Synthesis of the Isomeric Dinitro-*p*-phenylenediamines by Nitration of *NN'*-Bis(phenylsulphonyl)-*p*-phenylenediamine

By **Kwong-Yung Chu** and **John Griffiths,*** Department of Colour Chemistry, The University, Leeds L22 9JT

Mild nitration of *NN'*-bis(phenylsulphonyl)-*p*-phenylenediamine affords a mixture of the 2,3-, 2,5-, and 2,6-dinitro derivatives, which after separation and hydrolysis give the corresponding dinitro-*p*-phenylenediamines. Structural assignments are made on the basis of ^{1}H n.m.r. and chemical evidence.

ALTHOUGH great interest has been shown in nitro-*p*-phenylenediamine and its *N*-alkyl derivatives,[1] little is known about the corresponding dinitro-compounds. Much of the interest arises from the value of the former compounds as orange-to-violet hair dyes, and it was expected that a second nitro-group would provide an additional bathochromic shift of the visible absorption band, and that the resulting colours might fall in the violet-to-blue range. We now report the synthesis of the three dinitro-*p*-phenylenediamines by direct nitration.

Nitration of *p*-phenylenediamine itself is not feasible, and generally the *NN'*-diacetyl derivative has been used for preparation of the mononitro-compound. The only reported formation of a dinitro-compound by this procedure dates back to 1874,[2] when Biedermann and Römer claimed the isolation of a product which on hydrolysis gave a dinitro-*p*-phenylenediamine. However, as the reported m.p. (294 °C) is appreciably higher than those of the three isomers we now describe, the nature of this material is uncertain.

There have been few other attempts to prepare the dinitro-*p*-phenylenediamines, and these have relied on nucleophilic substitution procedures rather than direct nitration. Thus Macleod *et al.*[3] have claimed the synthesis of 2,3- and 2,5-dinitro-*p*-phenylenediamine by the action of ammonia on the appropriate dichlorodinitrobenzenes. However, the products were not well characterised, and the reported properties are at variance with those which we now describe. Using a similar approach, Hodgson and Crook[4] have synthesised 2,6-dinitro-*p*-phenylenediamine, by the action of ammonia on 3,5-dinitro-4-methoxyaniline.

DISCUSSION

From our own studies of the nitration of protected *p*-phenylenediamines, it was evident that the *NN'*-bis(phenylsulphonyl) derivatives were more useful than the corresponding diacetyl compounds, and proved more reactive towards substitution by the nitronium ion. This high reactivity enabled nitration to be effected under relatively mild conditions, where unwanted side reactions could be minimised. Thus with fuming nitric

[1] J. F. Corbett, 'The Chemistry of Synthetic Dyes, vol. V,' ed. K. Venkataraman, Academic Press, New York, 1971, pp. 508—518.

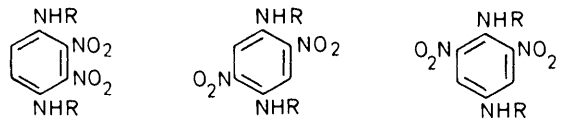
[2] R. Biedermann and H. Römer, *Ber.*, 1874, **7**, 1533.

[3] A. L. Macleod, M. C. Pfund, and M. L. Kilpatrick, *J. Amer. Chem. Soc.*, 1922, **44**, 2260.

[4] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1936, 1570.

acid in acetic acid–acetic anhydride at 5—10 °C, *NN'*-bis(phenylsulphonyl)-*p*-phenylenediamine gave a bright yellow product, which after removal of an insoluble material consisted of three components. Interestingly, no traces of the mononitro-compound were detected by t.l.c.

The three components were separated by chromatography on acidic alumina, giving the 2,3-, 2,5-, and 2,6-dinitro-derivatives (1a)—(3a) in yields of 24, 10, and



(1) (2) (3)

a ; R = $PhSO_2$
b ; R = H

16%, respectively. The molecular formulae were indicated by elemental analysis or mass spectrometry, and the substitution patterns were assigned after hydrolysis to the corresponding amines.

Hydrolysis was smoothly effected by maintaining solutions of the sulphonamides in concentrated sulphuric acid at room temperature for 30 h, and then pouring them into cold water. The three dinitro-*p*-phenylenediamines (1b)—(3b) were obtained in 51, 77, and 79% yields respecively.

2,6-Dinitro-*p*-phenylenediamine (3b) formed deep purple needles melting at 222 °C, these properties corresponding closely with those reported for the product from the reaction of 3,5-dinitro-4-methoxyaniline with ammonia.[4] The structure of this isomer was clearly indicated by the ^1H n.m.r. spectrum, which showed two different amino-groups, with singlets at $\delta(CDCl_3)$ 5.40 (2 H) and 7.90 (2 H), both removed by deuterium oxide. The two aromatic protons gave a singlet (2 H) at δ 7.87.

Distinction between the isomers (1b) and (2b) was more difficult, however, as both showed two ^1H n.m.r. singlets of relative area 2 : 4. The aromatic proton singlet of one of the isomers occurred at higher field (δ 7.05) than that of the other (δ 7.74), which suggested that the former could be assigned structure (1b). Thus in (1b), each ring proton experiences the effect of one *meta*- and one *para*-nitro group, whereas in (2b) each proton has one *meta*- and one *ortho*-nitro group; the latter situation should afford the greater deshielding.

Proof that this assignment was correct was forthcoming from chemical tests. Thus the two isomeric sulphonamides (1a) and (2a) were reduced with iron powder in acetic acid, and the solutions were treated with phenanthraquinone. The isomer (1a) afforded bright yellow needles of the phenazine derivatives, indicating the presence of an *ortho*-diamino grouping in the reduced product, whereas (2a) gave no reaction.

2,3-Dinitro-*p*-phenylenediamine (1b) formed dark red needles, melting at 202—204 °C. These properties are not in agreement with those reported by Macleod *et al.*,[3] who claimed to have prepared (1b) as yellow crystals of m.p. 241—250 °C. The 2,5-dinitro-isomer (2b) formed dark purple crystals, m.p. 240—241 °C, whereas Macleod *et al.* describe this compound as reddish-brown needles, melting at 295—300 °C.

The 2,3-dinitro-isomer (1a) is formed seemingly in greater amounts than both (2a) and (3a) in the nitration reaction. In view of the *meta*-directing effect of the first nitro-group introduced into the system, (3a) would be expected to predominate, and because of the steric crowding in (1a), one would also expect the 2,5-dinitro-isomer to be formed in preference to the 2,3-isomer. Although the isolated yields only account for approximately 50% of the starting material, it is difficult to explain the anomalous isomer distributions in terms of widely differing rates of decomposition of the three isomers under the conditions of the nitration reaction. Similar observations have been made for the nitration of 2-nitroquinol 1-benzenesulphonate,[5] where the 2,3-dinitro-product is formed in considerably greater yields than the 2,5-isomer, and none of the 2,6-isomer is detected.

EXPERIMENTAL

Melting points are corrected. ^1H N.m.r. spectra were recorded at 220 MHz, with $CDCl_3$ as solvent.

Nitration of NN'-*Bis*(*phenylsulphonyl*)-p-*phenylenediamine*.— *NN'*-Bis(phenylsulphonyl)-*p*-phenylenediamine (3.0 g) was added in small portions over 1 h to a mixture of fuming nitric acid (s.g. 1.52; 1.2 ml), glacial acetic acid (2 ml), acetic anhydride (5 ml), and urea (0.2 g) at 5—10 °C, with stirring and cooling. The yellow suspension was stirred at 5 °C for 1 h, and at 15 °C for 24 h, and then poured over ice (200 g). After stirring for several hours, the yellow solid was filtered off, washed well with water, and dried (3.05 g). The solid was digested with boiling methylene chloride (1.2 l) and the insoluble solid removed by filtration. The concentrated solution was chromatographed over acidic alumina in benzene–methylene chloride (1 : 1). The first orange-brown band afforded 2,5-*dinitro*-NN'-*bis*(*phenylsulphonyl*)-p-*phenylenediamine* (2a) (0.35 g, 10%) as orange needles, m.p. 212—213° (Found: C, 45.1; H, 2.9; N, 12.0; S, 12.9. $C_{18}H_{14}N_4O_8S_2$ requires C, 45.2; H, 2.9; N, 11.7; S, 13.3%); $\nu_{max.}$ (KBr) 3 265 cm^{-1}.

The second orange band gave 2,3-*dinitro*-NN'-*bis*(*phenylsulphonyl*)-p-*phenylenediamine* (1a) as bright yellow plates (0.87 g, 24%), m.p. 231° (decomp.); M^+ 478; $\nu_{max.}$ (KBr) 3 280 cm^{-1}.

The residual pale yellow alumina was extracted with acetone acidified with several drops of hydrochloric acid, and the extracts were evaporated to dryness to give 2,6-*dinitro*-NN'-*bis*(*phenylsulphonyl*)-p-*phenylenediamine* (3a) (0.59 g, 16%) as pale yellow needles, m.p. 196—197° (from ethanol); M^+ 478; $\nu_{max.}$ (KBr) 3 245 and 3 310 cm^{-1}.

2,3-, 2,5-, *and* 2,6-*Dinitro*-p-*phenylenediamines* (1b)—(3b).—The appropriate phenylsulphonyl derivative (1a)—(3a) (0.10 g) was dissolved in concentrated sulphuric acid (10 ml) with cooling. The solution was kept at 20 °C for 30 h, then poured onto ice and neutralised with ammonia solution, with the temperature maintained below 10 °C. In the case of (2b) and (3b), the amines were filtered off

[5] E. M. Kampouris, *J. Chem. Soc.*, (*C*), 1967, 1235.

directly. The 2,3-dinitro-isomer (1b) gave a clear orange solution, which was extracted with diethyl ether. The dried extracts were evaporated to give the *product* (1b) (0.021 g, 51%), dark red needles, m.p. 202—204° (from methanol) (Found: C, 36.7; H, 3.1; N, 28.7. $C_6H_6N_4O_4$ requires C, 36.4; H, 3.0; N, 28.3%); $\nu_{max.}$ (KBr) 3 420 and 3 300 cm^{-1}.

2,5-*Dinitro*-p-*phenylenediamine* (2b) was obtained as dark purple crystals from benzene (0.032 g, 77%), m.p. 240—241 °C (Found: C, 36.3; H, 3.0; N, 28.2%); $\nu_{max.}$ (KBr) 3 380 and 3 485 cm^{-1}.

2,6-*Dinitro*-p-*phenylenediamine* (3b) formed dark purple crystals from benzene (0.033 g, 79%), m.p. 222 °C (lit.,[4] 225 °C) (Found: C, 36.3; H, 3.1; N, 28.4%); $\nu_{max.}$ (KBr) 3 300, 3 340, 3 360, and 3 440 cm^{-1}.

Phenazine Derivative of N^1N^4-*Bis*(*phenylsulphonyl*)*benzene*-1,2,3,4-*tetra-amine*.—Iron powder (2.5 g) was added in portions over 15 min to a solution of (1a) (0.239 g) in boiling acetic acid (40 ml), and heating was continued until the dark brown solution became pale yellow. The mixture was rapidly filtered, and to the hot filtrate was added immediately a solution of phenanthraquinone (0.104 g) in acetic acid (8 ml). The mixture was boiled for 10 min and cooled. The golden yellow leaflets of the *phenazine derivative* were filtered off and dried (0.130 g, 44%); m.p. 320 °C (decomp.) (Found: C, 65.3; H, 3.7; N, 9.8. $C_{32}H_{22}N_4O_4S_2$ requires C, 65.1; H, 3.8; N, 9.5%).

When an identical procedure was followed with the 2,5-dinitro-isomer (2a), no precipitate formed after prolonged treatment with phenanthraquinone.

We thank the S.R.C. for n.m.r. and mass spectrometry services.

[7/1055 *Received*, 20th *June*, 1977]