X.—*Formation of Monomethylaniline from Dimethylaniline.*

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THE conversion of a tertiary aromatic base into a derivative of a secondary base has been observed by Hess (*Ber.*, 1885, **18**, p. 685), who found that, by boiling dimethylaniline with benzoic chloride, benzoylmethylaniline is formed, and the methyl group eliminated as methylic chloride. A similar reaction was described by Staedel (*Ber.*, 1886, **19**, 1947), who showed that acetic bromide converts dimethylaniline into acetylmethylaniline. In neither case are the yields given. We find that the conversion of dimethyl- into monomethyl-aniline may be effected in quite another way.

In attempting to elucidate the constitution of the substance which we described a short time ago under the name of *phenylnitrocarbinol* (*Trans.*, 1897, **71**, 1050), we studied its behaviour with various substances, and found that, in most cases, its action closely resembled that of nitrous acid, which is scarcely remarkable, seeing that phenylnitrocarbinol evolves nitrous fumes on standing. Its action on dimethylaniline is, however, sufficiently curious to merit a brief description.

On adding phenylnitrocarbinol to an equivalent quantity of dimethylaniline, the mixture becomes very dark coloured, and the temperature rises rapidly, whilst at the same time there is a rapid evolution of nitrogen gas entirely free from carbon dioxide.

This evolution of gas occurs whether the mixture is cooled down or allowed to become hot, and the quantity appears to be independent of temperature and, within certain limits, of the amount of dimethylaniline present.

In one experiment, 1.0015 grams of phenylnitrocarbinol and 2 grams of dimethylaniline gave 13.5 c.c. of gas, and, in a second experiment, performed under similar conditions, 2.2225 grams of the nitrocarbinol gave 27 c.c. of gas, the proportion of substance and gas being in both cases the same. The product of the action, which is deep red by transmitted light and a deep green by reflected light, was mixed with sufficient hydrochloric acid to combine with the unchanged dimethylaniline, and then extracted with ether. By adding sodium carbonate to the acid solution and distilling with steam, the unchanged dimethylaniline could be recovered; the tarry liquid which remained in the distilling vessel did not invite further investigation.

The ethereal extract contains benzaldehyde, benzylic alcohol, and nitrosomethylaniline. Four experiments, in each of which 30 grams of phenylnitrocarbinol were employed, gave on the average 5 grams of benzaldehyde, 4.5 grams of benzylic alcohol, and 5.5 grams of nitrosomethylaniline. Thus about half of the nitrocarbinol disappears, and is probably represented by the tarry material already referred to.

That the nitrosomethylaniline is not due, as was at first supposed, to the presence of methylaniline in the dimethylaniline used, was shown by the fact that a sample of dimethylaniline which had been carefully freed from monomethylaniline gave a result precisely similar to the above.

The three substances contained in the ether were separated and identified, as follows. The ethereal extract was treated with sodium hydrogen sulphite solution until nothing further crystallised. The ethereal solution was then separated from the bisulphite compound, the ether removed by distillation, and the residue distilled with steam; an oil of a yellow colour, and possessing the fragrant smell of nitrosomethylaniline, passed over, leaving a yellow, crystalline compound in the distilling flask, and this, when recrystallised from water, formed brilliant, golden plates which melted with decomposition at 150° . The minute quantity of this crystalline compound precluded its further investigation.

The nitrosomethylaniline was extracted from the distillate by ether, the ether removed, and the residual oil warmed with $2\frac{1}{2}$ times its weight of stannous chloride previously dissolved in three times the quantity of strong hydrochloric acid; the nitrosomethylaniline is thus reduced to methylaniline and remains in solution, whereas the whole of the benzylic alcohol is converted into benzylic chloride and separates as an oil. The liquid is then diluted with water and distilled in a current of steam. The benzylic chloride which distils was identified by converting it into benzaldehyde, and the latter into the phenylhydrazone melting at 153° . The solution of methylaniline was made alkaline with caustic soda, extracted with ether, and the ethereal solution,

after dehydrating over potash, was distilled; the methylaniline thus obtained was then converted into the platinochloride, which gave the following result on analysis.

0.1358 gave 0.0438 Pt. Pt = 31.2 per cent.

$(C_7H_9N)_2, H_2PtCl_6$ requires Pt = 31.4 per cent.

It is difficult to formulate in any satisfactory fashion the above reaction. If we assume that the half, of the nitrocarbinol which is converted into tar, has been oxidised at the expense of the other half, then the equation

will represent very closely the quantities involved. What becomes of the methyl group which is detached from the dimethylaniline cannot be at present explained, seeing that no carbon dioxide is formed.

The evolution of nitrogen is generally associated either with the action of a nitroso- on an amido-group or with the decomposition of a diazo-compound, which practically represents an intermediate stage of the same process. As there appears no reason to anticipate the formation of a diazo-compound, we are led to assume that the first process is responsible for the production of nitrogen. This could only occur by the reduction of an original nitro- or nitroso-group to an amido-group, that is, by the reduction of the nitrocarbinol to benzylamine, which, by the action of nitrous acid evolved from another molecule of the nitrocarbinol would produce benzylic alcohol, whilst benzaldehyde would be formed simultaneously. By what chemical change the reduction occurs, it is impossible at present to conjecture.

Action of Nitrogen Trioxide on Dimethylaniline.

The above result suggested the possibility of a similar reaction occurring when nitrogen trioxide acts on dimethylaniline in an indifferent solvent. A brief reference to the action of nitrogen trioxide on dimethylaniline dissolved in alcohol or acetic acid occurs in a paper by Lippmann and Lange (*Ber.*, 1880, 13, 2136), in which they state that the base is partly converted into a resinous matter (*partielle Verharzung*). Having a small quantity of the trioxide dissolved in chloroform at hand, the gas was driven over into a solution of dimethylaniline dissolved in ether by a current of nitric oxide in order to remove traces of the peroxide. The ether rapidly changed colour, passing from green to black, and a black and sticky deposit ultimately separated. This method was afterwards modified, and liquid nitrogen

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trioxide* was allowed to drop into the dimethylaniline dissolved in five times its weight of dry ether.

Each drop of the trioxide on coming in contact with the ether produced a hissing noise like a red-hot wire plunged into water, but in spite of the apparent vigour of the action, there was a scarcely perceptible rise of temperature. In both cases, the same result was obtained.

In order to test the product for nitrosodimethylaniline, the ether, which was coloured brown, was decanted from the black deposit, shaken with hydrochloric acid to remove dimethylaniline, the ether removed by distillation, and the residue distilled with steam. The aqueous distillate was yellow; but no drops of oil were visible, and no smell of nitrosomethylaniline could be detected. The distillate was extracted with ether, and the minute quantity of residue left on removing the ether gave no nitroso-reaction. Nitrosodimethylaniline is therefore not formed by this reaction, and the action of nitrogen trioxide is distinct from that of phenylnitrocarbinol.

In the distilling flask, a small quantity of yellow, needle-shaped crystals separated, which were apparently identical with the substance obtained in the action of phenylnitrocarbinol on dimethylaniline, and previously referred to.

The black, tarry-looking product, although of such an uninviting appearance, is nevertheless easily purified; it was first extracted with small quantities of benzene until the latter was nearly colourless. A little resinous matter is thereby removed; and as prolonged boiling with alcohol decomposed the substance, the residue was repeatedly extracted with small quantities of alcohol just heated to boiling. On cooling, long, steel blue needles separate; these decompose with slight explosion when heated, evolving nitrous fumes. The substance dissolves readily in alcohol and in water with a bright yellow colour. On boiling with glacial acetic acid for a short time, a rapid evolution of nitrous fumes takes place, and the product, which contains nitrogen, when poured into water forms a yellowish-green, crystalline mass, consisting of fine needles. These, when recrystallised from dilute alcohol, are pale brown, and melt at 155—157°.

As these products are readily obtainable, we have thought it worth while to investigate more fully this somewhat curious reaction, which we reserve for a future communication.

* The liquid trioxide is most conveniently prepared by acting upon arsenic trioxide with ordinary concentrated nitric acid, whereby a considerable quantity of peroxide is formed, and allowing the gas to meet a current of pure and dry nitric oxide on its way to the cooled receiver. If a more dilute nitric acid is used, the yield is very much diminished, as the gas evolved consists mainly of nitric oxide. By operating in the manner described, the trioxide is obtained of a pure blue colour.

It is interesting to note the entire dissimilarity between the action of anhydrous nitrogen trioxide and that of its aqueous solution, and it seems not unlikely that analogous results may be met with in the case of other bases, and possibly also in the case of phenols.