126. *The Apparent Anomalous Lability of the 2-Nitro-group in 2 : 3-Dinitrotoluene. An Example of the Reversed-field Effect.*

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In 3 : 4-dinitrochlorobenzene and 3 : 4-dinitrotoluene it is the 3-nitro-group which undergoes displacement by such groups as NH_2 and OMe, since, in terms of the modern electronic theory, the 4-carbon atom in the activated molecule is less kationoid than its 3-carbon neighbour owing to the availability of an anionoid electromeric effect from the 1-substituent.

With 2 : 3- and 2 : 5-dinitrotoluene, however, an apparent anomaly arises, Kenner and Parkin (J., 1920, **117**, 852) having found that the 2-nitro-group reacts with hot alcoholic ammonia under pressure. To test whether this reaction can be effected by less drastic means, and therefore is to be regarded as normal, 2 : 3-dinitrotoluene has been subjected to the action of sodium mono- and di-sulphide at room temperature and also of hot aqueous caustic soda; in each case the 2-nitro-group was replaced.

This phenomenon seems to be an example of the effect of the widely spread electron-attracting field outside the methyl group (Bennett and Mosses, J., 1930, 2364), which, by reducing the intensity of the negative field of the 2-nitro-group, increases the kationoid character of the 2-carbon atom beyond that of its 3-carbon neighbour. The anionoid reagent, therefore, attracted initially by the positive field of the methyl group, attacks the 2-carbon in preference to the less kationoid 3-carbon atom. Similar examples are 2 : 5-dinitrotoluene and 2-chloro-5 : 6-dinitrotoluene (Morgan and Drew, J., 1920, **117**, 786). The co-ordination between the groups in *o*-toluidine suggested by Peacock (*Nature*, 1932, **129**, 57; cf. also Hodgson and France, this vol., p. 296) receives a like explanation.

Experimental.

Improved Preparation of 2 : 3-*Dinitrotoluene.*—3-Nitro-*o*-toluidine was prepared by a modification of Meisenheimer and Hesse's method (*Ber.*, 1919, **52**, 1170). Aceto-*o*-toluidide (30 g.) was added gradually to HNO_3 (66 c.c.; *d* 1·5) in AcOH (36 c.c.) at 30—35°, followed by Ac_2O (10 c.c.); after 6 hr., the mixture was poured into H_2O ($1\frac{1}{2}$ l.), the ppt. washed, dried, and boiled with conc. HCl (200 c.c.) for 6 hr., and 3-nitro-*o*-toluidine (15 g.) finally pptd. by dilution with H_2O ($1\frac{1}{2}$ l.).

The above product (10 g.) was converted into 3 : 3′-*dinitro*-2 : 2′-*azoxytoluene* (10 g.) by pouring its solution in EtOH (100 c.c.) into H_2O (375 c.c.) containing K_2SO_4 (50 g.) and conc. H_2SO_4 (100 g.), and shaking the mixture for 3 days; the product crystallised from EtOH, in which it was sparingly sol., in buff-coloured plates, m. p. 121° (Found : N, 17·9. $C_{14}H_{12}O_5N_4$ requires N, 17·7%). Treatment with 10 parts of HNO_3 (*d* 1·5) below 20° gave 2 : 3-dinitrotoluene, which was removed from the diluted mixture by steam distillation and then crystallised from aq. EtOH in white needles, m. p. 61° (Found : N, 15·5. Calc. : N, 15·4%).

Action of Sodium Hydroxide on 2 : 3-*Dinitrotoluene*.—The compound (1 g.) was heated for 3 hr. on the water-bath with 20% aq. NaOH (20 c.c.), the mixture steam-distilled to remove unchanged initial material, acidified, and again steam-distilled; the volatile 2-hydroxy-3-nitrotoluene (3-nitro-*o*-cresol) obtained crystallised from 50% aq. EtOH in bright yellow prisms, m. p. and mixed m. p. with authentic specimen, 69° (Found : N, 9·4. Calc. : N, 9·2%).

Action of Sodium Monosulphide on 2 : 3-*Dinitrotoluene*.—The substance (0·5 g.), dissolved in acetone (10 c.c.), was mixed with $Na_2S,9H_2O$ (1 g.) in H_2O (3 c.c.), kept at room temp. for 24 hr., and diluted with H_2O, and the pptd. 3 : 3′-dinitro-2 : 2′-ditolyl sulphide crystallised from EtOH; pale yellow micro-rhombs, m. p. 152° (Kenner and Parkin, *loc. cit.*, give m. p. 150°) (Found : S, 10·5. Calc. : S, 10·5%).

Action of Sodium Disulphide on 2 : 3-*Dinitrotoluene*.—The compound (1·5 g.) in acetone (30 c.c.) was mixed with a solution of $Na_2S,9H_2O$ (3 g.) and S (0·3 g.) in H_2O (10 c.c.), and kept for 3 days at room temp.; the deep red liquor was then acidified with dil. HCl, the ppt. dissolved in 20% aq. NaOH, and the solution shaken with sodium hyposulphite until colourless and oxidised with $K_3Fe(CN)_6$.

3 : 3′-*Diamino*-2 : 2′-*ditolyl disulphide* was pptd.; it crystallised from aq. EtOH in buff-coloured needles, m. p. 123° (Found : S, 23·3. $C_{14}H_{16}N_2S_2$ requires S, 23·2%).

The *acetyl* derivative formed colourless needles from aq. AcOH, m. p. 167° (Found : S, 18·0. $C_{18}H_{20}O_2N_2S_2$ requires S, 17·8%); and the *dipicrate*, deep orange-yellow needles, m. p. 158° (Found : S, 9·0. $C_{14}H_{16}N_2S_2,2C_6H_3O_7N_3$ requires S, 8·7%).

Preparation of 3 : 3′-*Dinitro*-2 : 2′-*ditolyl Disulphide*.—2 : 3-Dinitrotoluene (1 g.) in acetone (10 c.c.) was kept for 24 hr. after addition of $Na_2S,9H_2O$ (4 g.) in H_2O (3 c.c.), the deep red solution diluted with H_2O and filtered, and $K_3Fe(CN)_6$ added until colourless; 3 : 3′-dinitro-2 : 2′-ditolyl disulphide separated, and, after three crystns. from 80% AcOH, had m. p. 145° (Found : S, 19·2. $C_{14}H_{12}O_4N_2S_2$ requires S, 19·0%).

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