451. *Bromination of* 2-*Nitro*-p-*cresol.*

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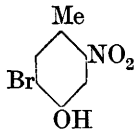
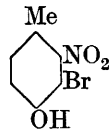
2-Nitro-*p*-cresol (Copisarow, J., 1929, 251), when brominated in chloroform solution, yields two monobromo-derivatives, m. p. 104° and 77° respectively. The former is 5-*bromo*-2-*nitro*-p-*cresol* (I) for the following reasons. (1) The compound is formed by nitration of

3-*bromo*-p-*tolyl* p-*toluenesulphonate* or carbonate and subsequent hydrolysis. (2) 3-Acetamido-*p*-tolyl methyl ether, on nitration and subsequent hydrolysis, yields 2-nitro-5-amino-*p*-tolyl methyl ether, from which 5-*bromo*-2-*nitro*-p-*tolyl methyl ether*, m. p. 94°, is obtained identical with the methylation product of the compound, m. p. 104°.

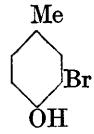
The compound, m. p. 77°, almost certainly has the formula (II).



(I.)



(II.)



(III.)

When nitrated, 3-bromo-*p*-cresol (III) yields 5-bromo-3-nitro-*p*-cresol but, as shown above, its carbonate yields the carbonate of 5-bromo-2-nitro-*p*-cresol (compare *p*-cresol and its carbonate, which are nitrated in position 3 and 2 respectively).

The bromine atom in compounds (I) and (II) and their derivatives is relatively inactive. For instance, 5-*bromo*-2-*nitro*-p-*tolyl acetate*, when treated in boiling acetic anhydride with sodium acetate and a trace of copper, loses less than 2% of its bromine in 12 hours, whereas under parallel conditions *p*-bromonitrobenzene loses about 35%. Also, when 5-bromo-2-nitro-*p*-tolyl methyl ether was heated with piperidine on a boiling water-bath for 6 hours, scarcely any bromine ions were produced, whereas under similar conditions at least 75% of the bromine was liberated from *p*-bromonitrobenzene.

Experimental.

All the compounds described below are sol. in EtOH and C_6H_6 and slightly sol. or insol. in ligroin and H_2O. Unless stated otherwise, they were crystallised from C_6H_6–ligroin.

5-*Bromo*-2-*nitro*-p-*tolyl Methyl Ether*.—The suspension obtained from 2-nitro-5-amino-*p*-tolyl methyl ether (10 g.) and HBr aq. (15 c.c., *d* 1·49; 8 c.c. H_2O) was diazotised at room temp. (4 g. $NaNO_2$ in 5 c.c. H_2O), and the filtered solution heated with CuBr (3 g. $CuCO_3$ in 20 c.c. HBr, *d* 1·49; Cu turnings). Et_2O then extracted the *bromo-ether*, which formed pale yellow needles, m. p. 94° (Found: N, 5·9. $C_8H_8O_3NBr$ requires N, 5·7%).

Bromination of 2-*Nitro*-p-*cresol*.—The cresol (1 mol.) in $CHCl_3$ (500 c.c.) and Br (1 mol.) in $CHCl_3$ (50 c.c.) were mixed at 35°, the $CHCl_3$ was distilled after 3 hr., the residue dissolved in hot 10% NaOH aq., 50% NaOH aq. added to raise the concn. to about 20%, and the orange-yellow cryst. Na salt collected after cooling, dissolved in H_2O, and treated with HCl aq. 5-*Bromo*-2-*nitro*-p-*cresol* was obtained, after several recrystns., as light yellow needles, m. p. 104° (Found: N, 6·3. $C_7H_6O_3NBr$ requires N, 6·0%), giving a dark greenish-brown colour with alc. $FeCl_3$.

The alkaline mother-liquor, on acidification, yielded a brown oil, which solidified and when crystallised (several times) formed straw-yellow prismatic

needles, m. p. 77°, presumably of 3-*bromo*-2-*nitro*-p-*cresol* (Found : N, 5·9%); these gave a light greenish-brown colour with alc. $FeCl_3$.

Methylation of the Bromo-derivatives.—5-Bromo-2-nitro- or 3-bromo-2-nitro-*p*-cresol (2·3 g.) was treated with Me_2SO_4 (1·2 c.c.) in boiling xylene (15 c.c.) and K_2CO_3 (1·2 g.) (cf. Haworth and Lapworth, J., 1923, **123**, 2986); the product separated from the filtered, cooled solution. On recrystn., 5-bromo-2-nitro-*p*-tolyl methyl ether formed pale yellow needles, m. p. 94°, and 3-*bromo*-2-*nitro*-p-*tolyl methyl ether* straw-yellow needles, m. p. 74° (Found : N, 5·4. $C_8H_8O_3NBr$ requires N, 5·7%).

5-*Bromo*-2-*nitro*-p-*tolyl Acetate*.—This was prepared in boiling Ac_2O (2 hr.). It formed thin, hexagonal, white plates with a faint, greenish iridescence; m. p. 121° (Found : N, 4·9. $C_9H_8O_4NBr$ requires N, 5·12%).

3-*Bromo*-2-*nitro*-p-*tolyl acetate*, similarly prepared from 3-bromo-2-nitro-*p*-cresol, formed small white plates, m. p. 81° (Found : N, 5·3%).

3-*Bromo*-p-*tolyl* p-*toluenesulphonate*, prepared from 3-bromo-*p*-cresol (9·3 g.) in pyridine (20 c.c.), and *p*-toluenesulphonyl chloride (10·3 g.), finally on the water-bath (½ hr.), and pptd. by H_2O, crystallised from EtOH in small, thick, rectangular prisms (15 g.), m. p. 121°, slightly sol. in C_6H_6 (Found : Br, 22·0. $C_{14}H_{13}O_4BrS$ requires Br, 22·4%).

3 : 3′-Dibromodi-*p*-tolyl carbonate, obtained by passing $COCl_2$ into a slightly alkaline solution of sodium 3-bromo-*p*-tolyloxide at 50—60°, crystallised from aq. EtOH in thick, white, hexagonal prisms, m. p. 77°.

Nitration of 3-*Bromo*-p-*tolyl* p-*Toluenesulphonate*.—The ester (3·4 g.), in 100% H_2SO_4 (20 c.c.) at 0°, was treated slowly, below 10°, with a mixture of HNO_3 (0·5 c.c., *d* 1·49) and 100% H_2SO_4 (3 c.c.). Kept at room temp. for 2 hr. and then poured on ice, the solution gave a nitro-derivative, which was hydrolysed with hot 10% NaOH aq. The orange-yellow sodium salt which separated on cooling was dissolved in hot H_2O; and acidification then gave 5-bromo-2-nitro-*p*-cresol, m. p. 104° after recrystn.

Nitration of 3 : 3′-*Dibromodi*-p-*tolyl Carbonate*.—The carbonate (6 g.), in 100% H_2SO_4 (100 c.c.), nitrated (1·8 c.c. HNO_3, *d* 1·49; 5 c.c. 100% H_2SO_4) and treated as described above, gave a product which, purified through the Na salt, proved to be 5-bromo-2-nitro-*p*-cresol, m. p. 104°, after recrystn.

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