

BROMINATION OF COMPOUNDS CONTAINING TWO AROMATIC NUCLEI

Part IX. Bromination of Aryl Esters of 3-Nitro Salicylic Acid

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THIS work was undertaken with a view to study towards bromination the effect of a negative group like $-\text{NO}_2$ in the acidic part of aryl esters of salicylic acid. It has been observed in the case of aryl esters of 3-nitro salicylic acid that bromine enters the acid part only when bromination is carried out in presence of a solvent like acetic acid and no bromine enters the phenolic part even when excess of bromine is used.

On the other hand bromination with liquid bromine always gives compounds with bromine in the phenolic part only. Phenyl ester gives a di-bromo derivative whilst *o,m*-cresyl esters give mono bromo derivatives only, even with a large excess of bromine. This points out that the course of bromination is controlled by the conditions of the reaction and not by the total quantity of bromine.

The constitutions of these bromo derivatives are proved by alkaline hydrolysis and confirmed by their synthesis.

EXPERIMENTAL

Bromination in acetic acid medium: Phenyl 5-bromo-3-nitrosalicylate.—Phenyl 3-nitrosalicylate (3 g.) was dissolved in acetic acid (10 c.c.) and solution of 2 g. of bromine in 5 c.c. acetic acid was added to it. The mixture was heated on a boiling water-bath for four hours. Solid that separated on cooling the solution was crystallised from carbon tetrachloride, m.p. 123–24°. Found: Br, 23.9; $\text{C}_{13}\text{H}_8\text{O}_5\text{NBr}$ requires Br, 23.7 per cent.

o-Cresyl 5-bromo-3-nitrosalicylate.—This was prepared in the same way as the phenyl ester. It crystallised from methyl alcohol, m.p. 138–39°. Found: Br, 22.8; $\text{C}_{14}\text{H}_{10}\text{O}_5\text{NBr}$ requires Br, 22.7 per cent.

m-Cresyl 5-bromo-3-nitrosalicylate was prepared in the same way as the ortho isomer. It crystallised from ethyl alcohol, m.p. 131–32°. Found: Br, 22.9; $\text{C}_{14}\text{H}_{10}\text{O}_5\text{NBr}$ requires Br, 22.7 per cent.

Bromination with liquid bromine

2: 4-Dibromophenyl 3-nitrosalicylate.—Liquid bromine (6 g.) was gradually added to phenyl 3-nitrosalicylate (4 g.) and the mixture was shaken for half an hour and then left overnight. The mixture was diluted with water and then treated with dilute solution of sodium bisulphite and the solid obtained crystallised from ethyl alcohol, m.p. 157–58°. Found: Br, 38.5; $C_{13}H_7O_5 NBr_2$ requires Br, 38.4 per cent.

4-Bromo-*o*-cresyl-3-nitro-salicylate, m.p. 123–24°, and 4-bromo-*m*-cresyl 3-nitro-salicylate, m.p. 131–32°, were prepared in the same way as the phenyl derivative by using 4 g. of ester and 3 g. of liquid bromine. Both crystallised from alcohol. The former gave Br, 22.8 and the latter gave Br, 22.9 whilst $C_{14}H_{10}O_5 NBr$ requires Br, 22.7 per cent.

Hydrolysis

All bromo derivatives described above were hydrolysed by boiling (1 g.) of the substance with 100 c.c. of 5 per cent. sodium hydroxide solution for about five to six hours. The solution was cooled in ice and carbon dioxide was passed through it when the phenolic component separated. It was removed by extraction with ether. The residual aqueous solution was then acidified and the acid obtained was crystallised and identified by mixed melting point.

Synthesis

The esters of 5-bromo-3-nitrosalicylic acid were also prepared by condensing the acid (2 g.) with the appropriate phenol (2 g.) in presence of phosphorus oxychloride (1 c.c.) by heating the mixture at 120–30° for about half an hour. Their mixed melting points with the bromination products showed no lowering.

Melting point of the bromo aryl esters of 3-nitro-salicylic acid showed no lowering, when mixed with the synthetic products described by Jadhav and Thakkar¹.

REFERENCES

1. Jadhav and Thakkar .. *J. Univ. Bom.*, 1949 18 (3), 30-32.