

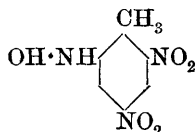
IV.—*Note on the Reduction of Trinitrobenzene and Trinitrotoluene with Hydrogen Sulphide.*

By JULIUS B. COHEN and HENRY D. DAKIN.

THE reduction of the 2:4:6-trinitrotoluene was originally undertaken with the object of producing an amino-group in the para-position, and by its removal of obtaining eventually 2:6-dinitrotoluene, a compound which we required in the study of the chlorination products of toluene.

The reduction of trinitrotoluene to 2:6-dinitro-4-toluidine by means of ammonium sulphide is described by Tiemann (*Ber.*, 1870, **3**, 218) and Beilstein (*Ber.*, 1880, **13**, 243), but the yield we obtained was small, and we did not succeed in improving it or in suppressing a quantity of tarry impurity which makes its appearance at the same time. After many unsuccessful attempts to effect reduction with ammonium sulphide and other agents, we tried a methyl alcoholic solution of crystallised ammonium sulphide, passing in hydrogen sulphide at the same time to displace air and keeping the whole well cooled. We found that the reaction proceeded vigorously even when the quantity of ammonium sulphide present was very far below the theoretical amount. Finally, we simplified the method by adding a few drops of concentrated ammonia to an alcoholic solution of the trinitro-

compound and saturating with hydrogen sulphide. The product, filtered from sulphur and poured into water, formed a bright yellow, crystalline precipitate, which was not the anticipated dinitrotoluidine, but, as we eventually discovered, 2 : 4-dinitro-6-tolyhydroxylamine,



Precisely the same reaction occurs with trinitrobenzene.

2 : 4-Dinitro-6-tolyhydroxylamine.

Twenty grams of finely powdered trinitrotoluene were suspended in about 100 c.c. of absolute alcohol, about 0.5 c.c. of concentrated ammonia was added, and the mixture cooled in ice. Hydrogen sulphide was then passed in with frequent shaking. In a short time, the colour of the solution deepened and the heavy crystals of trinitrotoluene, which at first settled to the bottom, were soon replaced by a thick, bulky, deep yellow precipitate, which filled the liquid. After about an hour, no further increase in the quantity of precipitate appeared, and the mixture was warmed for a moment on the water-bath and filtered quickly into a flask standing in ice. The precipitate was washed with hot alcohol until the filtrate was colourless. A residue of sulphur remained which weighed 6.3 grams. The alcoholic filtrate deposited, on standing, a mass of needle-shaped crystals, which were separated and amounted to 4.7 grams. This fraction contained a small proportion of dinitrotolyhydroxylamine, mixed with some compound of high melting point, and melted indefinitely from 130—160°. The product of high melting point is 2 : 6-dinitro-4-toluidine, for, on boiling 0.5 gram of this fraction for 2 hours with concentrated hydrochloric acid so as to convert the hydroxylamine compound into the insoluble 2 : 4-dinitro-6-toluidine, diluting and filtering, 0.3 gram of orange crystals melting at 167—169°, which is the melting point of the 2 : 6-dinitro-base, was deposited from the filtrate.

The filtrate was poured into water, which precipitated the bulk of the hydroxylamine compound. It was filtered, washed with water, and carefully dried. The weight was 11.5 grams. It was extracted with successive quantities of benzene, in which it all eventually dissolved, each portion being kept separate. The last extracts yielded crystals melting sharply at 143—145°, which did not change by successive recrystallisations and were therefore regarded as pure. The substance was analysed with the following results :

28 REDUCTION OF TRINITROBENZENE WITH HYDROGEN SULPHIDE.

0·2377 gave 39·5 c.c. moist nitrogen at 17° and 764 mm. N = 19·45.

0·1595 „ 27·25 „ „ „ 17° „ 760 mm. N = 19·79.

$C_7H_7O_5N_3$ requires N = 19·71 per cent.

A molecular weight determination by the boiling point method gave the following result :

0·181 gram in 11·43 grams of benzene raised the boiling point by 0·197°.

Mol. wt., found = 215 ; calculated = 213.

The compound reduces alcoholic silver nitrate, depositing a mirror ; it also reduces Fehling's solution. It readily dissolves in alcohol, but is less soluble in benzene and insoluble in light petroleum. From benzene, it crystallises in rhombohedra. It dissolves in boiling dilute hydrochloric acid unchanged and then crystallises in small, pale yellow needles. On prolonged boiling, it becomes insoluble and changes to a colourless, crystalline compound. The same result is much more rapidly effected by concentrated hydrochloric acid. Half a gram of the hydroxylamine compound, boiled with about ten times its weight of strong hydrochloric acid for half an hour, yielded 0·3 gram of the colourless substance.

2 : 4-Dinitro-6-toluidine.

The colourless compound was crystallised from benzene, from which it separated in needles melting at 212—213°. It was analysed with the following results :

0·1857 gave 0·2884 CO_2 and 0·0575 H_2O . C = 42·35 ; H = 3·44.

0·1475 „ 27·7 c.c. moist nitrogen at 26° and 759 mm. N = 20·8.

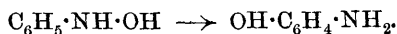
$C_7H_7O_4N_3$ requires C = 42·6 ; H = 3·5 ; N = 21·3 per cent.

0·220 gram in 8·1 grams of benzene raised the boiling point by 0·160°.

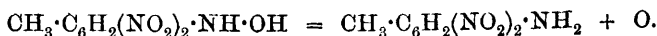
Mol. wt., found = 221 ; calculated = 197.

The substance is insoluble in sodium hydroxide solution or in dilute hydrochloric acid. Neither stannous chloride nor sodium nitrite in acid solution has any action on it. It dissolves unchanged in strong sulphuric acid and is reprecipitated by water.

The conversion of *p*-phenylhydroxylamine into *p*-aminophenol by mineral acids has been studied by Bamberger (*Ber.*, 1894, 27, 1349), and takes place by intramolecular rearrangement :



In the present case, the substance produced is not a phenol, but, according to analysis, a dinitrotoluidine. The conversion must therefore be accompanied by the removal of oxygen.



This is precisely what happens, for if the hydroxylamine compound be boiled with hydrochloric acid and indigo solution, the colour is slowly discharged, or with hydrochloric acid and potassium iodide, iodine is liberated.

As the amino-compound melts at $212-213^{\circ}$, it must be the 2:4-dinitro-6-toluidine, as the only other possible isomeride melts at $166-168^{\circ}$. This substance has not been previously prepared. As we have seen, the hydroxylamine compound acts both as a reducing and an oxidising agent. It is also worthy of remark that, whereas ammonium sulphide converts trinitrotoluene into 2:6-dinitro-4-toluidine, in which the *p*-nitro-group is reduced, the action of hydrogen sulphide is to reduce the nitro-group in the ortho-position.

1:3-Dinitro-5-phenylhydroxylamine.

This substance is prepared from 1:3:5-trinitrobenzene in exactly the same way as the tolyl derivative, but although the yield is smaller, the product is more readily obtained in a pure state. It forms dark orange crystals melting at $114-116^{\circ}$. Nine grams of trinitrobenzene yielded 4.5 grams of pure hydroxylamine derivative. Dinitrophenylhydroxylamine reduces alcoholic silver nitrate solution. On analysis, the following result was obtained:

0.113 gave 20.8 c.c. moist nitrogen at 15° and 756 mm. $N = 21.53$.
 $C_6H_5O_5N_3$ requires $N = 21.10$ per cent.

On boiling with concentrated hydrochloric acid, the substance at first passes into solution, but very soon a precipitate appears. The product is then poured into water, boiled up, and allowed to crystallise. On cooling, dark orange needles separate out, which melt sharply at $158-159^{\circ}$. This is the melting point of 3:5-dinitroaniline, with which it is undoubtedly identical, a fact which serves to confirm the nature of the reaction in the case of the tolyl derivative. We propose to continue this investigation.

THE YORKSHIRE COLLEGE.
