

CLXXXI.—*The Formation of 2:3:6-Trinitrotoluene in the Nitration of Toluene.*

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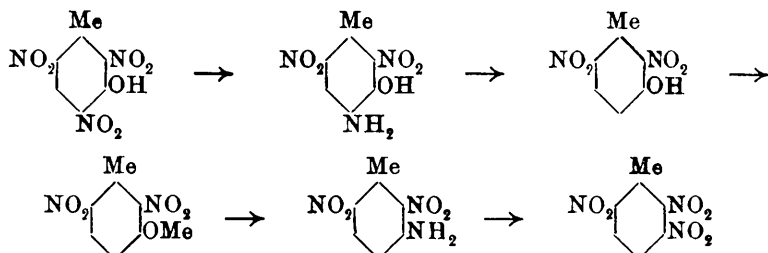
IN the mixture of trinitrotoluenes obtained by the direct nitration of toluene, previous workers have identified only 2:4:6-, 2:3:4-, and 3:4:6-trinitrotoluenes of the six possible isomerides. Molinari and Giua (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1914, **9**, 239) claimed to have isolated the 2:3:6-compound, previously unknown, to which they assigned a melting point of 79.5°, but this compound has been synthesised by Körner and Contardi (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 339) and by Brady and Taylor (this vol., p. 876), and found to melt at 111°; the latter authors have suggested that Molinari and Giua's compound was probably a molecular compound of 2:3:4- and 3:4:6-trinitrotoluenes. Will (*Ber.*, 1914, **47**, 704) has studied the nitration of 2:3- and 3:6-dinitrotoluenes, and states that the sole products of their nitration are 2:3:4- and 3:4:6-trinitrotoluenes. More recently, however, Marqueyrol, Koehler, and Jovinet (*Bull. Soc. chim.*, 1920, [iv], **27**, 420) have obtained a third trinitrotoluene, in addition to the 2:3:4- and 3:4:6-compounds, from the nitration of *m*-nitrotoluene. Their results are incomplete, and they have not identified the compound, but, as they found it was formed to a small amount in the nitration of 2:3- and 2:5-(or 3:6-)dinitrotoluenes, they conclude it must be either the 2:3:6- or the 2:3:5-trinitro-derivative. The present author, previous to the publication of Marqueyrol, Koehler, and Jovinet's results, had investigated the nitration of 2:3- and 3:6-dinitrotoluenes, and found that in each case the product contains about 15 per cent. of 2:3:6-trinitrotoluene.

Other workers have shown that about 4 per cent. of *m*-nitrotoluene is formed in the mono-nitration of toluene under the usual conditions, and that, on further nitration of this compound, about half the product is a mixture of 2:3- and 2:5-dinitrotoluenes. In crude trinitrotoluene, obtained by the direct nitration of toluene, there must be, therefore, about 0.3 per cent. of 2:3:6-trinitrotoluene. Opportunity, however, has not arisen to isolate this small amount from commercial samples of trinitrotoluene.

Further, a new method of preparing 2:3:6-trinitrotoluene has been devised, which is easier than that described by Körner and Contardi (*loc. cit.*), and starts from trinitro-*m*-cresol; this is more

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readily obtainable than the 2:6-dinitrotoluene required in Brady and Taylor's synthesis (*loc. cit.*). The reactions involved are as follows:



Methylpicramic acid, obtained by the reduction of trinitro-*m*-cresol, has been oriented only indirectly by Borsche and Heyde (*Ber.*, 1906, **39**, 4092), and the above synthesis fully confirms the view of these authors.

## EXPERIMENTAL.

*Nitration of 3:6-Dinitrotoluene.*—Forty grams of 3:6-dinitrotoluene were added to 250 c.c. of a mixture of sulphuric and nitric acids ( $\text{HNO}_3=17.5$ ;  $\text{H}_2\text{SO}_4=78$ ;  $\text{H}_2\text{O}=4.5$  per cent.). The mixture was mechanically stirred, and the temperature raised to  $80^\circ$  and kept at that point for an hour, when the temperature was raised to  $100^\circ$  for a further two hours, and finally to  $120^\circ$  for fifteen minutes. The mixture was then cooled and poured into water, the solid collected, and washed repeatedly under water with the injection of steam until free from acid.

The freezing point of the product after drying was found to be  $95.4^\circ$ , as against  $103^\circ$  for pure 3:4:6-trinitrotoluene. The mixture was recrystallised from acetic acid to remove most of the 3:4:6-trinitrotoluene, and, by diluting the filtrate, a mixture richer in 2:3:6-trinitrotoluene was obtained. Attempts were made to separate this mixture by crystallisation from various solvents, but without success, a mixture melting constantly at  $78^\circ$  being obtained. A portion was treated with alcoholic ammonia in the hope that it would be possible to separate the corresponding dinitrotoluidines, but an oily, intractable product was obtained. A successful separation was ultimately brought about by the action of hydrazine hydrate. It had been observed by Brady (*private communication*) that hydrazine hydrate reacts readily with 2:3:4- and 3:4:6-trinitrotoluenes, giving red, crystalline compounds sparingly soluble in alcohol. It has been found that 2:3:6-trinitrotoluene behaves in a different manner towards this reagent,

which can therefore be used to effect a separation. The mixture of 3:4:6- and 2:3:6-trinitrotoluenes was dissolved in methyl alcohol, a solution of hydrazine hydrate added, and the mixture warmed on the water-bath for some time. On cooling, the red precipitate was collected and fractionally crystallised from alcohol, and from the more readily soluble portion a colourless compound was isolated, which was identified as 2:3:6-trinitrotoluene by the method of mixed melting points with a sample of this compound prepared by Brady and Taylor's method.

*Nitration of 2:3-Dinitrotoluene.*—This was effected in an exactly similar manner to the nitration of 2:6-dinitrotoluene. The product had a freezing point of 100°, as compared with 112° in the case of pure 2:3:4-trinitrotoluene. The separation was brought about by means of hydrazine hydrate, and the 2:3:6-trinitrotoluene isolated and identified. The approximate amount of 2:3:6-trinitrotoluene present in the mixtures obtained by the nitration of 3:6- and 2:3-dinitrotoluenes was determined by making up mixtures of pure 3:4:6- and 2:3:4-trinitrotoluenes with 2:3:6-trinitrotoluene, and determining their freezing points. It was found that these corresponded with the freezing points of the products of nitration when about 15 per cent. of the 2:3:6-compound was present.

*2:6-Dinitro-m-cresol.*—This was prepared from 2:6-dinitro-4-amino-*m*-cresol. The method given for the preparation of this compound by Kellner and Beilstein (*Annalen*, 1863, **128**, 166) did not give good yields, so a modified method was adopted. Twenty grams of trinitro-*m*-cresol were dissolved in 50 c.c. of boiling methyl alcohol, and 200 c.c. of 15 per cent. ammonium sulphide slowly added. Vigorous action took place, and, when it subsided, the mixture was cooled, diluted, and acidified with hydrochloric acid. The sulphur was filtered off, and the filtrate evaporated to small bulk. On keeping, the 2:6-dinitro-4-amino-*m*-cresol separated, and was crystallised from alcohol with the addition of animal charcoal. It was found that the usual method for the removal of the amino-group by the action of sodium nitrite on a boiling alcoholic solution of the amine containing sulphuric acid did not give good results with this compound, owing to the stability of the diazo-compound formed; accordingly, the following method was adopted.

Ten grams of 2:6-dinitro-4-amino-*m*-cresol were dissolved in 70 c.c. of hot alcohol, 20 c.c. of concentrated hydrochloric acid added, and then, gradually, 10 grams of sodium nitrite dissolved in a minimum amount of water. As soon as the reaction ceased, the mixture was cooled and the precipitate collected. There was

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thus obtained a stable, greenish-yellow, crystalline material, which deflagrated on heating, and was probably the diazo-oxide corresponding with that obtained from picramic acid. This compound was treated with 30 c.c. of concentrated formic acid, and a small quantity of copper powder added, when a violent reaction took place, nitrogen and carbon dioxide being evolved. After filtering from the copper and diluting the filtrate, an oil separated, which slowly crystallised; the crystals were pressed on a porous tile and recrystallised from benzene, when 2:6-dinitro-*m*-cresol separated as a white, crystalline compound melting at 133° (Found: N=14·1.  $C_7H_6O_5N_2$  requires N=14·1 per cent.).

2:6-Dinitro-*m*-tolyl Methyl Ether.—The ammonium salt of 2:6-dinitro-*m*-cresol was prepared by dissolving the cresol in alcoholic ammonia and evaporating the solution on the water-bath until crystallisation took place on cooling. The filtered crystals were dissolved in the minimum amount of alcohol, and the calculated quantity of alcoholic silver nitrate was added, when the silver salt separated in lustrous, grey crystals, which deflagrate violently on heating. Five grams of the silver salt were added to a solution of 5 c.c. of methyl iodide in alcohol, when immediate action took place, and, after removal of the silver iodide, the solution was diluted and the precipitated 2:6-dinitro-*m*-tolyl methyl ether crystallised from alcohol, when it was obtained in white needles melting at 115° (Found: N=13·4.  $C_8H_8O_5N_2$  requires N=13·2 per cent.).

2:6-Dinitro-*m*-toluidine and 2:3:6-Trinitrotoluene.—Five grams of 2:6-dinitro-*m*-tolyl methyl ether were heated to 130° with 5 c.c. of ammonia and 20 c.c. of alcohol. On cooling and diluting, 2:6-dinitro-*m*-toluidine was precipitated, and identified by the method of mixed melting points with a sample of this compound prepared by Cook and Brady (this vol., p. 750). 2:6-Dinitro-*m*-toluidine can be converted into 2:3:6-trinitrotoluene by Körner and Contardi's method (*loc. cit.*).

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