litmus-paper, &c., containing little free acid, zinc-dust is added in excess, and warmth is applied to further the formation of the zinc compound of the hydrosulphide. Acid is again added (hydrochloric acid), and the hydrosulphide finally distils over with the vapour of water. By attention to the directions, an excellent yield is obtained. As might be expected, this new method of converting benzene disulphide into benzene hydrosulphide by means of zinc-dust will be of universal applicability, and will also permit the conversion of halogen-substituted disulphides (which are not reducible by nascent hydrogen without substitution of halogen by hydrogen) into the corresponding hydrosulphides. The author has employed the method for preparing paratoluene hydrosulphide.

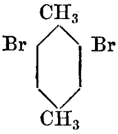
By the action of compact or granulated zinc, only traces of benzene disulphide are converted into the zinc-compound of the hydrosulphide.

W. S.

**Preparation of Durene from Paradibromo-benzene.** By PAUL JANNASCH (*Deut. Chem. Ges. Ber.*, x, 1354—1357). By heating together for some time, by means of a paraffin-bath at 160—170°, a benzene solution of dibromo-paraxylene, methyl iodide, and sodium, the author has obtained durene (tetramethyl-benzene) together with a little pseudocumene. Dibromo-paraxylene is prepared by the action of bromine in presence of iodine upon paraxylene, which again is most easily formed synthetically from dibromo-benzene by the action of methyl iodide and sodium. Full particulars of the process are given.

Two years ago the author obtained, by the action of methyl iodide and sodium upon monobromo-mesitylene, a compound which he has named β-tetramethylbenzene (*Deut. Chem. Ges. Ber.*, viii, 355). Durene being an isomeride of this body, it follows that the dibromoparaxylene, from which it is prepared—

(1)



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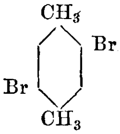

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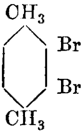
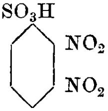


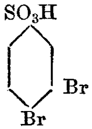
can only have the constitution (2) or (3), since the dibromoxylene of constitution (1) must yield β-tetramethylbenzene. Mesitylene is here assumed to be symmetrical trimethyl-benzene.

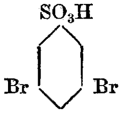
The author purposes studying the derivatives of β-tetramethyl-benzene, as well as those of the isomeric paradiethyl-benzene, which he hopes to obtain by the action of ethylbromide and sodium upon dibromobenzene.

Ch. B.

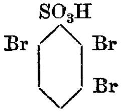
**Dinitrobenzeensulphonic Acid.** By A. SACHSE (*Liebig's Annalen*, clxxxviii, 143—157).—Metanitrobenzenesulphonic acid, prepared from benzene, was separated from the ortho- and para-acids by crystallisation of the calcium salt, regeneration of the acid by means of alcohol and sulphuric acid, and finally by recrystallisation of the barium salt and regeneration by sulphuric acid. By treating this acid with sulphuric and fuming nitric acids the dinitro-acid 

is formed, together with some dinitrophenol. This dinitro-acid is converted into barium salt and crystallised. The free acid is a brownish syrup solidifying to a crystalline mass on cooling; it is very soluble in alcohol and highly deliquescent. The ammonium salt (anhydrous), the potassium salt (containing $1\frac{1}{2}H_2O$), and the barium and lead salts (containing $3H_2O$) were prepared and examined. The chloride melted at 89° (Limpricht found 97°), and the amide at 283° (235°, Limpricht). Reducing agents gave rise to *diamidobenzenesulphonic acid*, $C_6H_3\left\{\begin{matrix}(NH_2)_2\\SO_3H\end{matrix}\right. + 1\frac{1}{2}H_2O$, a well-marked acid, although it combines with hydrochloric, hydrobromic, sulphuric acids, &c., to form crystallised salts; it also forms a stannosochloride. By conversion into diazo-derivative and treatment with hydrobromic acid, it yields *dibromobenzenesulphonic acid*, of which the potassium salt is anhydrous; the barium and lead salts crystallise with $3H_2O$ and the calcium salt with $2H_2O$; the chloride melts at 127° and the amide at 215° (with browning). Since there are but four possible dibromobenzenesulphonic acids obtainable from *meta*-nitrobenzenesulphonic acid, and three of them are already known, viz.:—

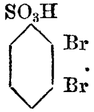




and



the chlorides of which melt respectively at 34°, 57·5°, and 71°, and the amides at 175°, 203, and 193°, it follows that the acid must be the fourth modification,



C. R. A. W.

**Condensation in the Ortho Series.** By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1123—1131).—4. *Tolylenediamine and Formic Acid.*—When equal parts of orthotolylenediaminic (m. p. 89°) and formic acid are digested together for some time, and the product is distilled, an oil of high boiling point is obtained which becomes crystalline after a time. These crystals could not be obtained in a pure state, but a solution of them in hydrochloric acid yielded with platinum tetrachloride a yellow precipitate, which, after being crystallised from boiling water, was found to have the composition $(C_8H_8N_2HCl)_2.PtCl_4$. The base therefore has the composition, $C_8H_8N_2$, and is *methenyltolylenediamine:* its formation may be thus represented, $C_7H_6(NH_2)_2 + CH_2O_2 = C_7H_6N_2H.CH + 2H_2O$. It melts at 98—101°.

5. *Orthoamidophenyl and Formic Acid.*—Equal parts of these two compounds when digested together and subsequently distilled yield, above 150°, a colourless oil of high refractive power, which after being freed from formic acid by means of potassium carbonate solidifies to a mass of crystals. This substance may be purified by repeated rectification when it boils at 182·5°, and the crystals fuse at 30·5°. It has the composition of *methenylamidophenol*, $C_7H_5NO$, and is formed thus: $C_6H_4(NH_2).OH + CH_2O_2 = C_6H_4NO.CH + 2H_2O$. The crystals appear to be monoclinic prisms. They are only slowly acted on by water, but are easily decomposed when heated with concentrated hydrochloric

acid: on cooling the solution solidifies to a mass of crystals consisting of amidophenol hydrochloride.

6. *Orthoamidophenol and Oxalic Acid.*—These two substances when heated together until gas ceases to be evolved, yield a dark-coloured product, from which colourless needles were obtained by repeated crystallisation from alcohol. Their examination is not yet completed.

7. *Orthotolylenediamine and Phthalic Anhydride.*—The product obtained on heating one part of the diamine with two of the anhydride until water ceased to be given off and it fused quietly, was powdered when cold and treated with a warm solution of potassic carbonate. The residue, on repeated crystallisation from dry acetic acid yielded thick lustrous yellowish prisms of *diphthalyltolylenediamine*, $C_{23}H_{14}N_2O_4$ or $C_7H_6(NC_8H_4O_2)_2$, corresponding with phthalanil, $C_6H_5.NC_8H_4O_2$. It melts at 270°, and is but slightly soluble in most solvents; attempts to obtain condensation-products from this substance by removal of $CO_2$ failed.

8. *Orthotolylenediamine and Benzoic Aldehyde.*—On mixing one part of the former with two of the latter heat is evolved, and the mixture on being heated for several hours at 180° gives off water. The product exhausted with hot dilute hydrochloric acid yields a solution which on cooling deposits *dibenzyltolylenediamine hydrochloride* in an impure state. By repeated crystallisation from dilute acid with aid of animal charcoal it is obtained in colourless needles. The free base, $C_{21}H_{18}N_2$, may be obtained by decomposing the salt with ammonia; it crystallises from alcohol in transparent lustrous prisms, which melt at 188—191°, and are almost insoluble in water. It is easily soluble in alcohol, especially when warm, and in dilute acids. The platinum salt is almost insoluble in water and hydrochloric acid, but crystallises from alcohol in nodules which have the formula $(C_{21}H_{18}N_2HCl)_2.PtCl_4$.

Tolylenediamine appears to form condensation-products with other aldehydes; the author has obtained such a base with salicylic aldehyde which he is at present investigating.

The object with which the examination of condensation-products in the ortho series was originally undertaken, was the synthesis of indigo, and the following are some of the experiments made in that direction. When an aqueous solution of orthotoluidine hydrochloride is mixed with ferric chloride and left at rest, blue flocks are deposited which gradually increase in number. After 24 hours these were collected and washed successively with hot dilute hydrochloric acid, dilute soda-solution, hot water, and alcohol. The violet-blue powder thus obtained is insoluble in ordinary solvents, and is free from chlorine: in contact with hydrochloric acid it becomes greenish, probably from formation of a hydrochloride, as the blue colour is restored by alkalis. It dissolves in aniline with a magnificent blue colour, and dyes silk and wool blue. This toluidine-blue differs from indigo in that it cannot be volatilised without decomposition, and it cannot be reduced and reoxidised moreover, although it dissolves in sulphuric acid with a blue colour, the solution when diluted soon becomes colourless. The analyses that have hitherto been made of this substance are not concordant, which is accounted for by the difficulty of purifying it. This reaction would seem to be characteristic of the ortho series, as paratoluidine under similar treatment does not yield a trace of a blue precipitate. The reaction which takes place with aniline, the author believes to be due to the presence of pseudotoluidine, or to be connected with the formation of aniline black.

*Formorthotoluide.*—A compound having the composition of formorthotoluide was prepared by distilling a mixture of equal parts of oxalic acid and orthotoluidine, and crystallising the distillate from alcohol, or better by merely heating the mixture until gas ceased to be evolved, and after cooling and pulverisation, extracting it with alcohol, ether, and dilute hydrochloric acid, and finally crystallising it from toluene or dry acetic acid. It forms colourless needles of the formula, $C_7H_7NH.CHO$, which melt at 211°, and are almost insoluble in ether and in cold alcohol. An investigation of this substance soon showed that it was not the true formorthotoluide, which may be obtained by the action of formic acid on orthotoluidine; for the present, the author proposes to call it isoformorthotoluide. When orthotoluidine and formic acid in molecular proportions are digested for some hours and then distilled, a liquid passes over between 278° and 292°, which solidifies on standing, and on repeated rectification may be obtained of constant boiling point, 288°. The crystals are purified by pressure, washing with dilute hydrochloric acid, and crystallisation from alcohol, in which they are easily soluble. They are large tables which melt at 56·5—57·5°. This compound, the true formorthotoluide, is resolved into formic acid and orthotoluidine, when boiled with dilute sulphuric acid, whilst the isomeric body remains unchanged even at 150°. Formorthotoluidine, when distilled with phosphoric anhydride, or when heated alone at 300°, yields orthotoluidine, but in the latter case another compound is formed in small quantity. It may be more conveniently prepared by digesting the formotoluide for a long time at the boiling temperature, and then distilling off the toluidine and unaltered toluide until the thermometer indicates 300°. The residue crystallised successively from alcohol and from toluene, yields the new substance in colourless glistening prisms which melt at 153°. It dissolves with difficulty in boiling alcohol, easily in hot toluene. The analyses agree with the formula, $C_8H_9N$, the other products of the reaction being toluidine, CO and $CO_2$—

$$2(C_7H_7NH.CHO) = C_9H_9N + C_7H_7.NH_2 + CO_2$$
$$C_7H_7NH.CHO = C_7H_7NH_2 + CO.$$

The constitution of the body $C_8H_9N$ is not yet known, but the author remarks that it has a composition intermediate between that of methyltoluidine and indol; it dissolves in hydrochloric acid, yields toluquinone on oxidation, and appears to form an addition-product with bromine. Formorthotoluide and orthamidoethylbenzene hydrochloride yield blue compounds when treated with ferric chloride, whilst the body $C_8H_9N$ is but slowly altered, and isoformorthotoluide is not acted on at all. The author finds that indol treated with ferric chloride yields a greenish-grey substance soluble in aniline with a brown colour: it is not volatile. C. E. G.

**On Ammonium Compounds.** By A. LADENBURG (*Deut. Chem. Ges. Ber.*, x, 1152—1153).—This is a reply to Meyer's objection that the compounds $N(C_2H_5)_3.C_7H_7I$ and $NC_7H_7(C_2H_5)_2.C_2H_5I$ obtained by the author, are one and the same compound, the slight differences observed being due to a small quantity of resin or like impurity. The author states that when triethylbenzylammonium chloride is converted into the corresponding iodide by means of silver oxide and hydriodic acid, and the neutral solution concentrated on the water-bath, a clear solution is obtained which gives off benzyl iodide on boiling with concentrated hydriodic acid. If, however, the clear solution is evaporated under an exsiccator, it solidifies to a crystalline mass, which no longer gives benzyl iodide when heated with hydriodic acid. From this the author infers that the compound undergoes isomeric change when evaporated to dryness. C. E. G.

**Monomethylaniline.** By E. Nölting and J. B. Boasson (*Deut. Chem. Ges. Ber.*, x, 795—796).—Kern declares that he has been unable to prepare monomethylaniline from either methyl alcohol and aniline chloride, or methyl iodide and aniline. Hepp also failed to obtain monomethylaniline according to the latter method. These facts not harmonising with the earlier observations of Hofmann, Girard and De Laire, &c., the authors determined to put the matter to a practical test. They found that monomethylaniline is abundantly formed in both reactions. In order to separate the secondary amine from the product of the reaction, which contains at the same time unaltered aniline and dimethylaniline, use was made of nitrous acid. Sodium nitrite was in fact added to a not too concentrated acid solution of the bases, which was well cooled. Thus, aniline is converted into diazobenzene-chloride, dimethylaniline into nitrosodimethylaniline chloride, which remains in solution, whilst the methylphenylnitrosamine formed at the same time is separated as a yellow oil, which can be extracted from the solution by means of ether. By reducing agents (tin and hydrochloric acid, or iron and acetic acid) monomethylaniline is easily obtained, and with quantitative exactness. This body was dissolved by sulphuric acid, forming an absolutely clear solution. It distilled over almost completely between 190—192°, gave with chloride of acetyl the acetyl-derivative described by Hofmann and Hepp, and when treated in acid solution with sodium nitrite, nitrosamine. The platino-chloride, precipitated from the hydrochloric acid solution by platinum tetrachloride, gave without further purifying, correct numbers on analysis. The following numbers testify to the fact that the yield of monomethylaniline is considerable.

(1.) 50 grams of mixed bases obtained by the action of 1 mol. of methyl iodide on 1 mol. of aniline, yielded 21 grams of the dry nitrosamine, corresponding to 16·5 grams of methylaniline.

(2.) 50 grams mixed bases, obtained by the action of 1 mol. of methyl iodide on 2 mols. of aniline, and separated from the crystals of the aniline iodide by means of ether, yielded 23·5 grams of nitrosamine, corresponding to 18·5 grams of methylaniline.

(3.) The product of the reaction of 25 grams of methyl alcohol on 100 grams of aniline chloride at 235—240°, gave 41 grams of nitrosamine, corresponding to 32·3 grams of methyl aniline. There is no doubt that in the preparation of dimethylaniline in quantity, monomethylaniline may be formed also. In two samples of commercial dimethylaniline the presence of small quantities of monomethylaniline was detected by the formation of nitrosamine, and in like manner some commercial diethylaniline yielded a small quantity of ethylphenylnitrosamine. The reaction is very delicate. Artificial mixtures were prepared of absolutely pure dimethyl- and monomethylaniline, and it was then found that one per cent. of the latter could be detected with certainty. One gram of the bases was dissolved in excess of tolerably dilute hydrochloric acid, a couple of drops of sodium nitrite solution added, the whole shaken with ether, and the ethereal extract was dried with calcium chloride, and evaporated on a watch glass. The methylphenylnitrosamine remains behind in yellow drops, and is recognised by a characteristic odour, and by means of Liebermann's reaction. Pure dimethylaniline leaves no oily drops, but a trace of a yellow crystalline body, probably nitrosodimethylaniline chloride, of which a small quantity might have been taken up by the ether. With the nitrosamine this body cannot be confounded. Probably this nitrosamine reaction will give rise to a method of quantitative estimation of the monomethylaniline contained in commercial methylaniline.

W. S.

**Nitro-derivatives of Diphenylamine.** By P. T. Austen (*Amer. Jour. Sci.* [3], xiii, 279).—Pisani (*Ann. Chem. Pharm.*, xcii, 326) found that trinitrochlorobenzene acts on ammonia with formation of trinitraniline. Clemm (*J. pr. Chem.* [2], i, 145) obtained trinitrodiphenylamine by using aniline in place of ammonia, and a dinitrodiphenylamine by the action of dinitrobromobenzene on aniline.

The trinitrochlorobenzene was made in the following manner. 100 grams of picric acid were well mixed with 200 grams of phosphorus pentachloride in a flask with reversed condenser. On applying a gentle heat the mixture fused, and the reaction took place violently and without further heating. After the action had ceased, most of the phosphorus oxychloride was distilled off. The heavy red liquid remaining in the retort was then poured into a large quantity of cold water and violently agitated. The impure substance thus obtained was purified by washing with ether and crystallisation from absolute alcohol. It then formed bright yellow crystals, becoming darker on drying. The yield is from 30—40 per cent. of the theoretical amount.

Better results were obtained by simply heating the substances in a tall beaker, and by using half the previous quantities. The trinitrochlorobenzene thus obtained fused at 82·5—83°.

*α-Trinitrophenylmetanitraniline*, $C_{12}H_7N_5O_8$

$$= NH[C_6H_4(NO_2).C_6H_2(NO_2)_3].—$$

25 grams of metanitraniline and 27 grams of chloropicryl were dissolved in boiling absolute alcohol; after a few minutes' boiling a heavy yellow crystalline sand began to separate. The solution was allowed to cool, and the precipitate was separated by filtration, and crystallised from glacial acetic acid. The formation of this compound is expressed by the following equation:—

$$C_6H_2(NO_2)_3Cl + 2C_6H_4(NO_2)NH_2 = NH[C_6H_4(NO_2)][C_6H_2(NO_2)_3] + C_6H_4(NO_2)NH_2.HCl.$$

α-Trinitrophenylmetanitraniline is almost insoluble in hot water, colouring it yellow, however; nearly insoluble in boiling ether, carbon disulphide, carbon tetrachloride, chloroform, and absolute alcohol; insoluble in hydrochloric and dilute nitric and sulphuric acids; easily soluble in strong sulphuric acid with deep wine-red colour, separating unchanged on addition of water; easily soluble in aniline, with red colour; also in hot amyl alcohol, but crystallises badly therefrom; soluble in hot glacial acetic acid, and separates on cooling as an orange crystalline sand. From acetyl chloride it separates in small wine-yellow transparent crystals.

Aqueous ammonia dissolves it very easily, the solution attaining a splendid scarlet colour. By evaporation it separates unchanged. With weak solutions of the alkalis it behaves as with ammonia; concentrated solutions, especially on heating, decompose it, with evolution of ammonia.

The compound consists of a heavy, crystalline, yellow sand, melting at 205° to a red liquid, which solidifies at about 175°. By careful heating it volatilises as a yellow powder. When thrown on a hot surface it explodes like gunpowder, but it is not exploded by percussion.

*α-Trinitrophenylparanitraniline*, $C_{12}H_7N_5O_8$ $= NH[C_6H_4(NO_2)][C_6H_2(NO_2)_3]$.— This compound was made in a manner similar to the preceding. Paranitraniline, with the calculated amount of picryl chloride, was dissolved in absolute alcohol; on boiling, a red crystalline powder separated, which was washed, and crystallised from glacial acetic acid. It melts at 216°, and resembles in solubility the preceding compound. In aqueous ammonia it dissolves easily, with red colour, and is reprecipitated unchanged by acids. From alcoholic ammonia it crystallises in beautiful glittering leaves. It dissolves in a hot solution of sodium carbonate, with scarlet colour; on cooling, violet needles separate, which are doubtless the sodium salt of α-picrylparanitraniline, $NNa[C_6H_4(NO_2)][C_6H_2(NO_2)_3]$. The needles are soluble in water and alcohol, and are decomposed by acids.

The trinitro-base is insoluble in aqueous ammonium carbonate, easily soluble in amyl alcohol, and crystallises therefrom in glittering yellow scales. In aniline it dissolves easily, and separates on evaporation in a crystalline form; dissolves also in benzoyl chloride, acetyl chloride, benzyl chloride, and chlorobenzene.

*Dinitrophenylmetanitraniline*, $C_{12}H_8N_4O_6$, $= NH[C_6H_4(NO_2)][C_6H_3(NO_2)_2]$.— Calculated amounts of dinitrobromobenzene (produced by nitration of bromobenzene) and metanitraniline were rubbed to a pulp with absolute alcohol, and the mixture heated to 100° for twenty hours in a sealed tube. On cooling, the tube contained hard brown crystals, which were washed with warm alcohol and crystallised from glacial acetic acid.

The substance is insoluble in water, alcohol, and ether, difficultly soluble in boiling glacial acetic acid, soluble in an excess of boiling chloroform, and separates on cooling in small yellow crystals, melting at 189°,* to a red liquid. With alkalis it behaves in the same manner as trinitrophenylparanitraniline.

*Dinitrophenylparanitraniline*, $C_{12}H_8N_4O_6$
$= NH[C_6H_4(NO_2)][C_6H_3(NO_2)_2]$.—The calculated quantities of dinitrobromobenzene and paranitraniline were treated as in the preparation of the preceding compound. On cooling, the tube contained a mass of dark-red crystals. They were washed with dilute alcohol, and purified by precipitation with water from their acetic acid solution. The substance is *easily soluble in cold glacial acetic acid*, thus showing a marked difference from the *meta*-compound, which is *difficultly soluble in boiling glacial acetic acid*. It is difficultly soluble in cold alcohol, easily in hot. It is a very light, pale yellow, elastic, and electric powder. Melting point 181°.

Since the picrylnitranilines contain the mononitrophenyl group, it appears extremely probable that a further nitration can be effected. In this case, since the trinitrophenyl group seems to be the limit of direct nitration of the phenyl group, it may be predicted that by the direct nitration of the picrylnitranilines higher nitro-members would be formed, and that the nitro-groups would enter into the mononitrophenyl group. If, then, by the nitration of the picrylnitranilines, higher isomeric nitro-compounds were obtained, the isomerism must reside in the nitrated mononitrophenyl group, since the trinitrophenyl group remains unchanged during the nitration. It is, however, very possible that in one of the resulting compounds the two picryl groups may be identical.

Since the positions of the nitro-groups in these dipicrylamines has not been ascertained, the trinitrophenyl group of picric acid will be represented as $\alpha$, and the dinitromononitrophenyl groups of meta- and paranitraniline as $\beta$ and $\gamma$ respectively. Only two of these picryl groups can be identical.

*$\alpha$-Picryl-$\beta$-picrylamine.*—$C_{12}H_5N_7O_{12} = NH[C_6H_2(NO_2)_3]_2$.—The $\alpha$-picryl-metanitraniline was added in small portions to a cooled mixture of equal volumes of fuming nitric and concentrated sulphuric acid. The liquid became hot, and a violent reaction set in. After the reaction had subsided the liquid was poured into cold water, whereupon a bright sulphur-yellow cream was obtained. After washing out the acid with water, the cream was well washed with alcohol, which removed a resin, then dissolved in boiling glacial acetic acid, and precipitated by strong hydrochloric acid, the precipitate washed with the dilute acid, and dissolved in boiling glacial acetic acid, with addition of animal charcoal, the solution filtered, and left to crystallise.

The substance is an impalpable sulphur-yellow powder; by careful crystallisation from glacial acetic acid it is obtained in small transparent glittering crystals, melting at 261°, to a red liquid, which solidifies at 175—170° to a red glass. On touching it with a hard body when in the liquid state, it solidifies to a yellow amorphous mass.

It is almost insoluble in hot water, and in dilute hydrochloric, nitric, and sulphuric acids. In hot amyl and ethyl alcohols it is almost in-

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* Willgerodt announced (*Deut. Chem. Ges. Ber.*, ix, 1178), a dinitrophenylmetanitraniline which he had produced by the action of $\alpha$-$C_6H_3(NO_2)_2Cl$ on metanitraniline. M. p. 194·5°. Perhaps identical with the above.

soluble, hardly soluble in ether, carbon tetrachloride, chloroform, and carbon disulphide; difficultly soluble in cold glacial acetic acid, easily on boiling; easily soluble in aniline. In aqueous ammonia, soda, and potash it dissolves easily, with a splendid scarlet colour; when boiled with the fixed alkalis it gives off ammonia. In sodium carbonate it dissolves easily, forming the sodium salt.

By addition of water to the solution in boiling glacial acetic acid, a thick precipitate is formed, which after crystallisation from glacial acetic acid has a melting point of 205°, and on analysis proved to be the original picrylmetanitraniline, from which this dipicrylamine was prepared. *By the addition, then, of water to the boiling solution in glacial acetic acid, the α-β-picrylamine loses two nitro-groups, and is reconverted into the picrylmetanitraniline.*

The dipicrylamine does not explode by percussion. When heated, it puffs with a white luminous flame, and leaves a light porous coal. It explodes with violence when thrown on to hot platinum foil.

*α-Picryl-γ-picrylamine*, $C_{12}H_5N_7O_{12} = NH[C_6H_2(NO_2)_3]_2$.—This compound was prepared by nitration of picrylparanitraniline in the same manner as in the case of the preceding compound. On pouring the resulting mixture into cold water, the substance separated as a light greenish-yellow cream, which was extracted with alcohol and crystallised from glacial acetic acid. It then forms small, transparent, glittering, light-yellow prisms, with a green reflex. It fuses at 230°, with decomposition. Its solubility is about the same as that of the preceding compound. It puffs on being heated, and explodes with violence when thrown on a hot surface. With alkalis it behaves like the α-β-compound.

It has already been mentioned that these compounds, especially the dipicrylamines, give fine scarlet colours with alkalis. The author finds that these colours are caused by the formation of salts of the nitrodiphenylamines. The hydrogen-atom of the imido-group becomes so strongly negative by the introduction of the nitro-groups, that it can easily be replaced by basic atoms.

Of the numerous salts prepared, one only has been examined, viz., *Barium α-picryl-β-picryldiamine*, $C_{24}H_8N_{14}O_{24}Ba$

$$= \left.\begin{matrix}\alpha\text{-}C_6H_2(NO_2)_3\\ \beta\text{-}C_6H_2(NO_2)_3\end{matrix}\right\} N—Ba—N \left\{\begin{matrix}C_6H_2(NO_2)_3\ \alpha\\ C_6H_2(NO_2)_3\ \beta\end{matrix}\right. \cdot —$$

The α-β-picrylamine was added to a cream of barium hydrate; it dissolved immediately with a deep red colour. The solution was boiled for a few minutes, and then evaporated to the crystallising point. On cooling, dark red needles were formed, which were purified by recrystallisation from water.

This compound appears to have sufficient basic properties to form salts with weak acids. Thrown on a hot surface it explodes violently.

*Ammonium-α-γ-picrylamine* crystallises in fine deep red transparent rhombohedrons.(?) It is possibly identical with the dye-stuff "aurantia." By treatment of the sodium salts of the dipicrylamines with picryl chloride, a reaction takes place, doubtless with the formation of the tertiary picrylamine, $N[C_6H_2(NO_2)_3]_3$.

The following table will show the various nitrodiphenylamines known, their mode of preparation, and their properties.

| No. | Rational formula. | Empirical formula. | Remarks. |
|---|---|---|---|
| I ...... | $N\left\{\begin{array}{l}C_6H_5\\C_6H_4(NO_2)\\CO.C_6H_5\end{array}\right.$ | $C_{19}H_{14}N_2O_3$ | By the action of $HNO_3$ on $N\left\{\begin{array}{l}(C_6H_5)_2\\CO.C_6H_5\end{array}\right.$. Light-yellow crystals. |
| II ..... | $N\left\{\begin{array}{l}C_6H_5\\C_6H_4(NO_2)\\H\end{array}\right.$ | $C_{12}H_{10}N_2O_2$ | NaHO on No. I. |
| III .... | $N\left\{\begin{array}{l}C_6H_4(NO_2)\\C_6H_4(NO_2)\\CO.C_6H_5\end{array}\right.$ | $C_{19}H_{13}N_3O_5$ | Fuming $HNO_3$ on $N\left\{\begin{array}{l}(C_6H_5)_2\\CO.C_6H_5\end{array}\right.$. Deep-yellow crystalline substance. |
| IV ..... | $N\left\{\begin{array}{l}C_6H_4(NO_2)\\C_6H_4(NO_2)\\H\end{array}\right.$ | $C_{12}H_9N_3O_4$ | NaOH on No. 3. Reddish-yellow needles with metallic blue reflex. |
| V ...... | $N\left\{\begin{array}{l}C_6H_5\\C_6H_3(NO_2)_2^{m.}\\H\end{array}\right.$ | $C_{12}H_9N_3O_4$ | $C_6H_3(NO_2)_2Br$ on $C_6H_5NH_2$. Long thin scarlet or red-yellow needles, m.-p. 153° (Clemm)<br>$\alpha$-$C_6H_3(NO_2)_2Cl$ on alcoholic $H_2S$ solution of aniline, m.-p. 156—157° (Willgerodt). |
| VI .... | $N\left\{\begin{array}{l}C_6H_5\\C_6H_2(NO_2)_3^{\alpha}\\H\end{array}\right.$ | $C_{12}H_8N_4O_6$ | $C_6H_2(NO_2)_3Cl$ on $C_6H_5NH_2$. Sparkling prisms. Scarlet by reflexion; reddish-yellow by refraction. M.-p. 175°. |
| VII .... | $N\left\{\begin{array}{l}C_6H_4(NO_2)^m\\C_6H_3(NO_2)_2^m\\H\end{array}\right.$ | $C_{12}H_8N_4O_6$ | $C_6H_3(NO_2)_2Br$ on *m*-nitraniline. Small glittering yellow crystals. M.-p. 189°. |
| VIII ... | $N\left\{\begin{array}{l}C_6H_4(NO_2)^p\\C_6H_3(NO_2)_2^m\\H\end{array}\right.$ | $C_{12}H_8N_4O_6$ | $C_6H_3(NO_2)_2Br$ on *p*-nitraniline. Light electrical yellow powder. Easily soluble in cold glacial acetic acid. M.-p. 181°. |
| IX .... | $N\left\{\begin{array}{l}C_6H_4(NO_2)^m\\C_6H_2(NO_2)_{3\alpha}\\H\end{array}\right.$ | $C_{12}H_7N_5O_8$ | $C_6H_2(NO_2)_3Cl$ on *m*-nitraniline. Heavy cryst. yellow sand or wine-yellow transparent prisms. M.-p. 205°. |

| No. | Rational formula. | Empirical formula. | Remarks. |
|---|---|---|---|
| X...... | $N\left\{\begin{matrix}C_6H_4(NO_2)p\\ C_6H_2(NO_2)_3\alpha\\ H\end{matrix}\right.$ | $C_{12}H_7N_5O_8$ | $C_6H_2(NO_2)_3Cl$ on *p*-nitraniline. Red crystalline powder or crystalline scales. M.-p. 216°. |
| XI .... | $N\left\{\begin{matrix}C_6H_2(NO_2)_3\beta\\ C_6H_2(NO_2)_3\alpha\\ H\end{matrix}\right.$ | $C_{12}H_5N_7O_{12}$ | By nitration of IX, m.-p. 261°. Impalpable bright yellow powder or small transparent glittering yellow crystals. |
| XII.... | $N\left\{\begin{matrix}C_6H_2(NO_2)_3\gamma\\ C_6H_2(NO_2)_3\alpha\\ H\end{matrix}\right.$ | $C_{12}H_5N_7O_{12}$ | By nitration of X. Small transparent glittering bright-yellow prisms with a green reflex. M.-p. 230°. |
| XIII ... | $Ba\left\{\begin{matrix}N\left\{\begin{matrix}C_6H_2(NO_2)_3\beta\\ C_6H_2(NO_2)_3\alpha\end{matrix}\right.\\ N\left\{\begin{matrix}C_6H_2(NO_2)_3\beta\\ C_6H_2(NO_2)_3\alpha\end{matrix}\right.\end{matrix}\right.$ | $C_{24}H_8N_{14}O_{24}Ba$ | $Ba(OH)_2$ on XI. Dark saffron-red glittering needles. Explodes on heating. |
| XIV ... | $N\left\{\begin{matrix}C_6H_2(NO_2)_3\,?\\ C_6H_2(NO_2)_3\,?\\ H\end{matrix}\right.$ | $C_{12}H_5N_7O_{12}$ | Nitration of diphenylamine. Transparent light-yellow prisms. M.-p. 238°. |
| XV .... | $N\left\{\begin{matrix}C_6H_2(NO_2)_3\,?\\ C_6H_2(NO_2)_3\,?\\ NH_4\end{matrix}\right.$ | $C_{12}H_8N_8O_{12}$ | $NH_3$ on XIV. Beautiful red leaves. |
| XVI ... | $N\left\{\begin{matrix}C_6H_2Br(NO_2)_2\,?\\ C_6H_2Br(NO_2)_2\,?\\ H\end{matrix}\right.$ | $C_{12}H_5N_5BrO_8$ | Nitration of— $HN\left\{\begin{matrix}C_6H_4Br\\ C_6H_3Br_2\end{matrix}\right.$. Yellow pearly leaves or rhombic tablets. M.-p. 235—240—242°. |
| XVII .. | $N\left\{\begin{matrix}C_6H_2(NO_2)_2Br\\ C_6H_5\\ H\end{matrix}\right.$ | $C_{12}H_8N_3BrO_4$ | $C_6H_5NH_2$ on— $C_6H_2\left\{\begin{matrix}(NO_2)_2\beta\\ Br_2p\end{matrix}\right.$. Beautiful red-orange fine hairy needles. M.-p. 120.° |
| XVIII.. | $N\left\{\begin{matrix}C_6H_2(NO_2)_2Br\,?\\ C_6H_3(NO_2)_2\\ H\end{matrix}\right.$ | $C_{12}H_5N_5BrO_8$ | Nitration of XVII. Small brown scales. M.-p. 167·5°. |

| No. | Rational formula. | Empirical formula. | Remarks. |
|---|---|---|---|
| XIX ... | $N\left\{\begin{array}{l}C_6H_3(NO_2)_2?\\C_6H_4.C_6H_4.NH_2?\\H\end{array}\right.$ | $C_{18}H_4N_4O_4$ | $\alpha$-$C_6H_3(NO_2)_2Cl$ on benzidine. Short bluish brown-red needles. M.-p. 255°. |
| XX .... | $N\left\{\begin{array}{l}C_6H_3(NO_2)_2?\\C_6H_4.C_6H_4.NH.C_6H_3(NO_2)_2\\H\end{array}\right.$ | $C_{24}H_{16}N_6O_8$ | Formed from XIX. Yellow pulverulent powder. Sol. in conc. $H_2SO_4$ with violet colour. M.-p. 330°. |
| XXI ... | $N\left\{\begin{array}{l}C_6H_3(NO_2)Cl^m\\C_6H_5\\H\end{array}\right.$ | $C_{12}H_9N_2ClO_2$ | Action of—<br>$C_6H_3(NO_2)Cl^m(NO_2)$ on aniline. Long glittering alizarin-red needles. M.-p. 108·5°. |

C. W. W.

**Base derived from a Waste-product in the Aniline Manufacture.** By C. Loring Jackson (*Amer. Jour. Sci.*, xiii, 449).—This body is found in the distillate from the highest boiling fractions of the aniline-distillation and passes over after the toluidine.

The substance, a black oily liquid, was dissolved in hydrochloric acid and filtered from tarry matters; the oily base set free by sodium hydrate was fractioned, and yielded at first xylidine and allied bodies; afterwards a fraction from 280—320°, which, after removal of naphthylamine with dilute sulphuric acid, was converted into the nitrate and purified by crystallisation; it then formed radiate groups of white needles which gave on analysis the composition $C_{13}H_{14}N.NO_3$.

The *sulphate* is very soluble. The *chloride*, $C_{13}H_{14}NCl$, crystallised in flat white needles. The *platinum salt*, $(C_{13}H_{14}NCl)_2PtCl_4$, crystallises in very characteristic fan-like groups of sparingly soluble light-yellow needles.

The free base, $C_{13}H_{13}N$, was obtained as an oil, which gave with chloroform and potassium hydrate a smell similar to that of the isocyanides; it is therefore a primary amine, $C_{13}H_{11}NH_2$. An acetyl-compound, $C_{13}H_{11}.NH.C_2H_3O$, was prepared and crystallised in white needles melting at 114·25°.

This base differs from the one which Carnelley prepared (this *Journal*, 1876, i, 21) by the reduction of synthetically formed mononitrotolylphenyl, in the following properties. Carnelley found that on adding sodium hydrate to a salt of his base, extracting with ether, and evaporating the ether, an oily body was first produced, from which there separated out a small quantity of needle-shaped tufts melting at 93—97°. The crystals obtained by treating a salt of the present base in a similar manner melted at 46—70°, and were moderately large prismatic crystals arranged in pennate groups, breaking up on pressure into rough octohedral masses. The crystals were insoluble in water, freely soluble in alcohol, ether, and benzene, and instantly converted by hydrochloric acid into a chloride easily soluble in water, and separating therefrom in white flattened needles melting with decomposition at about 200°; whereas Carnelley's crystalline base, when heated with hydrochloric acid, dissolved only after long boiling, and separated from the solution in small needles, melting with decomposition at 280—283°.

From this comparison it is evident that the two bases are not identical but isomeric. C. W. W.

**Metamorphoses of Aniline-Black.** By F. Goppelsröder (*Dingl. polyt. J.*, ccxxiv, 439—448).—1. *On Aniline-black vat.* The basis of electrolytic aniline-black obtained by treating the black formed at the positive pole, after purification with boiling water and alcohol, with solution of potash or soda dissolves in fuming sulphuric acid, and, according to the quantity of acid used, the solution has a bluish-violet or dark-green colour. If the action of the fuming acid has taken place in a satisfactory manner, a green precipitate should be produced by adding water to the solution, while the latter should be colourless or coloured slightly reddish-violet. After washing the precipitate until it no longer shows an acid reaction, it is dissolved by continuing the washing with water, the solution formed having a green colour. Cotton (mordanted or not mordanted) is not dyed by this solution, but wool is turned blue on the addition of ammonia. Caustic potash or soda changes the green solution to blue, and, after warming, to violet; acids bring the blue back to its original colour. The green solution is rendered colourless by hydrogen sulphide or by zinc-powder. The colourless liquid assumes a green colour on addition of fuming nitric acid. The following table gives various other reactions of the green solution:—

| Green Solution. | | Green Solution from Green Precipitate. | |
|---|---|---|---|
| Reagents. | Change. | Reagents. | Change. |
| Sodium amalgam. | Bluish-violet; then slowly discoloured. | Sulphuretted hydrogen | Green. |
| Ferrous sulphate. | No reduction. | Chlorine-water.. | Violet. |
| Sulphuric acid .<br>Thiosulphate of sodium ..... | No reaction. | Acetate of lead..<br>Tetrachloride or dichloride of tin | Green precipitate.<br>Green precipitate. |
| Hyposulphite of zinc or calcium. | Yellow colour. | Bichromate of potassium | Black precipitate. |
| Hypochlorite of sodium | Red when cold; orange-red on warming. Addition of $SO_2$, yellow. | Hypochlorite of potassium | Bluish-violet, then reddish-violet colour; $SO_2$, green |
| Bichromate of potassium | Green. | Excess of the former | Reddish-yellow; $SO_2$, no change; $Na_2S_2O_3$, brown colour. |

| Green Solution. | | Green Solution from Green Precipitate. | |
|---|---|---|---|
| Reagents. | Change. | Reagents. | Change. |
| Permanganate of potassium | Discoloured after adding sulphuric acid. | Sulphuretted hydrogen | The above bluish-violet or reddish-violet solution turns yellow. |
| Chlorine-water... | Intensely green, then bluish-violet, finally wine-red; $NH_3$, yellow. | Hypochlorite of sodium | Orange-yellow, |
| Ferricyanide of potassium and sodium | Brown. | Sodium amalgam | Yellowish-brown, and violet by adding hypochlorite of sodium. |
| Sulphate of copper | Green precipitate. | | |
| Baryta-water .... | Green precipitate. | | |

If the sulphuric acid used for treating the basis of aniline-black is not sufficiently concentrated, a green precipitate is produced which is insoluble in water. Neither of these green precipitates can be converted into aniline-black by ozone or other well-known reagents. The green precipitate or its green aqueous solution, when neutralised with alkalis, gives a blue liquid with violet tinge exhibiting the following reactions:—

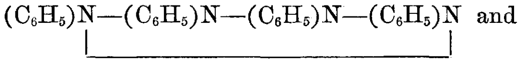
*Blue Alkaline Solution.*

| Reagents. | Change of Colour. |
|---|---|
| Hydrochloric acid ............ | Green. |
| Hypochlorite of sodium ....... | Reddish-violet when cold; orange-red when warm. Excess gives a yellow colour. |
| Ferricyanide of potassium ..... | Yellowish-brown; acetic acid, hydrochloric acid, &c. Green. |
| Bromine ................... | Bluish-violet. Excess destroys the colour. |
| Chlorine water ............... | The same. |
| Fuming nitric acid ........... | Green; then destroyed. |
| Glucose ..................... | Reduces the blue solution. |

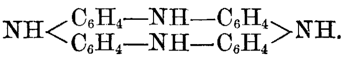
On introducing vegetable or animal fibres into a concentrated vat of aniline-black, they assume a violet colour, then a bluish-violet, and, finally, a blue colour, which is turned green by dilute acids, and not altered by alcohol. Alkalis, however, dissolve the blue colour with violet tinge. By treating the blue fibres in an oxidising bath a black is obtained which is not turned green by acids. If the blue was light, a grey colour is obtained; if it was dark, a black is formed. Calcium hyposulphite or metallic zinc reduces the alkaline bluish-violet solution in the same manner as glucose. The liquid assumes a yellow colour, while cotton dipped into it is dyed blue. The author has not yet succeeded in obtaining a black vat similar to the indigo vat with iron-vitriol and lime. He obtained a black deposit (coated with a bluish-violet precipitate) from a black lake containing lime and iron, as shown by the decomposition with hydrochloric acid, while the black was thrown down without any change. The following method gives a dark black colour in the vat:—The cloth is treated in the vat several times, and exposed to the air each time till a very dark blue colour has been obtained, which is then oxidised according to Jeanmaire's process with an acidulated solution of ferric chloride; this operation is repeated until the desired black shade is obtained. The reduced aniline-black may be used as ink; the letters are at first but slightly coloured, but afterwards assume a blue and, finally, a dark black colour. For instance, by painting on paper with the black vat containing an excess of glucose, we obtain shades varying according to the number of coats, from a light grey to a dark black colour. Sulphuretted hydrogen changes the black to brownish-yellow, which is blackened on oxidation in the air. Hypochlorite of calcium gives a reddish-violet colour, and afterwards destroys it; acids give a green colour, which ammonia turns black, and alkalis give a violet colour.

The above-described reduction by glucose in presence of alkali takes place also with the derivative of the basis of commercial aniline-black in the same way as with the basis of the electrolytic black. The commercial substance, however, requires purification with hot water and alcohol.

With regard to an illustration of the above facts and a theory as to the relation of aniline-black to various bodies connected therewith, the author can at present give only a provisional explanation. For the basis of electrolytic aniline-black he obtained the formula $C_{24}H_{20}N_4$. His analyses rested between the following two rational formulæ:—



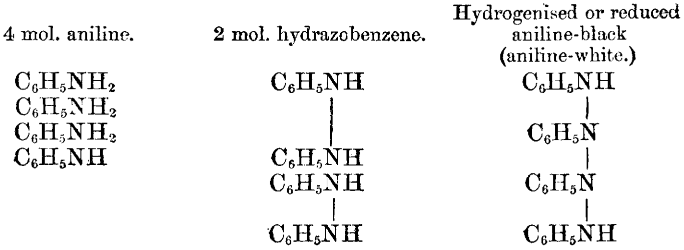
$$(C_6H_5)N—(C_6H_5)N—(C_6H_5)N—(C_6H_5)N \quad \text{and}$$



$$NH<\begin{matrix}C_6H_4—NH—C_6H_4\\C_6H_4—NH—C_6H_4\end{matrix}>NH.$$

The above facts are best explained by assuming the first formula as correct. The basis of aniline-black, a tetrazo-compound, is converted into the sulpho-acid by means of fuming sulphuric acid, which gives a colourless hydrogenised derivative, and with alkalis salts which dissolve in water, forming bluish-violet solutions. These are rendered colourless by hydrogenising agents, but become blue by dehydrogenation in the air, and give a black, which by superoxidation is converted into the above-named substance, not turned green by acids. As oxidising agents, aqueous solutions of potassium chlorate with addition of cupric sulphate and sal-ammoniac, or potassium chlorate with cupric chloride, or potassium bichromate, or, better, the well-known Jeanmaire agent, were employed. In the development of aniline-black in acid solutions of the aniline salts, the product first formed is emeraldine, a green body which should not be regarded as identical with that which is obtained by pouring the solution of aniline-black in fuming sulphuric acid into water.

The following bodies, therefore, have to be accurately investigated by analysis and metamorphoses:—(1.) Emeraldine, the mean between fugitive black and the aniline salts. (2.) The black which is turned green by acids. (3.) The oxidised true black. (4.) The green product of the action of fuming sulphuric acid on the black which turns green and on the real black. (5.) The colourless product of the hydrogenation of this green body (4) which may at present be called the sulpho-acid of the reduced aniline-black, or aniline-white. Taking the aniline salts as a starting-point, these various bodies are produced in the following order:—Aniline salts, emeraldine, black, sulpho-acid of the black, sulpho-acid of the hydrogenised black, and, by oxidation, once more the black. The following, at present purely hypothetical formulæ, may serve to explain the formation of aniline-black from the aniline salts, and the relation of the various bodies at present observed by the author:—



4 mol. aniline.

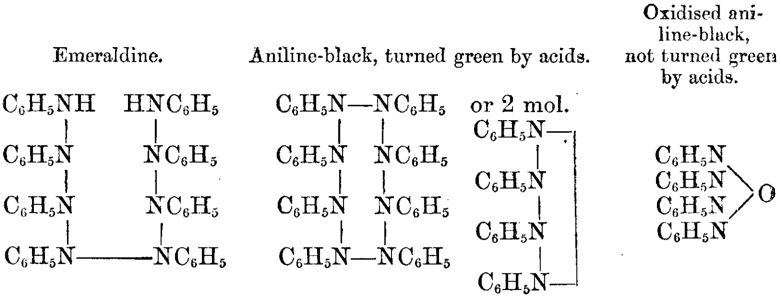
$$\begin{array}{l} C_6H_5NH_2 \\ C_6H_5NH_2 \\ C_6H_5NH_2 \\ C_6H_5NH \end{array}$$

2 mol. hydrazobenzene.

$$\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5NH \\ C_6H_5NH \\ | \\ C_6H_5NH \end{array}$$

Hydrogenised or reduced aniline-black (aniline-white.)

$$\begin{array}{c} C_6H_5NH \\ | \\ C_6H_5N \\ | \\ C_6H_5N \\ | \\ C_6H_5NH \end{array}$$



Emeraldine.

$$\begin{array}{lcr} C_6H_5NH & & HNC_6H_5 \\ | & & | \\ C_6H_5N & & NC_6H_5 \\ | & & | \\ C_6H_5N & & NC_6H_5 \\ | & & | \\ C_6H_5N & \text{———} & NC_6H_5 \end{array}$$

Aniline-black, turned green by acids.

$$\begin{array}{lcr} C_6H_5N & — & NC_6H_5 \\ | & & | \\ C_6H_5N & & NC_6H_5 \\ | & & | \\ C_6H_5N & & NC_6H_5 \\ | & & | \\ C_6H_5N & — & NC_6H_5 \end{array}$$

or 2 mol.

$$\begin{array}{c} C_6H_5N— \\ | \\ C_6H_5N \\ | \\ C_6H_5N \\ | \\ C_6H_5N— \end{array}$$

Oxidised aniline-black, not turned green by acids.

$$\begin{array}{l} C_6H_5N \\ C_6H_5N \\ C_6H_5N \\ C_6H_5N \end{array} \quad (C_6H_5N)_2{>}O$$

2. *Conversion of the Base of Aniline-black into a Pink fluorescent Colouring Matter.*—The basis of the electrolytic aniline-black was fused with potassium bisulphate. Sulphurous acid and nitrogen were given off, and the fused mass contained neither sulphite, thiosulphate, nor sulphide, and gave when boiled with water a slight yellow colour. The residue insoluble in water was treated on the water-bath with concentrated sulphuric acid, and yielded a copious black precipitate on the addition of water. The reddish-violet solution was rendered fluorescent by ammonia. The precipitate was treated with alcohol, which extracted a pink colouring matter showing the same fluorescence and giving the same chemical reactions and spectrum analysis as naphthalene-pink. The change of the black into the pink colouring matter is regarded by the author as an act of dehydrogenation. Should this

body prove to be naphthalene-pink, its formation would be explained by the following equation:—

$$5C_{24}H_{20}N_4 - 16H - 8N = 4C_{30}H_{21}N_3.$$

The reaction between the black and the bisulphate would be:

$$5C_{24}H_{20}N_4 + 16HKSO_4 = 8N + 16H_2O + 8SO_2 + 8K_2SO_4 + 4C_{30}H_{21}N_3.$$

The bisulphate is decomposed in the following manner:—

$$2KHSO_4 = K_2SO_4 + H_2O + O + SO_2.$$

In conclusion it is mentioned that on treating the basis of aniline-black with bichromate of potassium, and boiling it with water and then with alcohol acidified with sulphuric acid, the latter assumes a light violet colour. On treating the residue with caustic potash it assumes a violet-pink colour, while the residue when treated with alcohol gives a blue colouring matter. The same result was obtained with the basis of the aniline-black prepared in the usual way; but with the salt, *i.e.*, the deposit, as formed on the positive pole or with the commercial salt, different results were obtained. D. B.

**Amidazo-compounds in the Tolyl Series.** By R. NIETZKI (*Deut. Chem. Ges. Ber.*, x, 1155—1160).—The metatoluidine employed was prepared by Beilstein and Kuhlberg's method from metanitro-paratoluidine, the yield being about 10 per cent. of the paratoluidine. When treated with nitrous acid, either in alcoholic solution or floating on a solution of salt, it is easily converted into meta-amidazo-toluene, the hydrochloride of which is much less soluble than that of the corresponding ortho-compound previously described. The hydrochloride forms dark steel-blue needles, which are only slightly soluble in boiling alcohol, and are decomposed by water. The base itself crystallises in golden-yellow needles, which melt at 80°. The platinum salt, $(C_{14}H_{15}N_3.HCl)_2PtCl_4$, forms thin plates almost insoluble in water and in alcohol. On mixing alcoholic solutions of metatoluidine and paradiazoamidotoluene, paratoluidine is liberated, and metadiazoamidotoluene is formed. This base crystallises from alcohol in large yellow plates which melt at 127°. The hydrochloride forms small steel-blue plates grouped in stars; and the platinum salt, $(C_{14}H_{15}N_3.HCl)PtCl_4$, small bronze needles difficultly soluble.

It was important to ascertain what the reduction-products of the amidazo-compounds were, as if the amido- and azo- groups were 1 : 4, the resulting diamidotoluenes should yield toluquinone on oxidation.

In a former communication the author noticed that the action of oxidizing agents on paradiamidotoluene gave a beautiful green colour, but he now finds that when perfectly pure it no longer gives the colour reaction, although toluquinone melting at 67° is readily obtained. The hydroquinone melts at 124°. Pure paradiamidotoluene, obtained from the acetyl-derivative by heating it at 150° with hydrochloric acid, crystallises from hot dilute alcohol in large colourless prisms, which melt at 64° and boil at 273—274°. The green colour reaction is due to the presence of a trace of orthotoluidine, and as the same effect is produced with orthotoluidine and the base obtained by the reduction of meta-amidoazotoluene, he considers there can be no doubt as to its being the same diamidotoluene. These facts tend to strengthen the opinion that the quinones are 1 : 4 or para-compounds, and it would also seem that in all the amido-azo compounds the amido- and azo-groups occupy the positions 1 : 4 respectively.

C. E. G.

## Paradibromobenzenesulphonic Acid and some Derivatives.

By H. Borns (*Liebig's Annalen*, clxxxvii, 350—372).—1. *Paradibromobenzenesulphonic acid*, $C_6H_3Br_2SO_3H,3H_2O$.—The author obtains this acid by heating paradibromobenzene (melting at 89°) to 100° with fuming sulphuric acid for several days. On evaporating its aqueous solution over sulphuric acid it crystallises in fine transparent prisms, soluble in water and alcohol, and melting about 98°. It gives off 2 mols. of water at 100°, and the rest at 130°. The anhydrous acid melts at 128°.

The *ammonium salt*, $C_6H_3Br_2SO_3NH_4$, forms delicate needles very easily soluble in water and alcohol.

The *potassium salt*, $C_6H_3Br_2SO_3K,H_2O$, crystallises in long prisms or needles, which dissolve easily in water, and fall to powder when dried.

The *sodium salt*, $C_6H_3Br_2SO_3Na,1\frac{1}{2}H_2O$, forms delicate silky needles.

The *barium salt*, $(C_6H_3Br_2SO_3)_2Ba,H_2O$, forms pearly laminæ, which lose their water at 140° only.

The *calcium salt*, $(C_6H_3Br_2SO_3)_2Ca,10H_2O$, crystallises from concentrated solutions in pointed needles, and from weaker solutions in laminæ, easily soluble in water and alcohol. The crystals effloresce rapidly in the air.

The *lead salt*, $(C_6H_3Br_2SO_3)_2Pb,3H_2O$, forms yellowish laminæ, which dissolve sparingly in water, but are gradually deposited from the solution on standing.

The *silver salt*, $C_6H_3Br_2SO_3Ag,5H_2O$, crystallises in white prisms or in long pointed needles, which when dry do not alter in the air.

The *chloride*, $C_6H_3Br_2SO_2Cl$, is easily obtained by treating the potassium salt with phosphorus pentachloride. It crystallises from ether in tables, or in pearly laminæ, which melt at 71—72°.

The *amide*, $C_6H_3Br_2SO_2NH_2$, formed by the action of strong ammonia on the chloride, crystallises in long needles which dissolve sparingly in cold water and melt at 193°.

2. *Nitroparadibromobenzenesulphonic acid*, $C_6H_2Br_2(NO_2)SO_3H,1\frac{1}{2}H_2O$. —This substance is obtained by boiling the foregoing acid with the strongest nitric acid in a retort. It crystallises from aqueous solution over sulphuric acid in small yellow hygroscopic prisms, which dissolve in alcohol and ether, and blacken at 100° without melting.

The *ammonium salt*, $C_6H_2Br_2(NO_2)SO_3NH_4,\frac{1}{2}H_2O$, forms small laminæ, which dissolve easily in water, alcohol, and ether, give off their water completely at 130°, and decompose at 150°.

The *potassium salt*, $C_6H_2Br_2(NO_2)SO_3K,H_2O$, crystallises in fine yellow needles, easily soluble in water and alcohol.

The *barium salt*, $[C_6H_2Br_2(NO_2)SO_3]_2Ba,1\frac{1}{2}H_2O$, forms yellow prisms, easily soluble in hot, sparingly in cold water. This salt crystallises also with 6 mol. and with 9 mol. of water.

The *calcium salt*, $[C_6H_2Br_2(NO_2)SO_3]_2Ca,3H_2O$, forms small yellow prisms, easily soluble in water and alcohol.

The *lead salt*, $[C_6H_2Br_2(NO_2)SO_3]_2Pb,3H_2O$, crystallises in yellow nodules, easily soluble in water and alcohol.

The *chloride*, $C_6H_2Br_2(NO_2)SO_2Cl$, is most easily obtained by heating the potassium salt to 120° with phosphorus pentachloride and oxychloride in a sealed tube. It dissolves freely in ether, and crystallises imperfectly on evaporating the solution.

The *amide*, $C_6H_2Br_2(NO_2)SO_2NH_2$, is formed with difficulty by warming the chloride with strong ammonia, or better, by heating the two substances to 100° in sealed tubes. When crystallised repeatedly from hot water and alcohol it forms greenish-yellow prisms, which dissolve easily in hot water and alcohol, and melt at 178°.

3. *Amidoparadibromobenzenesulphonic acid*, $C_6H_2Br_2(NH_2)SO_3H,\frac{1}{2}H_2O$.—Formed, together with other products, by the action of tin and hydrochloric acid on nitrodibromobenzenesulphonic acid. It crystallises from strong solutions in delicate white needles and from weak solutions in faint violet-coloured prisms, which decompose at 150° without melting. It is sparingly soluble in hot and cold water and in alcohol. The salts are all easily soluble.

The *potassium salt*, $C_6H_2Br_2(NH_2)SO_3K$, crystallises in fine monoclinic tables.

The *barium salt*, $[C_6H_2Br_2(NH_2)SO_3]_2Ba,H_2O$, forms transparent prisms, which turn red in the air. It dissolves easily in alcohol.

The *lead salt*, $[C_6H_2Br_2(NH_2)SO_3]_2Pb,8H_2O$, crystallises in small white needles or pale brown prisms.

4. *Tribromobenzenesulphonic acid*, $C_6H_3Br_3SO_3H$.—The author obtains this substance by passing nitrous acid into a solution of amidodibromobenzenesulphonic acid in weak spirit, and evaporating the diazo-compound thus formed with strong hydrobromic acid. The residue is converted into barium salt, which is purified by repeated crystallisation. The free acid has not been examined.

The *sodium salt*, $C_6H_2Br_3SO_3K,1\frac{1}{2}H_2O$, forms brilliant yellow prisms, freely soluble in hot water.

The *barium salt*, $(C_6H_2Br_3SO_3)_2Ba,2H_2O$, forms yellow prisms, which dissolve with great difficulty in water.

The *chloride*, $C_6H_2Br_3SO_2Cl$, and the *amide*, $C_6H_2Br_3SO_2NH_2$, have also been prepared. The latter crystallises in small needles, which dissolve easily in alcohol, and undergo decomposition above 200°.

5. *Paradibromobenzenedisulphonic acid*, $C_6H_2Br_2(SO_3H)_2$, is formed, together with the corresponding monosulphonic acid, by the action of fuming sulphuric acid on dibromobenzene. It crystallises in small, transparent, easily soluble prisms.

The *potassium salt*, $C_6H_2Br_2(SO_3K)_2$, forms white soluble needles.

The *barium salt*, $C_6H_2Br_2(SO_3)_2Ba,4\frac{1}{2}H_2O$, crystallises in small, white, easily soluble needles.

The *chloride*, $C_6H_2Br_2(SO_2Cl)_2$, forms transparent monoclinic crystals, melting at 161°.

The *amide*, $C_6H_2Br_2(SO_2NH_2)_2$, forms nodules of microscopic needlès, easily soluble in water and alcohol.

Dibromobenzenedisulphonic acid is converted by boiling with strong nitric acid into *nitrodibromobenzenedisulphonic acid*, which is easily reduced by tin and hydrochloric acid to the corresponding *amido-acid*, $C_6HBr_2(NH_2)(SO_3H)_2$. The latter forms small crystals easily soluble in water and alcohol; its potassium and barium salts are crystalline and easily soluble. The *chloride* crystallises in prisms melting at 148°. The *amide* forms small needles which melt at 206°.

6. *Amidobromobenzenesulphonic acid*, $C_6H_3Br(NH_2)SO_3H$ + aq., obtained by the action of fuming sulphuric acid on parabromacetanilide at 170—180°, crystallises in white silky needles or in large pale-brown prisms, which dissolve sparingly in water and alcohol.

The *ammonium salt*, $C_6H_3Br(NH_2)SO_3NH_4$, forms small, reddish, easily soluble needles.

The *potassium salt*, $C_6H_3Br(NH_2)SO_3K$, crystallises in transparent laminæ or prisms, easily soluble in water.

The *barium salt*, $[C_6H_3Br(NH_2)SO_3]_2Ba,HO_2$, forms pearly laminæ, which turn red while moist, and dissolve easily in water and weak spirit.

The *calcium salt*, $[C_6H_3Br(NH_2)SO_3]_2Ca,H_2O$, forms easily soluble small prisms.

Amidobromobenzenesulphonic acid suspended in a little strong alcohol and treated with nitrous acid, yields the *diazo-compound*, $C_6H_2BrN_2SO_3H$, which crystallises in small yellow prisms, turning red in the light. This compound, when heated with hydrobromic acid, yields paradibromobenzenesulphonic acid, identical with that formed by the action of sulphuric acid on paradibromobenzene. When heated with absolute alcohol it yields metabromobenzenesulphonic acid.

J. R.

**Iodobenzenesulphonic Acid.** By W. LENZ (*Deut. Chem. Ges. Ber.*, x, 1135—1137).—Körner and Paternò obtained paraiodobenzenesulphonic acid by the action of sulphuric acid on benzene. The author, however, prepared it by the action of hydriodic acid on the diazo-compound from sulphanilic acid. After removal of iodine and excess of hydriodic acid, it was converted into the barium salt, crystallised, and then exactly decomposed with sulphuric acid. It crystallises in needles, which are very soluble in water, alcohol, and ether. $Ca(C_6H_4ISO_3)_2$, $Ba(C_6H_4ISO_3)_2$, and $Pb(C_6H_4ISO_3)_2$, all form colourless microscopic crystals, the first being easily soluble, and the last two difficultly soluble in water. The potassium and ammonium salts crystallise in minute needles. The chloride, $C_6H_4I.SO_2Cl$, crystallises in large transparent prisms, which melt at 86—87°, whilst the amide, $C_6H_4ISO_2.NH_2$, forms microscopic plates melting at 183°. The author has also obtained a fluobenzenesulphonic acid by a similar process, but all its compounds are so soluble that they could not be purified, except the amide, $C_6H_4F.SO_2NH_2$. This forms colourless, microscopic, six-sided, rhombic plates, easily soluble in alcohol. Potassium cyanide also acts strongly on the diazo-compound of sulphanilic acid, but the author has not yet investigated the nature of the reaction.

C. E. G.

**Derivatives of Metabenzene-disulphonic Acid.** By G. HEINZELMANN (*Liebig's Annalen*, clxxxviii, 157—184).—The best way of preparing this acid is to heat benzene with its own volume of fuming sulphuric acid, and then to add to this solution an equal volume of the same acid, and heat the mixture in a retort with its neck directed upwards, for two or three hours to such a degree that whilst the retort is well filled with white vapours, little or none shall escape; if only one hour's heating be allowed, much benzenemonosulphonic acid is found in the product. The thick dark-coloured mass is dissolved in water and the solution is neutralized with slaked lime; the whole is then drained and freed from colouring matter by treating a portion with sulphuric acid to precipitate the calcium; boiling the filtrate with lead carbonate; adding the resulting lead salt to the remainder; and precipitating the lead with sulphuretted hydrogen. Nearly all colouring matter is thus removed, so that on adding potassium carbonate, a nearly colourless solution of potassium salt is obtained, yielding fine crystals on evaporation. These were recrystallised and converted into the chloride (melting at 63°), which was then decomposed by water at 130—140° after crystallisation from ether: benzenesulphonic chloride was found in the ethereal mother-liquors.

It was not found practicable to brominate the disulphonic acid, but on nitration it yielded two *nitrobenzenedisulphonic acids*, designated by the author as α and β. The barium salt of the first crystallises in needles, that of the latter in nodules, so that the two can be mechanically separated. The *ammonium salt* of this α-acid, $C_6H_3(NO_2)(SO_3.NH_4)_2$, crystallises anhydrous from the solution obtained by decomposing the barium salt with ammonium carbonate, forming slightly yellow, large flat prisms with sharp end-faces. The *potassium salt* is also anhydrous; it forms colourless fine needles, somewhat less readily soluble in water than the *barium salt*, which crystallises with 4, 5, and $6H_2O$. The *calcium salt*, $C_6H_3(NO_2)\{(SO_3)_2Ca\},2H_2O$, crystallises in slightly yellow, highly deliquescent monoclinic (?) prisms. The *lead salt* forms nearly colourless needles, readily soluble in water, and crystallises with $4H_2O$, whilst the *silver salt* forms anhydrous nodules, quickly blackening in daylight. The *chloride* produced from the potassium salt by heating with phosphorus pentachloride and oxychloride in sealed tubes at 120°, washing the product with water and then with ether, and finally crystallising from warm toluene, forms with the toluene a crystalline compound, $C_6H_3(NO_2)(SO_2Cl)_2.C_7H_8$, which rapidly loses toluene in the air. The pure chloride melts at 96°, and when heated to 140° with water, splits up into hydrochloric acid and nitrobenzenesulphonic acid; concentrated ammonia readily converts it into the diamide, $C_6H_3(NO_2)(SO_2.NH_2)_2$, melting at 242°.

*β-Nitrobenzenedisulphonic acid* is obtained from the barium salt by means of dilute sulphuric acid, as a syrup, from which very minute hygroscopic crystals form on standing over sulphuric acid for a long time; its salts are much more soluble than those of the α-acid. The *ammonium salt* is anhydrous; the *potassium salt*, $C_6H_3(NO_2)(SO_3K)_2.\frac{1}{2}H_2O$ (?), forms nodules consisting of fine microscopic needles; the *barium salt* crystallises with $5H_2O$, the crystals turning yellow in daylight, without losing water. The *lead salt*, $C_6H_3(NO_2)\{(SO_3)_2Pb\}.4H_2O$, is obtained as a crystalline magma by the spontaneous evaporation of a concentrated solution; weaker solutions effloresce strongly. The *β-chloride* is an oil not solidifying in a freezing mixture; with ammonia, or dry ammonium carbonate, it forms only a brown, insoluble resinous product.

Sulphide of ammonium converts these two nitro-acids into the corresponding amido-acids, crystallising respectively with $3H_2O$ and $2\frac{1}{2}H_2O$, and forming neutral and also acid salts. On treatment with bromine-water, the α-acid forms bromanil, the β-acid tribromaniline. Neutral α-amidobenzenedisulphonates are obtained by decomposing the carbonates of the metals with the free acid not in excess, and the acid salts by adding to the neutral ones another equivalent of acid; the *ammonium salts* are $C_6H_3(NH_2)(SO_3.NH_4)_2.H_2O$ and $C_6H_3(NH_2)(SO_3H)(SO_3.NH_4),xH_2O$, the former crystallising in six-sided prisms, very readily soluble in water and spirit, the latter either in colourless flat anhydrous prisms or in hydrated highly deliquescent needles. The *neutral potassium salt* crystallises with $3H_2O$ and $4H_2O$, the *acid salt* with $H_2O$; the former is not deliquescent, the latter is difficultly soluble in cold water. The *barium salts* are respectively $C_6H_3(NH_2)\{(SO_3)_2Ba\}.3\frac{1}{2}H_2O$ and $\{C_6H_3(NH_2)(SO_3H)SO_3\}_2Ba.5H_2O$, the former being readily, the latter diffiultly soluble in water. The *neutral lead salt* crystallises in slightly coloured six-sided prisms containing $3\frac{1}{2}H_2O$; the *acid salt* contains $6H_2O$; the *neutral silver salt* is anhydrous.

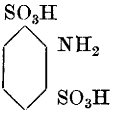
Of the salts of the β-acid the following have been examined: the *neutral barium salt*, $C_6H_3(NH_2)(SO_3)_2Ba.3H_2O$, forms concentric groups of brownish four-sided plates; the acid salt crystallises with $2H_2O$ and separates from hot concentrated aqueous solutions as a bulky mass of slender, shining, microscopic needles, redissolving very slowly in cold water. The *neutral lead salt*, $C_6H_3(NH_2)(SO_3)_2Pb.2H_2O$, forms hard crusts made up of nodules; the acid salt—

$$\{C_6H_3(NH_2)(SO_3H)SO_3\}_2Pb,6H_2O,$$

crystallises in crusts of small, shining, pointed rhombic plates, dissolving very slowly in cold water.

In order to elucidate the structure of these amido-acids, the α-acid was heated with hydriodic acid and phosphorus to 200°, without any result beyond explosion; the results obtained on treatment with bromine, however, point to the α-acid being indicated by No. 3 in the annexed formulæ, whilst the β-acid is indicated either by No. 1 or No. 2, of which the author prefers the latter, as this β-acid appears to be identical with the disulphanilic acid examined by Drebes.

No. 1.



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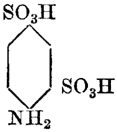

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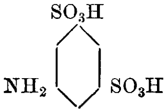

The *diazobenzenedisulphonic acid*, $C_6H_2(SO_3H)_2(N_2)$, obtained on treating the α-amido-acid with nitrous acid does not explode on heating; it decomposes in contact with metallic carbonates, but its acid salts can be obtained by treating the corresponding salts of the amido-acid with nitrous acid; in this way the ammonium salt, $C_6H_2(SO_2H)(SO_3NH_4)(N_2)$, is obtained, crystallising in anhydrous concentrically grouped needles; the potassium salt is anhydrous, whilst the barium salt is—

$$\{C_6H_2(N_2)(SO_3H)(SO_3)\}_2Ba,3H_2O$$

and the lead salt, $\{C_6H_2(N_2)(SO_3H)(SO_3)\}_2Pb,3H_2O$.

Similarly the β-amido-acid forms β-diazobenzenedisulphonic acid, and the acid salts of the β-amido-acid the corresponding β-diazobenzenedisulphonates on treatment with nitrous acid; the potassium salt is anhydrous, the barium salt crystallises with $2H_2O$, and the lead salt with $3H_2O$.

α-Diazobenzenedisulphonic acid boiled with hydrobromic acid forms α-bromodisulphonic acid, $C_6H_3Br(SO_3H)_2$: the ammonium salt of this acid is anhydrous; the potassium salt is very deliquescent and probably contains $4H_2O$; the barium salt crystallises in very soluble needles containing $2\frac{1}{2}H_2O$, and the lead salt in easily soluble, thin prisms containing $2\frac{1}{2}H_2O$. The *chloride*, $C_6H_3Br(SO_2Cl)_2$, crystallises from ether in crusts made up of small nodules melting at 99°; the *amide* melts at 245° and crystallises in white, silky small plates, difficultly soluble in cold, more readily in hot water. The corresponding derivatives of the β-acid have not yet been investigated.

*Bromamidobenzenedisulphonic acids.*—When 1 mol. bromine is added to an aqueous solution of α-amidobenzenedisulphonic acid, a mixture of mono- and dibromamidobenzenedisulphonic acids is produced, a portion of the amido-acid, however, remaining unchanged; if two or more molecules of bromine be added, bromanil is also formed, and separates in yellow laminæ, its quantity increasing in direct proportion to that of the bromine added. The two bromamido-acids are separated by evaporating the mixed solution to a syrup and leaving it over sulphuric acid for some days; the unaltered amido-acid separates in dense crystals, the mother-liquors of which solidify to a magma of slender needles grouped in nodules. These were converted into barium salt and then into ammonium salt, from the solution of which, prisms and tables separated, consisting of the *ammonium salt of dibromamidobenzenedisulphonic acid*; the last mother-liquors of these deposited the *monobromo-acid* as ammonium salt, crystallising in large, yellowish prisms; the mother-liquors yielded the ammonium salt of amidobenzenedisulphonic acid. The free acids are obtained, by converting the ammonium salts into lead salts, and decomposing with sulphuretted hydrogen, as crystallised masses, mostly consisting of colourless prisms, readily soluble in water and containing respectively $C_6H_2Br(NH_2)(SO_3H)_2.2\frac{1}{2}H_2O$ and $C_6HBr_2NH_2(SO_3H)_2.4H_2O$. *Bromamidobenzenedisulphonate of ammonium* is anhydrous (?); it forms large prisms, readily soluble in water. The *barium salt*—

$$C_6H_2Br(NH_2)\{(SO_3)_2Ba\}.8H_2O,$$

is highly deliquescent; the *lead salt* crystallises in nodules made up of fine prisms containing $3H_2O$. *Dibromamidobenzenedisulphonate of ammonium* forms dense colourless, anhydrous prisms, not readily soluble in cold water; the *potassium salt* is also anhydrous, whereas the *barium salt* contains $C_6HBr_2(NH_2)\{(SO_3)_2Ba\}.8H_2O$, and the *lead salt* crystallises in thin, flat, non-deliquescent prisms containing $3H_2O$. On passing nitrous acid into a solution of potassium α-dibromamidobenzenedisulphonate, the diazo-salt, $C_6(N_2)Br_2(SO_3H)(SO_3K)$, separates in anhydrous, microscopic, six-sided rhombic tables, but little affected by water or alcohol, but converted by hot hydrobromic acid into potassium α-tribrombenzenedisulphonate, $C_6HBr_3(SO_3K)_2$; this salt forms difficultly soluble minute prisms.

The corresponding derivatives of β-amidobenzenedisulphonic acid have not yet been examined. C. R. A. W.

**Action of Sulphuric Acid on Toluene.** By H. BECKURTS (*Deut. Chem. Ges. Ber.*, x, 943—947).—The action of sulphuric acid on toluene was first investigated by Jaworsky, who obtained a toluenesulphonic acid. Engelhardt and Latschinoff then took up the subject, and found that two isomeric toluenesulphonic acids were formed by the action of sulphuric acid on toluene. Wolkow next stated that these two acids, distinguished as α- and β-, belonged to the para- and meta-series. Finally Fittig and Ramsay demonstrated that the acid designated by Wolkow as the meta-acid, is undoubtedly tolueneorthosulphonic acid.

The subject has been finally taken up by the author, who directed his chief attention to the ortho-compound, and in the first place endeavoured to find a method of obtaining a good yield of it.

Sulphuric anhydride was introduced into toluene cooled by ice, and after solution of the toluene, the product was converted into potassium salt. Toluene was also introduced into fuming sulphuric acid in small quantities at a time, with continual cooling, till no more was taken up, and the potassium salts were prepared from the solution obtained. Both salts gave with phosphorus pentachloride, besides the solid sulphochloride melting at 69° (the tolueneparasulphonic chloride), an extremely small quantity of the liquid sulphochloride. When toluene was dissolved in ordinary sulphuric acid, the liquid being warmed on the water-bath—or in fuming sulphuric acid—potassium salts were formed which furnished a good quantity of liquid chloride corresponding nearly with Wolkow's results. The liquid chloride mechanically separated from the solid was freed from the portion of solid chloride still remaining dissolved in it, by cooling to —15°, and was then converted into the amide by aqueous ammonia. By fractional crystallisation from alcohol this amide was separated from another amide existing previously with it—the one being but slightly soluble in alcohol and fusing at 153—154°, the other very easily soluble in alcohol and fusing at 104°. The amide fusing at 137° could not be isolated. There could not, therefore, have been any more of the toluenepara-sulphochloride present in the sulphochloride employed. These observations show that by the action of sulphuric acid on toluene not two but three toluenesulphonic acids are formed. The amide fusing at 153° is named the ortho-compound; that at 104°, the meta-compound. The crude liquid chloride contained 80 per cent. by the first, and 20 per cent. of the second of these compounds.

*Tolueneorthosulphamide.*—Crystallises from alcohol in hard heavy octahedrons, from water in delicate prisms. It is but slightly soluble in water, much more easily in alcohol. Melting point between 153—154°. By heating with hydrochloric acid in a closed tube to 150°, the amide was converted into the ammonium salt of the corresponding acid, and from this the barium salt was prepared by means of barium hydrate.

*Barium Tolueneorthosulphonate* $(C_7H_7SO_2)_2Ba + H_2O$. — White shining scales, easily soluble in water, less easily in alcohol.

*Potassium Tolueneorthosulphonate.*—Tables, very easily soluble. The sulphochloride prepared from this salt by the action of phosphorus pentachloride forms a yellow oil which does not crystallise, even when cooled by a freezing mixture, and when treated with aqueous ammonia, yields the amide, melting at 153—154°.

*Toluenemetasulphamide.*—Crystallises from alcohol and water in slender shining needles and scales which are very soluble in alcohol and hot water, but difficult of solution in cold water. In the pure state it melts at 104—105°. Very small quantities, even traces, of impurities depress the melting point below 100°.

*Barium Toluenemetasulphonate*, $(C_7H_7SO_3Ba + H_2O$.—Prepared like the corresponding ortho-compound.* From dilute alcohol and from water the above barium sulphonate separates out as a white amorphous powder. It is easily soluble in water, less easily in alcohol.

The *sulpho-chloride* is a yellow oil which does not crystallise even in a freezing mixture. By aqueous ammonia it is converted into the *amide*, crystallising in white needles and scales, and fusing at 104°. The acid termed ortho-acid is identical with the acid obtained by Hübner and Post from β-parabromtoluenesulphonic acid, and by Jenssen from para-amidotolueneorthosulphonic acid. The properties assigned, by the chemists mentioned, to the chloride, amide, and barium salt of this acid completely coincide with those of these compounds derived by the author from the ortho-acid. The acid termed meta-acid is identical with the toluene-sulphonic acid obtained by Müller from the orthobromotoluenesulphonic acid, by Pagel from the orthotoluidinesulphonic acid, and by Pechmann from the para-

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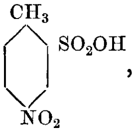
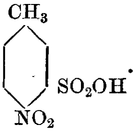
* The author observes in a foot-note that a small quantity of toluene was regenerated from both the ortho- and the meta-toluenesulphamide by heating with hydrochloric acid.—See Limpricht "Replacement of $SO_3H$ by H" (p. 191 of this volume).

amidotoluenemetasulphonic acid. This identity was proved by coinciding properties of derived compounds as in the preceding case. The amide (Hübner and Post) melts at 90—91°; at 104° (Pagel); at 100° (Pechmann). The chloride is described by all as an oil not crystallising at —10°. W. S.

**Isomeric Sulpho-acids from Paranitro-toluene.** By E. Hart and Ira Remsen (*Deut. Chem. Ges. Ber.*, x, 1046—1048).—Of the many possible modifications of nitrotoluenesulphonic acid, the following are known:—One from paranitrotoluene; one from orthonitrotoluene, which is identical with that from paratoluenesulphonic acid; and one from meta-nitroxylene. The first of these was prepared by Beilstein and Kuhlberg (*Annalen der Chem.*, clv, 11) by the action of fuming sulphuric acid on nitrotoluene; and they state expressly that only one sulpho-acid is formed during this reaction.

The authors, however (using a pure nitrotoluene), have obtained and separated two isomeric acids, or rather their calcium salts.

The first of these salts, containing four molecules of water, separates immediately from the concentrated solution in long slender needles; the other containing six molecules of water, is deposited on long standing in the form of monoclinic prisms. As it has been shown that the known sulpho-acid has the constitution , the only formula which remains for the second modification is—

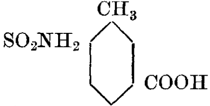


G. T. A.

**Oxidation of the Sulpho-acids of Metaxylene.** By M. W. Iles and Ira Remsen (*Deut. Chem. Ges. Ber.*, x, 1042—1046).—The difficulty of preparing pure xylene in large quantities was avoided by converting a tolerably pure coal-tar xylene into sulpho-acids, and these into the corresponding sulphamides, which could be separated by fractional crystallisation.

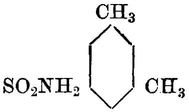
The authors find that three well-characterised sulphamides can be obtained from ordinary xylene, which melt respectively at 132°, 110°, and 143°. Some indications of a fourth amide were also found.

The first sulphamide, melting at 132°, is completely burnt away on oxidation. The second, melting at 110°, yields a monobasic acid—*sulphamine-metatoluic acid.* The fact that only one methyl-group undergoes oxidation, shows that the sulphamine group is not symmetrically situated with regard to the two methyl-groups in the molecule, but occupies the ortho-position with respect to one, and the para-position with respect to the other. There can be little doubt that it is the para-methyl which is oxidised into carboxyl, so that the formula of sulphamine-metatoluic acid is

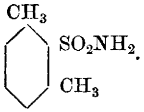


It is perhaps possible, by the introduction of carboxyl into the place of the sulphamine-group, to prepare xylidic acid.

The first amide melting at 132° is either—



or



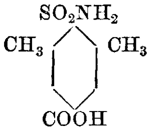
The investigation of these amides, including the third and fourth (?), will be continued.
G. T. A.

**Oxidation of Mesitylene-sulphonic Acid.** By L. B. Hall and Ira Remsen (*Deut. Chem. Ges Ber.*, x, 1039—1042).—Remsen has shown that the two isomeric toluene-sulphonic acids behave differently towards oxidising agents—the para-acid being converted into parasulpho-benzoic acid, whilst the ortho-acid yields simply carbon dioxide and water.

Mesitylene-sulphonic acid has the constitution of both the toluene-sulphonic acids, the sulpho-group being in the ortho-position with respect to two methyl-groups, and in the para-position with respect to the third methyl-group, and these methyl-groups must exhibit a different behaviour towards oxidising agents accordingly as they occupy the ortho- or the para-position. As potassium mesitylene-sulphonate when fused with potash exchanges a methyl-group for carboxyl, it was to be expected that the sulpho-acid itself would on oxidation be converted into an acid containing carboxyl, and such was found to be the case. For convenience the sulpho-acid was first converted into the corresponding sulphamide. The body obtained on oxidation melts at 247°. It possesses acid properties; is easily soluble in alcohol and ether, and nearly insoluble in cold water. Its most characteristic compound is the copper salt, which consists of groups of fine blue needles. These crystals lose water over sulphuric acid after they have been fully air-dried, but quickly take up the water again on exposure to air. Exposure to air at 200° produces no increase in weight. The anhydrous salt is of a bright-green colour. The formula of the hydrated salt is $(C_6H_2(SO_2NH_2)(CH_3)_2COO)_2Cu + 4H_2O$.

Since mesitylene-sulphonic acid on oxidation has only one methyl-group converted into carboxyl, it is in all probability the para-methyl which undergoes oxidation, and not one of the ortho-groups.

The amidated acid has the constitution expressed by the following formula:—



and is *parasulphamine-mesitylenic acid.*

This acid can be converted into mesitylenic acid by heating for a few hours to 200° in a sealed tube with concentrated hydrochloric acid.

The authors have prepared mesitylene from coal-tar oil, and found Jacobsen's method of separation (*Annalen der Chem.*, clxxxiv, 179) to answer very well. Further communications on mesitylene-sulphonic acid will be published shortly. G. T. A.

## Action of Bromine on Triamidophenol in presence of Water.

By H. WEIDEL and M. GRUBER (*Deut. Chem. Ges. Ber.*, x, 1137—1152).—As Schmitt and Bennewitz had obtained orthodichlorazophenol from orthoamidophenol by the action of chlorine, it seemed probable that a new class of azo-compounds might be obtained from the higher amido derivatives by similar means. This, however, was not found to be the case with triamidophenol. On gradually adding bromine (90 c.c.) to a solution of triamidophenol hydrochloride (200 grams) in 50 parts of water, the blue colour of the diimidoamidophenol first produced passes into yellow, and on allowing the filtered solution to stand, impure *bromodichromazin* is deposited in glistening brownish-yellow needles. The mother-liquors yield a little more of the substance on agitation with ether. It is purified by washing with boiling chloroform, and crystallising the residue from alcohol, with the aid of animal charcoal. The long yellow prismatic crystals formed on spontaneous evaporation of the alcoholic solution have been measured, as also most of the other crystalline compounds mentioned in this paper; they exhibit a feeble violet dichroism. It is very slightly soluble in ether, and insoluble in benzene, chloroform, and carbon bisulphide; boiling alcohol and acetic acid dissolve it with facility. When heated it is decomposed without previous fusion, giving off bromine vapour. The results of ten analyses lead to the formula $C_{18}H_8N_3Br_{11}O_7$ for this substance. It dissolves in concentrated sulphuric acid, but is precipitated by water unchanged, so that it is evidently not a hydrobromide of a compound of the formula $C_{18}H_7N_3Br_{10}O_7$.

Mercuric acetate, added to a solution of bromodichromazin in acetic acid or alcohol produces a pale-yellow crystalline precipitate of *mercury-bromodichromazin*, $C_{18}Hg_7N_3Br_{11}O_7 + 3Hg(C_2H_3O_2)_2$. Heated to 100°, it becomes brown, and evolves bromine, and at a somewhat higher temperature explodes. It is decomposed by sodium amalgam, with formation of ammonia, and when fused with potassium hydrate yields only oxalic acid.

Bromodichromazin, when boiled with a mixture of equal parts of sulphuric acid and water until it no longer separates on dilution, is converted into *bromodichroic acid*, $C_{18}H_7Br_{11}O_{11}$, which separates in crystalline crusts on long standing, the reaction being $C_{18}H_7Br_{11}N_3O_7 + 4H_2O = C_{18}H_7Br_{11}O_{11} + 3NH_3$. A further quantity may be obtained on extracting the acid liquors with ether. It may be purified by repeated crystallisation from a mixture of ether and benzene with the aid of animal charcoal; it then forms colourless tabular prismatic crystals of considerable size, which are easily soluble in water, alcohol, and ether. When heated they decompose below 100°, turning brown, and at a higher temperature evolve bromine, and char without previously melting. Its solution has an acid bitter taste, and easily decomposes carbonates. Bromodichroic acid yields precipitates with lead and silver salts, but they rapidly decompose, being transformed into the bromides; alkalis also decompose it very rapidly. The authors have succeeded in obtaining the calcium and barium salts by acting on their respective carbonates with a solution of the acid. They crystallise in slender needles, which are very hygroscopic, and quickly undergo change on contact with the air. Bromodichroic acid is reduced by sodium amalgam; but the authors were not able to obtain the product in a pure state, although they found that it yielded acetic acid and resorcin when fused with potassium hydrate.

When bromodichromazin is boiled for some time with dilute nitric acid, it is changed into an oil having the composition of *hexbromacetone*, $C_3Br_6O$, which crystallises on standing, whilst bromine and bromopicrin are produced at the same time. Chromic acid or chromic mixture acts in a similar manner; but an alkaline solution of permanganate completely decomposes it. Bromine acts strongly on bromodichromazin suspended in water, causing an evolution of carbonic anhydride, and although the action goes on slowly at the ordinary temperature, it may be completed in a few minutes by heating the mixture at 100°. On cooling, the hexbromacetone above mentioned separates in lustrous scales, which may be purified by crystallisation from chloroform. It may of course be prepared directly from triamidophenol by the action of excess of bromine, and this is the most convenient way when considerable quantities are required. It crystallises in large, colourless, highly refractive prisms, which melt at 107—109°. At a higher temperature it decomposes, only a small portion subliming unchanged. It is insoluble in water, easily soluble in ether, benzene, chloroform, and alcohol, but is decomposed by the latter. When boiled with a dilute solution of an alkaline hydrate, it yields bromoform and an alkaline carbonate, $C_3Br_6O + 2NaOH = 2CHBr_3 + Na_2CO_3$. It is decomposed in a similar manner when heated with water at 180°. It dissolves in boiling nitric acid, and separates again unchanged on cooling; but when the two are heated to 150°, bromopicrin is formed, together with carbonic anhydride and nitric peroxide, the reaction being $C_3Br_6O + 4HNO_3 = 2CBr_3(NO_2) + N_2O_4 + CO_2 + 2H_2O$*.

As Cloez found that the action of ammonia on pentabromacetone gave rise to bromoform and dibromacetamide, it seemed probable that hexbromacetone when similarly treated would yield tribromacetamide, $C_2Br_3O.NH_2$; such was found to be the case, the reaction taking place quantitatively when dry ammonia is passed over hexabromacetone in a tube. The crystalline product, when purified by crystallisation from dilute alcohol with aid of charcoal, forms white plates resembling benzoic acid, which melt at 119—121°. Large prismatic crystals may be obtained, however, by the spontaneous evaporation of its solution in benzene. It melts under boiling water, in which it is only slightly soluble; it is easily soluble in alcohol or

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* This equation is wrong: the quantities of oxygen on the two sides do not agree.—Ed.

ether, and in boiling benzene and chloroform. Tribromacetamide cannot be distilled unchanged, although it may be volatilised in a current of an indifferent gas. Alkaline solutions resolve it into bromoform and ammonia, with formation of an alkaline carbonate. Boiled with slightly diluted sulphuric acid (3 acid to 2 water) it yields ammonium sulphate and tribromacetic acid, $C_2Br_3O.NH_2 + H_2O = C_2Br_3O.HO + NH_3$. The crystals of the tribromacetic acid which separate on cooling, melt, after crystallisation from ether, at 128—130°, and are in all respects identical with the substance described by Schaeffer (*ibid.*, iv, 282). With alkalis it yields bromoform and a formate.

On dissolving hexbromacetone in pure methyl alcohol, adding water until the bromacetone begins to separate, and then treating the mixture with sodium amalgam, a powerful reaction takes place, and pseudopropyl alcohol is produced. It may be separated by fractional distillation, and then boils at 85°. These reactions of the compound $C_3Br_6O$ conclusively prove that it is really hexbromacetone, $CBr_3.CO.CBr_3$. Its formation from bromodichromazin may be represented by the equation—

$$C_{18}H_8N_3Br_{11}O_7 + 34Br + 14H_2O = 3C_3Br_6O + 3NH_4Br + 9CO_2 + 24HBr.$$

The constitution of bromodichromazin is at present unknown, but the author suggests that both it and bromodichroic acid are probably closely related to the compounds which Stenhouse obtained by the action of chlorine and bromine on pyrogallol. One of these compounds, mairogallol, $C_{18}H_7Cl_{11}O_{11}$, appears to be analogous to bromodichroic acid, $C_{18}H_7Br_{11}O_{11}$, whilst bromodichromazin, $C_{18}H_8N_3Br_{11}O_{11}$, is perhaps an azo-compound.

C. E. G.

**Note on Sordidin.** By E. Paternò (*Gazzetta chimica italiana*, vii, 281—284).—In a former paper the author noticed that the lichen *Zeora sordida* contained, besides usnic acid, two other compounds, zeorin, melting at 230°, and sordidin melting at 180° (this *Journal*, 1876, ii, 203). They were obtained from the ethereal extract by fractional crystallisation from alcohol, after the bulk of the usnic acid had been separated. The cold alcohol which had been employed to wash the extract in order to remove the resin, deposited, on standing, crystals which were suspected to be sordidin, but after purification were found to melt at 210°. The residue from a large quantity of usnic acid was therefore carefully examined; it contained—besides some usnic acid—zeorin, sordidin, and brown resin. It was washed, first with ether and then with alcohol to remove the resin, and the residue fractionally crystallised from chloroform, alcohol, and benzene. In this way it was separated into usnic acid, zeorin, and a substance of the formula $C_{13}H_{10}O_8$, melting at 210°, identical with that above described. From these results it would seem, either that in the lichen last examined, the sordidin had been replaced by the compound melting at 210°, which was also present in small quantity in the sample first examined, or, what was more probable, that the first specimen of sordidin obtained was impure, and that its true melting point was 210°. This latter supposition seemed the more likely, as an attempt to prepare sordidin from the second sample of lichen by crystallisation alone, yielded a product of lower melting point. All doubts were removed by the behaviour of the substances with a boiling solution of potassium hydrate. Zeorin is unaltered by this reagent, whilst the compound melting at 210° yields a product which crystallises in slender microscopic needles which do not melt at 250°, but char at a somewhat higher temperature. On submitting a small sample of the sordidin previously described and analysed, to similar treatment, it gave the crystals melting at 250°, and zeorin. The true melting point of sordidin, therefore, is 210°, and its empirical formula $C_{13}H_{10}O_8$. The yield obtained from the lichen amounted to only 0·1 per cent.

C. E. G.

**Oxidation of Cholesterin by Potassium Permanganate.** By LATSCHINOFF (*Bull. Soc. Chim.*, xxvii, 456).—The oxidation of cholesterin by potassium permanganate gives rise to three different acids—cholesteric acid, $C_{26}H_{42}O_4$; oxycholesteric acid, $C_{26}H_{42}O_5$; and dioxycholesteric acid, $C_{26}H_{42}O_6$. All, except the alkaline salts of these acids, are precipitated. The salts of the first acid dissolve in alcohol, ether, and benzene; those of the second in ether and benzene, but not in alcohol; those of the third in benzene, but not in ether and alcohol.

R. R.

**A Nitro-derivative of Paraoxybenzoic Aldehyde.** By G. MAZZARA (*Gazzetta chimica italiana*, vii, 285—286).—The aldehyde prepared by Reimer and Tiemann's method was heated with nitric acid diluted with five times its volume of water, and the brownish-black crystalline product was freed from oily matter as far as possible by pressure between filter-paper, and purified by crystallisation from alcohol with aid of animal charcoal. It forms long yellowish needles, which melt at about 140°, and are soluble in alcohol and in boiling water, only slightly soluble in ether, chloroform, and benzene. Its aqueous solution gives a red coloration with ferric salts. Nitroparaoxybenzoic aldehyde, $C_6H_3(NO_2)(OH).COH$, easily decomposes carbonates. The potassium compound $C_6H_3.NO_2.OK.COH + H_2O$, crystallises in magnificent plates of golden-yellow colour; they give off their water at 70°. The silver compound, $C_6H_3.NO_2.AgO.COH$, falls as a canary-yellow precipitate on adding silver nitrate to a solution of the potassium compound. C. E. G.

**Three Dichlorobenzoïc Acids.** By R. SCHULTZ (*Liebig's Annalen*, clxxxvii, 260—274).—Monochlorotoluene, the first product of the action of chlorine on toluene in presence of iodine, has been regarded by some chemists as the *para*-compound, mainly or exclusively. If this view were correct, it would follow that the substance is capable of yielding only two dichlorotoluenes when subjected to the further action of chlorine. But the author of the present paper shows that the dichlorotoluene thus formed is a mixture of at least three (and probably *only* three) isomerides, and that consequently monochlorotoluene is not a single product.

Dichlorotoluene, obtained by passing chlorine into dry warm toluene containing molybdenum pentachloride, was purified by distillation and then converted into dichlorobenzotrichloride, $C_6H_3Cl_2CCl_3$, by the action of chlorine on its vapour. The latter product, when heated to 200° with water in sealed tubes, yielded dichlorobenzoic acid, in accordance with the equation—

$$C_6H_3Cl_2.CCl_3 + 2H_2O = C_6H_3Cl_2.COOH + 3HCl.$$

This acid, after neutralisation with barium hydrate, yielded by fractional crystallisation the barium salts of the three following acids:—

1. An acid melting at 201°, and crystallising from water in needles, identical in its properties and in those of its barium salts with Beilstein's α-dichlorobenzoic acid.

2. An acid melting at 156°, crystallising from water in delicate needles, and subliming in small laminæ, apparently identical with the β-dichlorobenzoic acid of Beilstein, Claus, and Thiel.

3. An acid melting at 126·5°, distinguished by the author as γ-dichlorobenzoic acid. It dissolves sparingly in water, more freely in alcohol, and crystallises from the latter in small needles.

The *barium salt*, $(C_6H_3Cl_2COO)_2Ba + 3\frac{1}{2}$ aq., crystallises from alcohol in stellate groups of small needles.

The *potassium salt*, $C_6H_3Cl_2COOK + 5$ aq., crystallises from water, in which it is very freely soluble, in beautiful needles.

The *ammonium salt*, $C_6H_3Cl_2COONH_4 + 1$ aq., crystallises in fine needles.

The *zinc salt*, $(C_6H_3Cl_2COO)_2Zn + 1\frac{1}{2}$ aq., crystallises indistinctly. On boiling a concentrated solution the salt is deposited, but redissolves on cooling. The zinc salt of the β-acid behaves in the same manner, but not that of the α-acid.

The *chloride*, $C_6H_3Cl_2COCl$, obtained by distilling the barium salt with phosphorus pentachloride, is a clear liquid boiling without decomposition at 244°.

The *amide*, $C_6H_3Cl_2CONH_2$, formed by the action of alcoholic ammonia on the chloride, crystallises from alcohol and water in very fine white needles melting at 166°. J. R.

**Nitrobenzoic Acids.** By LEO LIEBERMANN (*Deut. Chem. Ges. Ber.*, x, 1036—1038).—Three isomeric nitrobenzoic acids may be obtained by nitration of benzoic acid. The melting point of these acids, when mixed, varies, but generally lies between 115—120°. The fourth acid described by Fittica (*Berichte*, x, 481), and melting at 127°, does not exist. Mixtures of organic acids behave like metallic alloys with respect to their melting points. Thus a mixture of equal parts of oxybenzoic and paroxybenzoic acids melts between 143° and 152° (melting point of oxybenzoic acid = 200°, of paroxybenzoic acid = 210).

A mixture of equal parts of oxybenzoic acid and salicylic acid melts at 126° to 134° (melting point of salicylic acid = 155°). Several other instances are given, and these tend to show that mixtures of the known nitrobenzoic acids may give rise to others with melting points lower than those of either constitutent, which are not, however, distinct acids. G. T. A.

**Nitrobenzoic Acids.** By E. Widnmann (*Deut. Chem. Ges. Ber.*, x, 1159—1160).—This contains the author's determinations of the melting points of the three nitrobenzoic acids, and of mixtures of the same:—

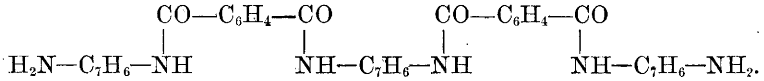
| | |
|---|---|
| Orthonitrobenzoic acid ........ | 149° |
| Metanitrobenzoic acid.......... | 140°—141° |
| Paranitrobenzoic acid.......... | 238° |

A mixture of the three isomeric acids began to melt at 137°, and was completely melted at 180°. In the following table, when two temperatures are given, the lowest indicates the commencement, and the highest the completion, of the fusion:—

| Proportions in mixture. | Ortho and Meta. | Ortho and Para. | Meta and Para. |
|---|---|---|---|
| 10 : 10 | 92°—98° | 200° | 165°—205° |
| 10 : 5 | 125° | 142°—190° | 127°—185° |
| 10 : 1 | 140° | 141° | 130°—155° |
| 10 : 0·5 | 144° | 145° | 132°—133° |
| 10 : 0·2 | 146° | 147° | 134°—135° |
| 10 : 0·1 | 146° | 145° | 135°—136° |
| 0·1 : 10 | 132°—135° | 233°—237° | 236°—238° |
| 0·2 : 10 | 132°—134° | 228°—235° | 232°—237° |
| 0·5 : 10 | 132°—140° | 222°—235° | 215°—234° |
| 1 : 10 | 132°—133° | 200°—225° | 205°—230° |
| 5 : 10 | 112° | 210°—216° | 195°—208° |

C. E. G.

**Action of Phthalic Anhydride on Aromatic Diamines.** By R. Biedermann (*Deut. Chem. Ges. Ber.* x, 1160—1166). The author finds that the action of phthalic anhydride on diacid bases is similar to that which takes place with succinic anhydride and metaphenylenediamine, namely, that the acid residue does not enter into the benzene nucleus of the aromatic diamene; but that condensation takes place, with elimination of hydrogen from the $NH_2$ groups in the latter. In this way *monophthalyl-tolylenediamine* $C_7H_6(NH)_2(CO)_2C_6H_4$, or  $C_7H_6<\begin{matrix}NH—CO\\NH—CO\end{matrix}>C_6H_4$, is formed on heating phthalic anhydride and tolylenediamine (m.p. 99°) together until water ceases to be given off. The product is exhausted with boiling alcohol, and the residue crystallised from dry acetic acid. The yellow silky needles, which separate from the alcoholic solution, are the monophthalyl compound. After repeated crystallisation from nitrobenzene, they melt at 192°. Boiled with soda solution, or with concentrated hydrochloric acid, is is resolved into phthalic acid and tolylenediamine. The portion which it insoluble in alcohol, but crystallises from acetic acid, is *diphthalyl-tolylenediamine* $C_7H_6[N(CO)_2C_6H_4]_2$. It is insoluble in alcohol, and separates from its solution in boiling acetic acid in small, snow-white, glistening crystals, which melt at 230—233°. It is only slowly attacked by soda solution, and not at all by hydrochloric acid. If the mixture of the anhydride and the diamine be heated with phosphoric anhydride, or if the hydrochloride be substituted for the base, the same result is obtained as that above described; but on boiling the two in alcoholic solution, and then evaporating to dryness, nothing but monophthalyl-tolylenediamine is formed. The latter, when boiled with dilute hydrochloric acid, is not at once resolved into phthalic acid and tolylenediamine, but an intermediate product is first formed of the formula,



$$H_2N{-}C_7H_6{-}NH{-}CO{-}C_6H_4{-}CO{-}NH{-}C_7H_6{-}NH{-}CO{-}C_6H_4{-}CO{-}NH{-}C_7H_6{-}NH_2.$$

the liberated phthalic acid acting on another molecule of the monophthalyl-tolylenediamine, to form the compound

$$C_7H_6[N{=}(CO)_2{=}C_6H_4]_2$$

above mentioned. The hydrochloride of the base crystallises in beautiful rhombic plates, and gives a reddish-yellow platinum salt $C_{37}H_{32}N_6O_4\,(HCl.)PtCl_4$. The base itself is very soluble in water, and difficult to purify.

The action of phthalic anhydride on para- and metaphenylenediamine takes place in a manner precisely similar to that with the tolylenediamine. *Diphthalylparaphenylenediamine* $C_6H_4[N(CO)_2C_6H_4]_2$, crystallises from acetic acid in needles which melt at 295°. The *monophthalylparaphenylenediamine* $C_6H_4(NH)_2(CO)_2C_6H_4$ is a crystalline powder melting at 182°. *Diphthalylmetaphenylenediamine* melts at 252°, and the *monopthalyl*-compound at 178°. The reactions of these compounds with alkaline solutions and with acids are strictly analogous to those of the compounds previously described.

Two compounds, melting at 104° and 272°, have been obtained by the action of phthalic anhydride on tolylenediamine melting at 80°. All the compounds described yield nitro derivatives, and yellow nitroso-compounds have been obtained from the bases. The author concludes the paper by stating that phthalic anhydride and urea fused together yield phthalimide, with evolution of ammonia and carbonic anhydride, whilst, if boiled in alcoholic solution, a molecular combination of phthalic acid with urea is formed. C. E. G.

**Oxyphthalic Acid.** By A. Baeyer (*Deut. Chem. Ges. Ber.*, x, 1079—1084).—The ethyl amidophthalate employed in this research was prepared by saturating an alcoholic solution of crude nitrophthalic acid with dry hydrochloric acid, separating the ethyl nitrophthalate thus formed by the addition of water, and after washing it with a solution of sodic hydrate, dissolving it in alcohol, and reducing it by means of hydrochloric acid and zinc powder. By this means crystallised ethyl amidophthalate was obtained equal to 80 per cent. of the theoretical for the amount of ethyl nitrophthalate employed.

The ethyl amidophthalate was converted into oxyphthalate by dissolving it in dilute sulphuric acid (40 parts), and after decolorising the solution by means of animal charcoal, gradually adding a solution of sodium nitrite, and heating to 100°. Great care must be taken not to employ excess of the nitrite, or yellow compounds will be formed, which greatly diminish the yield of the oxyphthalate. The ethyl oxyphthalate separates as an oil, which is soluble in alkaline solutions, and is reprecipitated by acids; it does not crystallise, neither does it volatilise without decomposition. The ether was saponified by boiling with a concentrated solution of potassium hydrate, and the acid precipitated as lead salt: the latter suspended in water and decomposed by sulphuretted hydrogen, gave a colourless solution, from which the oxyphthalic acid was extracted by concentration and agitation with ether. *Oxyphthalic acid*, $C_8H_6O_5$, or $C_6H_3(OH)(COOH)_2$, obtained by dissolving the anhydride in boiling water, and allowing the solution to cool, crystallises in tufts, which are readily soluble in hot water, but require 32·4 parts at 10°. It is very soluble in alcohol and acetone, less so in ether, and is almost insoluble in the hydrocarbons. It melts at about 180°, being resolved into water and the anhydride. The salts which oxyphthalic acid forms with the alkalis and alkaline earths are very soluble. Ferric chloride gives a reddish-yellow colour with the acid. When oxyphthalic acid is heated with concentrated sulphuric acid for four hours at 200°, and the dark-coloured product poured into water, a greenish-yellow precipitate is formed, from which three distinct substances have been obtained:—1. A yellow sublimable body, resembling anthraflavone. 2. A substance resembling a phthalideïn, soluble in sulphuric acid with a splendid red colour. 3. A colourless crystalline compound, which melts at 123°, and sublimes unchanged. Oxyphthalic acid in aqueous solution is easily reduced by sodium amalgam, but the product (presumably hydroxyphthalic acid) has not been examined.

*Oxyphthalic anhydride*, $C_8H_4O_4$, is formed when the acid is heated at 180°. It sublimes unaltered at 200—210°, in long needles, totally different in appearance from those of phthalic anhydride, but it cannot be distilled unchanged. The anhydride melts at 165—166°, and when heated with aniline, at 160—180°, yields a well crystallised anilide.

An *oxyphthaleïn of phenol*, which very closely resembles the corresponding phthaleïn, is formed on heating the anhydride with phenol and sulphuric acid, at 115°. It is somewhat more soluble in water than the phthaleïn, and its dilute alkaline solution is rose-red. It is reduced by zinc-dust to a colourless oxyphthalin, which, by the action of concentrated sulphuric acid, is converted into a greenish-yellow oxyphthalidin; the latter, like the phthalidin, is oxidised by sulphuric acid and manganese peroxide in the cold, yielding a colourless oxyphthalideïn, which dissolves in sulphuric acid, with a blue violet colour. Oxyphthalic anhydride heated with resorcin at 200°, yields *oxyfluoresceïn*, resembling fluoresceïn in every respect, and the brominated derivative resembles eosin, but gives a somewhat redder shade on silk. The *oxygalleïn* is also very similar to galleïn.

The author concludes with some theoretical considerations. The hydroxyl group in oxyphthalic acid may occupy two different positions, but this question is at present undetermined, the formation of meta-amidobenzoic acid from amidophthalic acid by boiling it with hydrochloric acid yielding no information. Perhaps the study of the second nitrophthalic acid indicated by O. Miller (*ibid.*, x, 709), may throw some light on the matter. As oxyphthalic acid so closely resembles phthalic acid in its reactions with resorcin, the formation of a fluoresceïn will serve to distinguish it from isomeric derivatives of isophthalic and terephthalic acids. C. E. G.

## A new Acid (Atranoric Acid) from Lecanora atra.

By E. Paternò and A. Ogliatoro (*Gazzetta chimica italiana*, vii, 189—192). The ethereal extract of this lichen, collected in the neighbourhood of Palermo, yielded, on evaporation, a crystalline mass mixed with a soft brown resin, which was easily removed by washing with cold ether. The crystals are a mixture of two acids, which were separated by means of chloroform; one (*atranoric acid*) is colourless, and but slightly soluble in cold chloroform; whilst the other, which is yellow, is very soluble.

Atranoric acid crystallises from chloroform in small, colourless, transparent prisms, which melt at 190°, and are only very slightly soluble in cold alcohol or ether; it is moderately soluble in boiling chloroform. The results of the analysis correspond closely with the formula $C_{19}H_{18}O_8$. It has feeble acid characters, although it does not affect litmus, dissolving in alkaline solutions, and being reprecipitated by acids. Boiled with aniline and alcohol, it yields a compound crystallising in lustrous yellow needles, which melt at 156°. Heated with alcohol at 150°, it is converted into a crystalline substance, very soluble in alcohol. It forms long needles, which melt at 115°.

The yellow acid accompanying atranoric acid in this lichen, closely resembles usnic acid in appearance, general characters, and behaviour with solvents, but melts at 175°, whilst usnic acid melts at 195—197°. Heated with alcohol at 150°, it yields a substance crystallising in slender needles, and melting at 175° just like the decarbusnic acid obtained from usnic acid by this process. With aniline and alcohol it also behaves like usnic acid. The product of the dry distillation of the acid, when extracted with water and filtered from tar, gives a yellow colour with ammonia and potash, brown with ferric chloride, and deep red with sodic hypochlorite. Usnic acid (from *zeora sordida*), gives results almost identical. This would tend to show that the acid is merely usnic acid whose melting point is lowered by the presence of some impurity in small quantity; the results of the analysis give carbon about 0·5 per cent. lower than that required by the formula $C_{18}H_{16}O_7$. The author suggests that the beta-usnic acid of Hesse, and the cladonic acid of Stenhouse, extracted from *Cladonia rangiferina*, may be merely impure usnic acid.

The authors have also obtained, from a variety of the same lichen, (*Lecanora atra panormitana:* De Notaris), another acid, melting at 91°, and which they propose to call *atralinic acid.* Its formula is $C_{16}H_{18}O_5$.

Appended to this paper is a note by Paternò, in which he refers to a substance, described in his memoir as usnate of aniline, obtained by boiling usnic acid with aniline. It crystallises in yellow needles, melting at 142°, and was considered to be an usnate of aniline. He now finds that, on boiling the acid with excess of aniline, another compound is produced, which crystallises in leafy plates, melting at

170°, and much less soluble in alcohol than the compound previously described. It is not an usnate of aniline, but it is at present under investigation. C. E. G.

**Isolepidene.** By M. ZININ (*Bull. Soc. Chim.*, xxvii, 546).—Isolepidene forms rather more than a third of the weight of oxylepidene submitted to distillation, and is always accompanied by a considerable quantity of oxylepidene. Treated with a mixture of zinc and acetic acid, isolepidene fixes two atoms of hydrogen, whilst the action of sodium amalgam on an alcoholic solution gives rise to an addition-product with four atoms of hydrogen. The oxidation of isolepidene by chromic anhydride produces at first an isomeride of oxylepidene, but afterwards the product is benzophenone. Benzoic acid and benzile are secondary products of the reaction. R. R.

**Anthraquinone.** By A CLAUS (*Deut. Chem. Ges. Ber.*, x, 925—928).—Several years ago the author observed that by passing chlorine, or dropping bromine, into a boiling alcoholic solution of anthracene, anthraquinone was formed and crystallised out after a short time. An endeavour to base a quantitative method of determining anthracene in the crude article on this fact failed, owing to the reaction going too far or not far enough. However, the reaction did not seem to lack interest, especially as by similar treatment naphthalene cannot be converted into naphthaquinone. The reaction is very well suited as a lecture experiment. 1 gram of anthracene is treated with 4 to 6 times its bulk of alcohol in a small flask, so that on boiling, only a part dissolves, and then a rapid stream of chlorine is passed through the boiling liquid, or bromine is introduced. After cooling, the liquid is filtered, the residue on the filter washed first with cold alcohol then with dilute soda-solution, and finally after drying sublimed between watch-glasses. The chlorinised products are recognised in the sublimate by their yellow colour.

Hydroanthraquinone was obtained by Böttger and by Graebe and Liebermann, by reduction of anthraquinone with zinc-dust and sodium hydrate. It may likewise be obtained from anthraquinone by treatment with sodium-amalgam. When the latter and anthraquinone are brought together, and the mixture is treated with water, a clear deep-red solution of sodium-hydroanthraquinone is obtained after a short time. This is especially the case if violent motion of the vessel be avoided. After pouring off the excess of amalgam and leaving the residue exposed to the air, the colour disappears gradually, or on shaking with air, quickly, fine needles of regenerated quinone separating out. This is said to make an excellent lecture experiment, and also to serve for detecting the smallest traces of anthraquinone. A few particles of anthraquinone (1 mgr. is amply sufficient) are placed in a test-tube with some sodium-amalgam, and treated with absolute ether free from alcohol, the whole being well shaken for some time. If now a drop of water be let fall into the ether and the vessel gently moved, a splendid red colour appears, which immediately disappears on shaking, so as to bring the red solution in contact with the air above the ether;

on leaving it at rest the colour soon reappears. This play of colour may be repeated as often as desired by alternately shaking the liquid and leaving it at rest. If absolute alcohol be used instead of ether, there appears at the point of contact of the alcohol and sodium amalgam, a dark-green zone, which on gently shaking extends to the whole solution, turning it to a splendid green. On shaking air through however, the colour entirely disappears. This reaction may also be repeated at pleasure with the same trace of anthraquinone, if enough amalgam be present. Should the alcohol, however, contain a trace of water, then a red colour appears instead of the green, and may be made to disappear and reappear the oftener the more water is present, by shaking air through as before mentioned. This reaction is recommended as an extremely good test for the presence of water in alcohol. These colour reactions merely prove that anthraquinone is always regenerated from the coloured products on shaking with air. This fact was proved experimentally by testing the melting point and other properties of the regenerated anthraquinone. The constitution of the green body is now a subject of investigation. The author has also commenced with Schnutz the investigation of the action of zinc-ethyl on anthraquinone. By causing 4 molecules of zinc-ethyl to act on 1 molecule of the quinone, a very lively reaction is set up and a brown plaster-like mass is obtained, easily soluble in alcohol and ether. This has not as yet been crystallised. It is easily soluble in nitric acid, and from the solution water precipitates a solid nitro-product, now under examination. Ethiodide of zinc acts more gently, and furnishes the same product. Other quinones have been likewise experimented on, as benzene-quinone and naphtho-quinone. The authors hope, by the help of these reactions, to find a means of throwing light on the often repeated supposition that the bodies going under the general name of quinones are not really analogously constructed. The reaction of hydrocyanic acid, and of this acid with hydrochloric acid, on the different quinones, has also been taken in hand. W. S.

**Munjistin, ε-Purpurin, and Purpuroxanthincarbonic Acid.** By E. Schünck and H. Römer (*Deut. Chem. Ges. Ber.*, x, 790—792).—The authors find that the munjistin discovered by Stenhouse is identical with their purpuroxanthincarbonic acid, and that munjistin gives a crimson and not a yellow barium-lake, as first reported by Stenhouse. Stenhouse discovered the substance and named it munjistin, whilst Schünck and Römer have settled its formula, $C_{15}H_8O_6$, and its position with regard to the other colouring matters of madder. These two chemists extracted their product from "munjeet," just as Stenhouse did, and compared the results of their analyses with those executed upon purpuroxanthincarbonic acid.

With respect to ε-purpurin, Rosenstiehl has stated that this body is identical with purpuroxanthincarbonic acid. This assertion appears to the authors not a little unscrupulous, inasmuch as Rosenstiehl thus makes his ε-purpurin $2\frac{1}{2}$ per cent. poorer in carbon, without giving any numbers to justify the alteration, and apparently forgets that the melting point of ε-purpurin is 180°, whilst that of purpuroxanthincarbonic acid is 231°, a difference of more than 50°. Rosenstiehl alters the formula of his ϵ-purpurin from $C_{14}H_8O_5$ to $C_{15}H_8O_6$, but unfortunately the synthetical method of preparation suitable to the previous formula is allowed to remain. He maintains (*Compt. rend.*, lxxxiii, 829) that ϵ-purpurin is formed by the oxidation of purpuroxanthin, and this he maintains after he has given the new formula, $C_{15}H_8O_6$, to the ϵ-purpurin. It is naturally an enigma to the authors how $C_{14}H_8O_4$ (purpuroxanthin) can by simple oxidation be converted into $C_{15}H_8O_6$ (purpuroxanthincarbonic acid). Another peculiar source for ϵ-purpurin is, according to Rosenstiehl, pseudo-purpurin, to which he has lately given the formula $C_{15}H_8O_7$. By boiling with water it is said to split up into $C_{15}H_8O_6$ and $C_{14}H_8O_5$ (purpurin hydrate). The madder-orange of Runge, Rosenstiehl has declared in his last communication to be also identical with ϵ-purpurin (corresponding to purpuroxanthincarbonic acid). Only a few months ago the same chemist declared that till then only contradictory statements had appeared about this body, and if the authors understood aright, he further stated it to be a mixture of ϵ-purpurin and purpuroxanthin. However, according to the latest results of Stenhouse and Stokes, the said orange is not identical with munjistin, and the authors have further already shown that it cannot also be identical with purpuroxanthincarbonic acid. Finally, ϵ-purpurin cannot be compared with any individual chemical body, as it is undoubtedly a mixture of an unknown number of bodies. W. S.

**Eterpene (Ethyl-eterpene).** By F. V. SPITZER (*Deut. Chem. Ges. Ber.*, x, 1034—1036).—The author described in a former paper (this *Journal*, 1876, ii, 514) a body derived from camphor chloride by means of ethyliodide and sodium, for which the name of eterpene (= ethyl-terpene) was proposed. He now finds that the same reaction takes place at the ordinary pressure and without the use of benzene as a solvent, but that the so-called eterpene, $(C_{10}H_{15}.C_2H_5)$, is a terpene, and that the ethyliodide does not take a part in the reaction. G. T. A.

**The Polythiohydrates of Strychnine.** By A. W. HOFMANN (*Deut. Chem. Ges. Ber.*, x, 1087—1894).—Some years ago the author described a compound of strychnine obtained in yellow crystals (*ibid.*, i, 81) on mixing an alcoholic solution of strychnine with one of yellow ammonium sulphide, and to which he assigned the formula, $C_{21}H_{22}N_2O_2.H_2S_3$. Since then Schmidt (*ibid.*, viii, 1267) has obtained what he believed to be a different compound, $(C_{21}H_{22}N_2O_2)_2(H_2S_2)_3$, by passing hydrogen sulphide into an alcoholic solution of strychnine and exposing it to the air. The author has compared these two substances and finds them to be identical. The question naturally arose, which of the two formulæ given is the correct one? This evidently could not be settled by the results of the elementary analysis, as the difference in the percentage of hydrogen would fall within the limits of experimental error; recourse was therefore had to a determination of the amount of hydrogen outside the strychnine molecule. If the compound contained $H_2S_2$ it would, when treated with arsenious acid in hydrochloric acid, yield $As_2S_6$, whilst if it contained $H_2S_3$ it would yield $As_2S_9$; on making the experiment the analytical results showed that the precipitate actually contained $As_2S_{18}$, indicating that the strychnine compound contained $H_2S_6$. Similar results were obtained on heating it with lead acetate and acetic acid. It would seem therefore that the correct formula for this compound is really $(C_{21}H_{22}N_2O_2)_2.H_2S_6$. This formula agrees with the results of the elementary analysis even better than the one originally proposed by the author.

The author considers it probable that this compound has a constitution analogous to that of the periodide, $C_{21}H_{22}N_2O_2.HI.I_2$, and that it may perhaps be $C_{21}H_{22}N_2O_2.H_2S_2.S_4$, in which case the oily drops liberated on treating the substance with an acid must be regarded as a solution of sulphur in hydrogen persulphide. C. E. G.

**Picrotoxin.** By E. PATERNÒ and A. OGLIALORO (*Gazzetta chimica italiana*, vii, 193—197).—After referring to their former paper on this subject (this *Journal*, 1877, i, 719), in which they mentioned that the action of bromine on picrotoxin did not appear to give rise to a dibrominated derivative, as supposed by Barth, the authors state that when bromine (2 mols.) is added to picrotoxin (1 mol.) suspended in ether, hydrobromic acid is given off, and the picrotoxin is converted into a mixture of two compounds, both insoluble in ether; the same compounds are formed by the action of bromine on picrotoxin in hot aqueous solution. One of the substances contains bromine, and may be readily separated by dissolving the mixture in boiling alcohol, when it separates in the crystalline state on cooling. The analytical results agree with the formula $C_{15}H_{15}Br.O_6$, that of *monobromopicrotoxide*, if the formula previously given for picrotoxide be changed to $C_{15}H_{16}O_6$. This monobromo-derivative forms small, transparent, colourless prisms which decompose at about 240° to 250° without melting. The second substance remaining in solution in the alcoholic mother-liquors, in which it is readily soluble, may be purified by repeated crystallisation from boiling water. It crystallises in long slender needles which melt at 246—248°, but are at the same time decomposed. The numbers obtained on analysis agree with the formula $C_{15}H_{18}O_7$ or $C_{15}H_{16}O_6 + H_2O$, that of a *hydrate of picrotoxide*. If this compound be boiled with acetyl chloride for about an hour, hydrochloric acid is given off, and after removing the excess of acetyl chloride, a soft viscous mass is left which, on treatment with boiling alcohol, yields picrotoxide and a compound having the composition $C_{15}H_{16}O_7(C_2H_3O)_2$. This crystallises in thin plates which melt at 202°. Hydrate of picrotoxide also appears to be formed, together with picrotoxide, when hydrochloric acid is passed into picrotoxin suspended in ether. It possesses acid properties, and seems to stand in the same relation to picrotoxide that santonic acid does to santonin. C. E. G.

**New Red Colouring Matter accompanying Chlorophyll.** By C. BOUGAREL (*Bull. Soc. Chim.*, xxvii, 442, 443).—After fresh leaves of the peach-tree had been treated with ether, the liquid was poured off and alcohol substituted. Two days afterwards there were observed on the leaves and on the sides of the vessel brilliant scales of a greenish colour by reflected light, but red by transmitted light. These crystals were found to be insoluble in water, nearly insoluble in alkalis, acids, alcohol, and ether, but very soluble in chloroform and benzene, to which they imparted a beautiful rose colour. The author proposes to call this red colouring matter *erythrophyll*. R. R.

**Colouring Matter of Velella Limbosa.** By A. and G. De Negri (*Gazzetta chimica italiana*, vii, 219).—This pelasgic mollusc, which is only rarely thrown up on the beach, gives a blue colouring matter which is readily distinguished from that of murex and aplysia by the absence of absorption-bands, when examined spectroscopically. The colouring matter is very fugitive, disappearing rapidly on the death of the animal. It is insoluble in ether, chloroform, benzene, and carbon bisulphide, but soluble in water, the solution turning yellow when heated; acids turn it red, and it is decolorised by the hypochlorites. C. E. G.

**The Colouring Matter of "Boletus Luridus."** By G. Cugini (*Gazzetta chimica italiana*, vii, 209—212).—In 1860 Phipson attributed the purple colour which the freshly-cut surface of *B. luridus* and *B. cyanescens* show when exposed for a short time to the air, to aniline; the author finds, however, that the coloration is not produced by oxidation, but by the action of ammonia. The extract obtained by treating the fungus with dilute alcohol yields nothing to ether, showing that no aniline is present. The extract is strongly acid, and is coloured blue by ammonia in small quantity, although excess of the alkali destroys the colour: potassium hydrate gives a deep wine-yellow. Ferric chloride gixes a green colour, and tincture of iodine a greenish-brown colour. The author did not succeed in isolating any crystalline substance. C. E. G.