

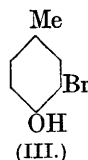
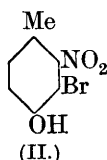
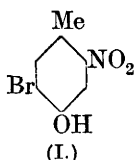
451. *Bromination of 2-Nitro-p-cresol.*

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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).



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. $C_9H_9O_3NBr$ 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. $C_7H_5O_3NBr$ 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. $\text{C}_8\text{H}_8\text{O}_3\text{NBr}$ 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. $\text{C}_9\text{H}_8\text{O}_4\text{NBr}$ 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 ($\frac{1}{2}$ 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. $\text{C}_{14}\text{H}_{13}\text{O}_4\text{BrS}$ 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*-tolyl oxide 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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