349. *The Replacement of the Diazonium by the Nitro-group. Part V. New Preparations of 2 : 3- and 2 : 5-Dinitrotoluene from Mono-amines and the Simultaneous Introduction of Two Nitro-groups into Some Homonuclear Diamines.*

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2 : 3- and 2 : 5-Dinitrotoluene are more readily prepared by the procedure described by Hodgson, Heyworth, and Ward (*J.*, 1948, 1512) from 3- and 5-nitro-*o*-toluidine than by previously described methods. The same procedure permits the preparation of the dinitro-compounds from bis-diazotised *m*- and *p*-phenylene- and *m*- and *p*-tolylene-diamines.

Previously reported methods for the preparation of 2 : 5-dinitrotoluene in moderately large quantities such as the oxidation of 2 : 5-dinitrosotoluene with cold fuming nitric acid (Fierz-David and Sponagel (*Helv. Chim. Acta*, 1943, **26**, 98), the nitration of *m*-nitrotoluene (Sirks, *Rec. Trav. chim.*, 1908, **27**, 211), and the reaction of nitrogen peroxide with *p*-toluquinone dioxime in ether (Olivieri-Tortovici, *Gazzetta*, 1900, **30**, I, 534), were found to be unsuitable. Grell's Sandmeyer procedure (*Ber.*, 1895, **28**, 2565), modified by neutralising the solution of 5-nitrotoluene-2-diazonium sulphate with calcium carbonate and subsequently decomposing it with cupro–cupri sulphite (Hodgson, Heyworth, and Ward, *loc. cit.*) gave a 52% yield of pure 2 : 5-dinitrotoluene.

The route from 5-nitro-*o*-toluidine was preferred to that from 6-nitro-*m*-toluidine. Nitration of aceto-*o*-toluidide and hydrolysis of the product gave a mixture of 3- and 5-nitro-*o*-toluidine, from which the 3-isomer was removed by steam-distillation of the mixed hydrochlorides. Preparation from aceto-*m*-toluidide, whereby the required 6-nitro-*m*-toluidine had to be separated from two accompanying isomers, was not so satisfactory. The initial nitration was less efficient than in the case of acet-*o*-toluidide and the conversion of the amino- into the nitro-group did not give such a good yield.

There appears to be no evidence in the literature of the simultaneous replacement of two diazo- by two nitro-groups in the same aromatic nucleus. The solid bisdiazonium sulphates of *m*- and *p*-phenylene- and *m*- and *p*-tolylene-diamines were prepared by the method of Hodgson and Mahadevan (*J.*, 1947, 325) and their aqueous solutions added to excess of aqueous sodium nitrite containing a suspension of cupro-cupri sulphite as catalyst, whereupon the corresponding dinitro-compounds were obtained in small yield. Failure, however, was experienced with *o*-phenylenediamine, 4-nitro-*o*-phenylenediamine, and 1 : 8-naphthylenediamine. When the amino-groups were in different nuclei, as in benzidine, the simultaneous replacement by two nitro-groups occurred in 27% yield (cf. Hodgson, Mahadevan, and Ward, *J.*, 1947, 1392, who give 16%).

EXPERIMENTAL.

2 : 5-*Dinitrotoluene*.—(a) *From aceto*-o-*toluidide*. To aceto-*o*-toluidide (24 g.) in sulphuric acid (50 c.c., *d* 1·84), nitric acid (10 c.c., *d* 1·42) in sulphuric acid (10 c.c., *d* 1·84) was gradually added. The nitration was initiated by the addition of 2 c.c. of the mixed acids to the toluidide solution at 60° together with a trace of sodium nitrite, whereupon the temperature rapidly rose to 70°. Thereafter the mixture was maintained at 30—40° during the addition of the remainder of the mixed acids. By this means, the nitration was carried out at as low a temperature as possible, and the production of 3-nitroaceto-*o*-toluidide kept at a minimum. After being stirred for a further hour to ensure completion of the nitration, the mixture was poured into iced water (2 l.), and the yellow mixture of solid 3- and 5-nitroaceto-*o*-toluidides (29 g.; 90% yield) filtered off and washed with cold water, aqueous sodium hydrogen carbonate, and finally with cold water. The solid was then heated under reflux for 3 hours with sulphuric acid (100 c.c., *d* 1·84) and water (300 c.c.), and the hot orange solution filtered and cooled, whereupon crude 5-nitro-*o*-toluidine crystallised. The mother liquor after being made just alkaline with 20% sodium hydroxide, gave a mixture of 3- and 5-nitro-*o*-toluidine, which was added to hydrochloric acid (30 c.c., *d* 1·18) in water (100 c.c.). 3-Nitro-*o*-toluidine (1·7 g.) was removed by steam distillation; the filtered residual liquor gave crystalline 5-nitro-*o*-toluidine on cooling (total yield, 18·6 g.) 5-Nitro-*o*-toluidine (5 g.) was diazotised in sulphuric acid (10 c.c., *d* 1·84), water (10 c.c.), and ice (10 g.), by addition at 0° of sodium nitrite (2 g.) in water (10 c.c.). The solution of the diazonium sulphate was poured on to calcium carbonate (15 g.) and a little ice, the mixture filtered, and the clear solution stirred into one of sodium nitrite (20 g.) in water (100 c.c.) containing freshly prepared cupro-cupri sulphite [made by the addition of crystallised copper sulphate (10 g.) in water (100 c.c.) to crystalline sodium sulphite (10 g.) in water (50 c.c.)]. The temperature rose to 30—40°, and nitrogen was evolved. When this had ceased, the mixture was steam-distilled and 2 : 5-dinitrotoluene (3·1 g., 52% yield), m. p. 49—51°, was obtained from the distillate. In further experiments yields of 48, 50, and 50% were obtained.

(b) *From aceto*-m-*toluidide*. This nitration was particularly difficult to start and afterwards became exceedingly violent and produced only tarry products, so that the initiation procedure had to be carried out at 70°. The mixture was then rapidly cooled to 20—30° and kept at that temperature until all the mixed acid had been added. Using the same quantities as for aceto-*o*-toluidide, a mixture of nitroaceto-*m*-toluidides (29 g.; 90% yield) was obtained, which was separated by the technique described above into 6-nitro-*m*-toluidine (12·8 g.), and a mixture of 2- and 4-nitro-m-toluidines (1·6 g.).

Nitro-compounds were obtained by the cupro-cupri sulphite procedure: 2 : 5-dinitrotoluene (2·5 g.; 40% yield) from 6-nitro-*m*-toluidine (5 g.), 3 : 4-dinitrotoluene (2·7 g.; 45% yield) from 4-nitro-*m*-toluidine (5 g.), and 3 : 4-dinitrotoluene (3·0 g., 50% yield) from *m*-nitro-*p*-toluidine (5 g.) (identical with the material prepared from 4-nitro-*m*-toluidine).

2 : 3-*Dinitrotoluene*.—2 : 3-Dinitrotoluene (3·0 g., 50%) was obtained from 3-nitro-*o*-toluidine (5 g.) by the procedure given under (a) above.

Simultaneous Replacement of Two Diazonium by Two Nitro-groups.—A cooled solution of the diamine (5 g.) in glacial acetic acid (50 c.c.) was added to one of sodium nitrite (7 g.) in sulphuric acid (40 c.c., *d* 1·84) at 0°, the mixture was warmed gradually from 0° to 20—30° during 30 minutes and then stirred in a thin stream into ice-cold dry ether (200 c.c.), whereupon crystals of the bisdiazonium sulphate (together with anhydrous sodium sulphate) separated. After being left for 15 minutes the mixture was filtered and the crystals washed with dry ether (20 c.c.), dissolved in iced water (30 c.c.), and added at 30° to a solution of sodium nitrite (30 g.) in water (50 c.c.) containing cupro-cupri sulphite (10 g.) as catalyst. *m*-Dinitrobenzene (0·4 g. from 5 g. of *m*-phenylenediamine) and *p*-dinitrobenzene (2·0 g., 25% yield from 5 g. of *p*-phenylenediamine) were obtained by steam-distillation of the crude products. Attempts to prepare picric acid from 4 : 6-dinitrobenzene-1 : 2-diazo-oxide, and 2 : 6-dinitro-1-naphthol from 6-nitronaphthalene-1 : 2-diazo-oxide were unsuccessful.

*Some additional and improved preparations using the technique described above for 5-nitro-*o*-toluidine.*

Amine diazotised.	% Yield of nitro-compound.	Amine diazotised.	% Yield of nitro-compound.
Aniline	68	3-Nitro-*o*-toluidine	50
m-Nitroaniline	45	4-Nitro-*o*-toluidine	55
o-Toluidine	27	4-Nitro-*m*-toluidine	45
p-Toluidine	49	6-Nitro-*m*-toluidine	50
o-Chloroaniline	81	2-Nitro-*p*-toluidine	42
m-Chloroaniline	89	3-Nitro-*p*-toluidine	50
p-Chloroaniline	70	β-Naphthylamine	20
o-Anisidine	24	Benzidine	27
p-Anisidine	28	2 : 2′-Dinitrobenzidine	13

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