CV.—*The Products of Diazotisation of the Trinitro-
p-anisidines.*

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Two trinitro-derivatives of *p*-anisidine are theoretically possible :

Of these the first was prepared by the nitration of the benzoyl derivative of *p*-anisidine (Reverdin and A. de Luc, *Arch. Sci. phys. nat.*, 1909, 27, 383), and the second by the methylation of the silver salt of the corresponding trinitroacetylaminophenol (Meldola and

Kuntzen, *Trans.*, 1910, **97**, 455). In view of the mobility of the nitro-group in certain nitroamino-compounds on diazotisation, a comparative study of these trinitroanisidines appeared to be of special interest, and the present research was undertaken with the object of obtaining definite information concerning the special influence of the methoxy-group in determining such mobility. From the results made known in former papers, it appears that the nitro-group (*) in the above formulæ complies with all the conditions requisite to insure mobility, being in the ortho-position with respect to the diazotisable amino-group, and having another nitro-group in the ortho-position with respect to itself. A comparative study of the products of diazotisation of 2:3-dinitro-4-aminophenol and its methyl ether has shown that the influence of the methoxy-group is predominant, the formation of a paraquinonediazide being prevented in the latter case (Meldola and Hay, *Trans.*, 1907, **91**, 1477; also Meldola and Eyre, *Trans.*, 1902, **81**, 988). The ortho-quinonediazide is accordingly formed under these conditions by the displacement of the ortho-nitro-group, whereas in the dinitroaminophenol itself, from which a para-quinonediazide can be obtained, no elimination of a nitro-group takes place. On the other hand, it has been shown that a methoxy-group in the para-position with respect to the diazotisable amino-group and in the ortho-position with respect to one or two nitro-groups is eliminated on diazotisation (Meldola and Stephens, *Trans.*, 1905, **87**, 1205; Reverdin and Bucky, *Ber.*, 1906, **39**, 2691). The existing state of knowledge concerning the configurations favourable respectively for the elimination of a nitro-group or of a methoxy-group was summarised in a former paper (Meldola and Hay, *Trans.*, 1907, **91**, 1474), and it has since been shown that in the trinitroaminophenol corresponding with No. II of the above formulæ, the trinitroquinonediazide is at once formed on diazotisation, no nitro-group being eliminated (Meldola and Hay, *Trans.*, 1909, **95**, 1383). The trinitroaminophenol corresponding with formula No. I has not yet been obtained, but this might also be expected to give a trinitroquinonediazide on diazotisation.

On comparing the formulæ of the two trinitroanisidines, it will be seen, in accordance with the general results of former researches, that not only is the nitro-group in both compounds in a favourable position for displacement, but that the methoxy-group is also in what may be called a critical position, and more especially in No. I, in which this group is between two ortho-nitro-groups and in the para-position with respect to the diazo-group. This pair of isomerides is therefore particularly suitable for determining the relative mobility of the nitro- and methoxy-groups under the

influence of a diazo-group. As will be seen from the experimental results, the question is answered decisively, both compounds losing the 3-nitro-group on diazotisation and giving rise to the dinitro-ortho-quinonediazides:

It is thus shown that under conditions equally favourable for the elimination of a nitro-group and a methoxy-group, the former is the more readily displaced when the diazo-group is formed in its neighbourhood. If the mechanism of the progress is expressed in terms of the hypothesis of "isomeric change," it may be said that the predominating influence is in favour of the second and not the first of the two possible schemes:

EXPERIMENTAL.

The diazotisation of the trinitroanisidines was effected in the usual way by dissolving the compounds in cold sulphuric acid, diluting with a little water, and adding solid sodium nitrite to the solution cooled in ice. On pouring the solution of diazonium sulphate into water, decomposition at once takes place, and the quinone-diazide is precipitated as a yellow, crystalline deposit.

2: 5-Dinitro-1-methoxy-3: 4-quinonediazide.

The compound prepared as above, after being washed and dried, was crystallised from hot glacial acetic acid. It is a fairly stable substance, crystallising in yellow prisms, melting and decomposing at 191—194°:

0.2277 gave 46 c.c. N_2 (moist) at 16° and 757.5 mm. $N = 23.47$.

$C_7H_4O_6N_4$ requires $N = 23.34$ per cent.

The compound is not explosive, but deflagrates on heating. It

combines slowly with β -naphthol in alkaline solution to form an *azo*-compound, which crystallises from boiling glacial acetic acid in brick-red needles, having a slight metallic lustre, and melting at 236° . From its mode of formation its constitution is:

0.0780 gave 9.9 c.c. N_2 (moist) at 17.5° and 764.1 mm. $\text{N} = 14.78$.

$\text{C}_{17}\text{H}_{12}\text{O}_7\text{N}_4$ requires $\text{N} = 14.58$ per cent.

The *azo*-compound is slightly phenolic, dissolving in dilute aqueous sodium hydroxide with a red colour. It is insoluble in cold alcohol, and very sparingly soluble in boiling alcohol. Its solution in concentrated sulphuric acid is violet, becoming redder on dilution with water.

2: 6-Dinitro-1-methoxy-3: 4-quinonediazide.

This compound was obtained by crystallisation from hot glacial acetic acid in orange prisms, melting at 197 — 198° . It deflagrates like its isomeride on heating:

0.0708 gave 14.35 c.c. N_2 (moist) at 16.8° and 755.8 mm. $\text{N} = 23.41$.

$\text{C}_7\text{H}_4\text{O}_6\text{N}_4$ requires $\text{N} = 23.34$ per cent.

The *azo*-compound formed by coupling the quinonediazide with β -naphthol is characterised by being non-crystalline, a somewhat exceptional property among *azo*-derivatives of β -naphthol. For this reason, and owing to the circumstance that we had only a very small quantity of the substance at our disposal, the compound has only been examined qualitatively. It is distinctly more soluble in alcohol and acetic acid than its isomeride; its solutions are red, and it separates from a hot saturated solution in glacial acetic acid in reddish-brown, amorphous nodules. It is distinctly phenolic, dissolving in dilute alkali with a violet colour, and forming a sodium salt, which is easily "salted out" by excess of sodium hydroxide or by more soluble salts. The sodium salt is also amorphous. The melting point of the compound obtained by deposition from acetic acid and washing with alcohol is about 197° . It dissolves in concentrated sulphuric acid with a fine blue colour, becoming violet on dilution with water.

We have great pleasure in acknowledging the co-operation of Mr. Harold Kuntzen in carrying out the experimental part of this investigation.