LIII.—*The Reduction of 2 : 6-Dinitrotoluene with Hydrogen Sulphide.*

By JULIUS BEREND COHEN and JOSEPH MARSHALL.

IN the course of an experiment in which 2 : 6-dinitrotoluene was reduced with hydrogen sulphide in alcoholic ammonia, a quantity of 6-nitro-2-amino-*m*-cresol was obtained together with 6-nitro-*o*-toluidine, these substances being separated in the following manner. The product, after reduction, was boiled with dilute hydrochloric acid and separated by filtration from sulphur. On adding ammonia in excess to the filtrate in order to precipitate the nitro-*o*-toluidine, a deep violet solution was obtained. The filtrate from the base was carefully neutralised, when a brown, crystalline precipitate was deposited, which was crystallised from alcohol. The new substance crystallises in dark, orange-coloured needles, which dissolve readily in dilute acids and alkalis and melt with decomposition at about 190°; it is completely precipitated by carbon dioxide from its solution in alkalis. With the mineral acids it forms well-crystallised, colourless salts; the hydrochloride crystallises in flat prisms with pointed ends, the sulphate, in fine needles, and the nitrate in clusters of acicular crystals. The compound is evidently an aminophenol and the analysis indicates a nitroamino-cresol.

0·1468 gave 22 c.c. moist nitrogen at 25° and 735 mm. $N = 16·73$.

$C_7H_8O_3N_2$ requires $N = 16·56$ per cent.

In order to determine the relative positions of the amino- and hydroxyl-groups, the compound was dissolved in dilute sulphuric acid and oxidised with an excess of lead peroxide at a temperature of about 60°. The orange-coloured liquid was extracted with ether, and on removing the solvent a mass of dark red crystals remained which had the characteristic odour of quinone. On crystallisation from a mixture of ether and light petroleum, the substance was deposited in the form of brilliant, ruby-red prisms which melted at 64—65°.

0·1801 gave 13·2 c.c. moist nitrogen at 17·5° and 747·5 mm. N = 8·54.
$C_7H_5O_4N$ requires N = 8·49 per cent.

When sulphur dioxide is passed through the quinone suspended in water, it dissolves to a yellow solution from which ether extracts the corresponding quinol; on removing the solvent the quinol is deposited in the form of bright scarlet needles which may be crystallised from ether and light petroleum and melt at 117—118°.

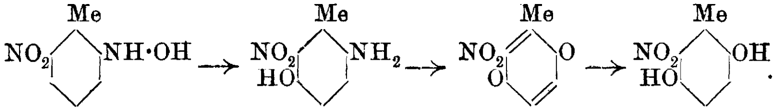
The solution of the quinol in caustic soda has a deep violet colour which disappears on saturating with carbon dioxide, the quinol being regenerated. When the nitroaminocresol is dissolved in dilute hydrochloric acid and a solution of bleaching powder gradually added, a light brown precipitate is formed, which separates from a mixture of ether and light petroleum in clusters of pale yellow, spear-shaped crystals melting at 70—71°. The compound is a chloronitrotoluquinone, $CH_3\cdot C_6HO_2Cl\cdot NO_2$.

0·1352 gave 0·096 AgCl. Cl = 17·67.
$C_7H_4O_4NCl$ requires Cl = 17·61 per cent.

The formation of nitroaminocresol from 2 : 6-dinitrotoluene is readily explained. Cohen and Dakin have shown (Trans., 1902, **81**, 26) that *s*-trinitrobenzene and 2 : 4 : 6-trinitrotoluene are readily reduced by hydrogen sulphide in faintly alkaline solution and yield the corresponding dinitrohydroxylamine compounds.

If the reduction of the 2 : 6-dinitrotoluene is not complete, 6-nitro-*o*-tolylhydroxylamine is formed and is converted by the boiling hydrochloric acid used in the extraction, into nitroaminocresol in the same way that phenylhydroxylamine yields *p*-aminophenol (Bamberger, *Ber.*, 1894, **27**, 1349).

The series of changes which have been described may be represented by the following formulæ :



6-Nitro-*o*-tolylhydroxylamine.   6-Nitro-2-amino-*m*-cresol.   6-Nitrotoluquinone.   6-Nitrotoluquinol.

We propose to continue the investigation of the above compounds and to extend the study of the action of hydrogen sulphide to other nitro-compounds.

THE YORKSHIRE COLLEGE.