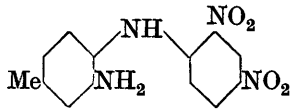
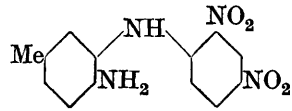
338. *The Isomeric 2 : 4-Dinitrophenyl Derivatives of 3 : 4-Tolylenediamine.*

By KENNETH C. ROBERTS.

THE mechanisms which have been invoked to account for the rearrangement of hydroxysulphones (Smiles and others, J., 1931, 2207, 3264; this vol., pp. 1040, 1488) and halogenohydroxybenzoyltoluic acids (Hayashi, J., 1927, 2516; 1930, 1513) suggested that the 4- and the 5-methyl derivative (I and II) of 2′ : 4′-dinitro-2-aminodiphenylamine might also be interconvertible through an intermediate quinonoid form (III).

Treatment with alkali, however, decomposed them, sulphuric acid had no effect on (I) and produced a readily hydrolysable sulphonic acid from (II), and less powerful agents were without action.

(I.) 

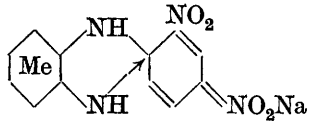


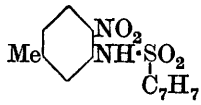
(II.)

The amine (I) has now been isolated by fractionation of the condensation product (a mixture of I and II) of 3 : 4-tolylenediamine and 4-chloro-1 : 3-dinitrobenzene (Ernst, *Ber.*, 1890, **23**, 3428): it has also been synthesised from 3-p-*toluenesulphonamido*-p-*toluidine* and 4-chloro-1 : 3-dinitrobenzene. The 5-methyl isomeride (II) has been obtained by an analogous synthesis from 4-*p*-toluenesulphonamido-*m*-toluidine (VI) (Ullmann and Gross, *Ber.*, 1910, **43**, 2698).

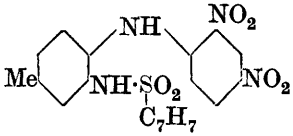
Synthesis of 2′ : 4′-Dinitro-2-amino-4-methyldiphenylamine (I).—4-Nitro-*m*-toluidine and *p*-toluenesulphonyl chloride (mol. quantities) were heated on the water-bath and then at 120° for a few mins. with pyridine (4 mols.). The product, treated with aq. alkali weaker than normal, yielded a red solution,

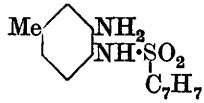
from which HCl aq. liberated p-*toluenesulphon-4′-nitro*-m-*tolylamide* (IV); pale yellow, monoclinic rhombs or needles, m. p. 135°, from Et_2O and EtOH (Found : C, 55·1; H, 4·7. $C_{14}H_{14}O_4N_2S$ requires C, 54·9; H, 4·5%).

(III.) 



(IV.)

(V.) 



(VI.)

Reduction of (IV) (2·5 g.) in fuming HCl aq. (6 c.c.) with $SnCl_2$ (6 g.) in EtOH (12 c.c.) on the water-bath, removal of EtOH, treatment with H_2O and Et_2O, and purification with $(NH_4)_2CO_3$ aq. gave 3-p-*toluenesulphonamido*-p-*toluidine*; colourless plates, m. p. 120°, from EtOH (Found : C, 60·8; H, 6·1. $C_{14}H_{16}O_2N_2S$ requires C, 60·8; H, 5·7%).

The above sulphonamidotoluidine, 4-chloro-1 : 3-dinitrobenzene, anhyd. NaOAc (1 mol. of each), and propyl alcohol were heated at 100° for 10 hrs. After removal of alcohol and treatment of the product with dil. HCl and C_6H_6, 2′ : 4′-*dinitro*-2-p-*toluenesulphonamido*-4-*methyldiphenylamine* (V) was obtained in yellow needles, m. p. 217° (Found : C, 54·6; H, 3·9; N, 12·6. $C_{20}H_{18}O_6N_4S$ requires C, 54·2; H, 4·0; N, 12·6%), insol. in HCl aq., and forming slowly a crimson sodium derivative in contact with NaOH aq.

The sulphonamide (V) was heated for 20 mins. at 130—140° with H_2SO_4 (3 parts) and H_2O (1 part) (cf. Witt and Uerménvi, *Ber.*, 1913, **46**, 296). Treatment of the product with Na_2CO_3 aq. yielded 2′ : 4′-*dinitro*-2-*amino*-4-*methyldiphenylamine* (I), which crystallised from cold EtOH in yellow needles, m. p. 162·5° (Found : C, 54·2; H, 4·3; N, 19·15. $C_{13}H_{12}O_4N_4$ requires C, 54·1; H, 4·1; N, 19·4%), and from hot EtOH in magenta prisms, m. p. 173° (Found : C, 54·0; H, 4·6%). Both forms were stable in air at room temp., but the yellow form was converted into the red when kept at 130—140° for several hrs. Observations with a Judd Lewis spectrometer showed that the isomerides formed optically identical solutions in EtOH at various temps. The ultra-violet absorption curves were of the same type as that of diphenylamine, but were displaced towards the red, the head of the band occurring at 3500 Å.

Synthesis of 2′ : 4′-*Dinitro*-2-*amino*-5-*methyldiphenylamine* (II).—A solution of 4-*p*-toluenesulphonamido-*m*-toluidine (VI) in propyl alcohol was treated as described above for the preparation of the 4-methyl isomeride. 2′ : 4′-*Dinitro*-2-p-*toluenesulphonamido*-5-*methyldiphenylamine*, isolated by usual methods, crystallised from C_6H_6 in yellow needles, m. p. 184° (Found : C, 54·2; H, 4·4; N, 12·3. $C_{20}H_{18}O_6N_4S$ requires C, 54·2; H, 4·1; N, 12·6%), insol. in hot conc. HCl and slowly forming an insol. deep purple sodium derivative, in contact with hot or cold NaOH aq.

The above sulphonamidodiphenylamine, hydrolysed by the method of Witt and Uerménvi (*loc. cit.*), yielded 2′ : 4′-*dinitro*-2-*amino*-5-*methyldiphenylamine* (II), which crystallised from hot EtOH in red-brown needles, m. p. 195°, and

from cold EtOH in orange needles, m. p. 191° (Found: C, 54·0; H, 4·4; N, 19·4. $C_{13}H_{12}O_4N_4$ requires C, 54·1; H, 4·1; N, 19·4%). The red-brown form became orange when kept and its m. p. fell: the orange form deepened in colour when maintained near its m. p. (cf. I); the absorption curves were indistinguishable from those of the 4-methyl isomeride. The amine (II) was not affected by ultra-violet light; its m. p. and the m. p. of a mixture with (I) were unchanged by prolonged heating. The red sodium derivative was also unchanged by the action of heat.

2′ : 4′-*Dinitro*-2-*aminodiphenylamine*.—This substance, prepared by the method of Borsche and Rantscheff (*Annalen*, 1911, **379**, 169), crystallised from EtOH in orange needles, m. p. 147°. Above the m. p. it became red and partly resolidified, and finally melted at 152°. The red form reverted to the orange form at room temp., and the orange form became red (m. p. 152°) when kept at 135—145° for 2 hrs. (cf. I and II above). The absorption curve of the substance was indistinguishable from that of (I) and (II).

No evidence of chromoisomeric forms of 2 : 4-dinitrodiphenylamine has been obtained.

KING'S COLLEGE, LONDON. [*Received, June 11th*, 1932.]