274. *The Nitration of 4-Nitro-*o-*tolyl* p-*Toluenesulphonate.*

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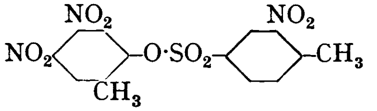
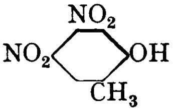
In the course of unsuccessful attempts to prepare 4 : 6-dinitro-*o*-cresol, the nitration of *4-nitro-*o-*tolyl* p-*toluenesulphonate* was investigated. It has been found that, although concentrated nitric acid gives a mononitro-derivative, which, in view of the well-known behaviour of the *p*-toluenesulphonyl residue on nitration, is undoubtedly the o-*nitro*-p-*toluenesulphonate* of 4-nitro-*o*-cresol, yet a mixture of nitric and sulphuric acids yields 4 : 5-*dinitro*-o-*tolyl* o-*nitro*-p-*toluenesulphonate* (I), which on hydrolysis forms *o*-nitro-*p*-toluenesulphonic acid and 4 : 5-*dinitro*-o-*cresol* (II). The orientation of (II), and hence

(I.)





(II.)

that of (I), was established by the fact that its *methyl* ether on nitration afforded 3 : 4 : 5-trinitro-2-methoxytoluene, indicating that the second nitro-group in (II) is in the 5-position (the 3-position is excluded on account of the effect of the *p*-toluenesulphonyl residue), and on reduction gave 5-*nitro-2-methoxy*-p-*toluidine* which was converted into 5-nitro-2-methoxytoluene.

Experimental.

*4-Nitro-*o-*tolyl* p-*Toluenesulphonate.*—This *ester* was prepared from 4-nitro-*o*-cresol (Ullmann and Fitzenkam, *Ber.*, 1905, **38**, 3790) (40 g.), *p*-toluenesulphonyl chloride (52 g.), water (100 c.c.), and anhydrous sodium carbonate (28 g.) by the method used by Ullmann and Nadai (*Ber.*, 1908, **41**, 1872) for the preparation of the 2 : 4-dinitrophenyl ester. Crystallised from alcohol, it formed rectangular prisms, m. p. 123—124°, sparingly soluble in hot methyl or ethyl alcohol and readily soluble in warm acetic acid (Found : C, 54·8; H, 4·5. $C_{14}H_{13}O_5NS$ requires C, 54·7; H, 4·2%).

*Nitration of 4-Nitro-*o-*tolyl* p-*Toluenesulphonate.*—(A) The foregoing ester was added with stirring to nitric acid (11 c.c.; *d* 1·5), and after having been kept at room temperature for 1 hour, the solution was poured on ice and the *nitro*-derivative crystallised from alcohol, forming rectangular prisms, m. p. 120—121° (Found : C, 47·4; H, 3·6. $C_{14}H_{12}O_7N_2S$ requires C, 47·7; H, 3·4%). The scission of this compound (1·6 g.) was effected with piperidine (1·5 c.c.) at 100° in the course of 1 hour, and a solution of the reaction mixture in 10% aqueous sodium hydroxide was kept for 20 minutes, filtered, and acidified, yielding almost pure 4-nitro-*o*-cresol, m. p. 117° after recrystallisation.

(B) The ester (35 g.) was carefully added to a mixture of concentrated sulphuric acid (170 c.c.) and nitric acid (255 c.c.; *d* 1·5) (agitate) maintained at below 40°. After having been kept at room temperature for 1 hour, the nitration mixture was poured on ice (1200 g.), and the resulting 4 : 5-*dinitro*-o-*tolyl* o-*nitro*-p-*toluenesulphonate* crystallised from alcohol, forming glistening, colourless, hexagonal plates (35 g.), m. p. 125—126°, readily soluble in acetone or hot acetic acid (Found : N, 10·0. $C_{14}H_{11}O_9N_3S$ requires N, 10·6%). Mixed with the nitro-derivative obtained by method (A), it melted at 109—110°. The same product, m. p. and mixed m. p. 125—126°, was obtained when the nitration was carried out at 0°.

The trinitro-ester (1·2 g.) and piperidine (1 c.c.) reacted vigorously, forming a dark red solution, which was heated on the steam-bath for ¾ hour and then dissolved in 5% aqueous sodium hydroxide (100 c.c.). Acidification of the filtered solution with hydrochloric acid gave an oil which was isolated with ether and dissolved in warm benzene. On cooling, 4 : 5-*dinitro*-o-*cresol* separated in almost colourless needles, m. p. 115°, readily soluble in hot toluene or alcohol (Found : C, 42·6; H, 3·3. $C_7H_6O_5N_2$ requires C, 42·4; H, 3·0%). On methylation with methyl sulphate and 10% aqueous sodium hydroxide, it formed the *methyl* ether, which crystallised from methyl alcohol in thick needles, m. p. 80—81° [Found : OMe, 14·6. $C_7H_5O_4N_2(OMe)$ requires OMe, 14·6%]. Treatment of this compound (1 g.) with a mixture of nitric acid (10 c.c.; *d* 1·5) and concentrated sulphuric acid (7 c.c.) during 1 hour at room temperature gave rise to 3 : 4 : 5-trinitro-2-methoxytoluene (precipitated with ice), which separated from alcohol in almost colourless prisms, m. p. 112°, identical with a specimen prepared from 4-nitro-2-methoxytoluene according to the directions of Kaufler and Wenzel (*Ber.*, 1901, **34**, 2241) [Found : OMe, 12·0. Calc. for $C_7H_4O_6N_3(OMe)$: OMe, 12·1%].

Hydrolysis of the trinitro-ester (30 g.) was also effected with a mixture of 10% aqueous potassium hydroxide (180 c.c.) and alcohol (80 c.c.) on the steam-bath during 15 minutes, and on cooling, the crystalline potassium *o*-nitro-*p*-toluenesulphonate was collected and converted into the characteristic barium salt, which separated from warm water as a hydrate in clusters of needles [Found, in material dried over sulphuric acid in a vacuum: Ba, 22·4. Calc. for $(C_7H_6O_5NS)_2Ba,2{\cdot}5H_2O$: Ba, 22·4%. Found, in anhydrous material: Ba, 24·2. Calc. for $(C_7H_6O_5NS)_2Ba$: Ba, 24·1%]. Acidification of the alkaline liquor left after the separation of the potassium salt gave 4 : 5-dinitro-*o*-cresol (10 g.), m. p. and mixed m. p. 115° after purification.

5-*Nitro*-2-*methoxy*-p-*toluidine*.—Stannous chloride (13 g.) was dissolved in methyl alcohol (50 c.c.) saturated with hydrogen chloride and carefully added to 4 : 5-dinitro-2-methoxytoluene (3 g.) and methyl alcohol (10 c.c.), the resulting solution boiled for ½ hour, and the *nitro-amine* precipitated with water. Recrystallised from benzene, it formed clusters of yellow needles, m. p. 152° (Found: C, 52·8; H, 6·0. $C_8H_{10}O_3N_2$ requires C, 52·8; H, 5·5%). The amine dissolved only in concentrated mineral acids; addition of water to a solution in concentrated hydrochloric acid precipitated the free base.

Reduction of the nitro-compound with ammonium sulphide did not give the nitro-amine, and treatment with sodium disulphide gave rise to a product containing sulphur, probably a diphenyl disulphide (cf. Kenner and Parkin, J., 1920, **117**, 852; Parijs, *Rec. trav. chim.*, 1930, **49**, 45).

A solution of the nitro-amine (1·5 g.) in sulphuric acid (15 c.c.) and water (15 c.c.) was diazotised at below 0° with sodium nitrite (1·2 g.); 10 minutes later boiling alcohol (35 c.c.) was added, and after the reaction had ceased, 5-nitro-2-methoxytoluene was precipitated with water and crystallised from methyl alcohol, forming clusters of needles, m. p. 62—63°, identical with an authentic specimen (Simonsen and Nayak, J., 1915, **107**, 828) [Found: OMe, 18·5. Calc. for $C_7H_6O_2N(OMe)$: OMe, 18·6%].

The authors are indebted to the Chemical Society, the Dixon Fund of London University, and the Department of Scientific and Industrial Research for grants.

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[*Received, June 3rd*, 1933.]