340. *Synthesis of Some Nitro-derivatives of Diphenylamine.*

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THE preparation of the di- and tri-nitro-derivatives of diphenylamine described by the authors (*J. Physical Chem.*, 1932, **36**, 1434) is herein recorded. The former were obtained by condensing 2 : 4-dinitrochlorobenzene (1 mol.) and 2 : 4-dinitro-5-chlorotoluene (1 mol.) with the appropriate amines (1·3 mols.). For the preparation of the trinitro-compounds, picryl chloride was used, and also in some syntheses 2 : 4 : 6-trinitrophenylmethylnitroamine, which in many cases was equally satisfactory (compare James, Jones, and Lewis, J., 1920, **117**, 1273) : it was not found necessary to add sodium hydroxide, as employed by Turpin (J., 1891, **59**, 714).

EXPERIMENTAL.

The following condensations were carried out with the aid of anhyd. NaOAc as condensing agent, no solvent being employed, the mixture being heated for 2 hrs. at 150—160°.

2 : 4-Dinitro-5-methyldiphenylamine (from dinitrochloro- or dinitrobromo-toluene; yield, 70%), yellow lustrous prisms, m. p. 148°, from EtOH (Found : N, 15·3. Calc. : N, 15·4%). Hepp (*Annalen*, 1882, **215**, 369) records orange needles, m. p. 142°. 2 : 4-*Dinitro*-5 : 2′-*dimethyldiphenylamine* (from dinitrochloro- or dinitrobromo-toluene; yield, 70%), long thin yellow plates, m. p. 111°, from EtOH (Found : N, 14·4. $C_{14}H_{13}O_4N_3$ requires N, 14·6%). 2 : 4-*Dinitro*-5 : 3′-*dimethyldiphenylamine*, deep yellow plates, m. p. 136·5°, from EtOH; yield, 80% (Found : N, 14·8%). 2 : 4-*Dinitro*-5 : 2′ : 4′-*trimethyldiphenylamine* (from dinitrochloro- or dinitrobromo-toluene and *m*-xylidine; yield, 70%), greenish-yellow needles, m. p. 138° (Found : N, 13·85. $C_{15}H_{15}O_4N_3$ requires N, 13·95%). 2 : 4-*Dinitro*-5 : 2′ : 5′-*trimethyldiphenylamine* (from dinitrochlorotoluene and *p*-xylidine; small yield), yellow prisms, m. p. 114·5°, from EtOH (Found : N, 13·9. $C_{15}H_{15}O_4N_3$ requires N, 13·95%). These four compounds are readily sol. in C_6H_6, AcOH, or Me_2CO. 2 : 4-Dinitro-2′-methoxy-5-methyldiphenylamine, recryst. from AcOH, had m. p. 146° (yield, 90%). It was sparingly sol. in light petroleum and was isolated in two modifications of different colour (Cullinane, Embrey, and Davies, *loc. cit.*). 2 : 4-Dinitro-3′-ethoxydiphenylamine, recryst. from Me_2CO–EtOH, formed yellow plates, m. p. 153° (yield, 75%), slightly sol. in EtOH (Reverdin and Lokietek, *Bull. Soc. chim.*, 1915, **17**, 406, describe orange-yellow crystals, m. p. 151°). These two compounds are readily sol. in C_6H_6, Me_2CO, $CHCl_3$, or C_5H_5N. 2 : 4-*Dinitro*-3′-*ethoxy*-5-*methyldiphenylamine*, thick orange-yellow plates, m. p. 115°, from EtOH (yield 70%); moderately easily sol. in EtOH or AcOH, easily in Me_2CO, $CHCl_3$, C_5H_5N, or C_6H_6 (Found : N, 13·3. $C_{15}H_{15}O_5N_3$ requires N, 13·25%). 2 : 4-Dinitro-4′-ethoxy-5-methyldiphenylamine, recryst. from AcOH, had m. p. 148·5°; yield, 90%. It exists in two modifications of different colour (Cullinane, Embrey, and Davies, *loc. cit.*).

2 : 4-*Dinitro*-5-*methylphenylbenzylamine* (from dinitrochlorotoluene and benzylamine; yield, 70%), bright yellow plates, m. p. 102°, from C_6H_6 (Found : N, 14·8. $C_{14}H_{13}O_4N_3$ requires N, 14·6%). A higher temp. (180°) was employed in the prep. of the three following compounds. 2 : 4-Dinitro-2′-methoxydiphenylamine (80% yield), m. p. 165·5° (Cullinane, Embrey, and Davies, *loc. cit.*). Schöpff (*Ber.*, 1889, **22**, 902) gives m. p. 151°. 2 : 4-Dinitro-4′-ethoxydiphenylamine, scarlet lustrous plates, m. p. 121—122°, from EtOH in 90% yield (compare Blom, *Helv. Chim. Acta*, 1921, **4**, 1036). 2 : 4-*Dinitrophenylbenzylamine* (from dinitrochlorobenzene and benzylamine; yield, 90%), yellow plates, m. p. 116°, from AcOH; sol. in EtOH, C_6H_6, or Me_2CO; alc. alkali produces a red colour (Found : N, 15·4. $C_{13}H_{11}O_4N_3$ requires N, 15·4%).

For the prep. of the two following substances the reaction mixture was heated to 200°. 2 : 4-Dinitro-4′-methoxydiphenylamine, deep red prisms, m. p. 141°; yield, 90% (compare Blom, *loc. cit.*). 2 : 4-Dinitro-2′ : 5′-dimethyldiphenylamine (from *p*-xylidine and dinitrochlorobenzene), orange-red hair-like needles, m. p. 144°, from EtOH (Found : N, 14·7. Calc. : N, 14·6%). Lesser (*Annalen*, 1913, **402**, 51) gives m. p. 150°.

The following compounds were prepared by refluxing the reactants with EtOH and NaOAc for 1—1½ hrs. 2 : 4-Dinitro-2′-ethoxydiphenylamine, red silky needles (from Me_2CO), m. p. 172°, readily sol. in C_6H_6, or AcOH, and moderately easily in EtOH (Found : N, 13·9. Calc. : N, 13·9%). Schöpff (*loc. cit.*) gives m. p. 164°. 2 : 4-*Dinitro*-2′-*ethoxy*-5-*methyldiphenylamine*, scarlet needles, m. p. 179·5°; yield, 75% (Found : N, 13·3. $C_{15}H_{15}O_5N_3$ requires N, 13·25%). 2′-*Bromo*-2 : 4 : 6-*trinitro*-4′-*methyldiphenylamine* (from picryl chloride and *m*-bromo-*p*-toluidine), orange prisms, m. p. 176°; yield, 90%. C_6H_6 or EtOH was suitable as a reaction medium (Found : Br, 20·1. $C_{13}H_9O_6N_4Br$ requires Br, 20·1%). 2 : 4 : 6-Trinitrophenylbenzylamine (from picryl chloride and benzylamine; yield, 90%), yellow flat prisms, m. p. 141·5°. James, Jones, and Lewis (*loc. cit.*) describe chocolate-coloured needles, m. p. 143·3°, and golden-yellow crystals, m. p. 144·8°.

In the three following condensations 2 : 4 : 6-trinitrophenylmethylnitroamine was substituted for picryl chloride. 2 : 4 : 6-Trinitro-4′-hydroxydiphenylamine, red prisms, m. p. 178°. Turpin (*loc. cit.*, p. 719) and Wedekind (*Ber.*, 1900, **33**, 433), who record m. p. 174° and 173° respectively, and Meldola (*J.*, 1917, **111**, 550) used picryl chloride in the condensation. 2 : 4 : 6-*Trinitro*-4′-*ethoxydiphenylamine* (yield, 90%), long thin red prisms, m. p. 138·5°, from EtOH (Found : N, 16·2. $C_{14}H_{12}O_7N_4$ requires N, 16·1%). 2 : 4 : 6-Trinitro-4′-aminodiphenylamine, red prisms, m. p. 194°; yield, 90%. Morgan and Micklethwait (*J.*, 1908, **93**, 608) give m. p. 185—187°.

Benzo-2 : 4 : 6-*trinitroanilide*.—Picryl chloride and benzamide, heated alone or in EtOH, gave a very small yield of product. Benzamide (1 mol.), picryl chloride (1·2 mols.), and NaOH (1·2 mols.) were refluxed in EtOH for 4 hrs. The solid that separated on cooling crystallised from EtOH in yellow rectangular prisms, m. p. 191°, sol. in Me_2CO, and moderately easily in AcOH (Found : N, 17·1. $C_{13}H_8O_7N_4$ requires N, 16·9%).

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