

Halogenation. Part IV. Bromination and Iodination of Aromatic Acids.

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Aromatic acids are not so easily brominated and iodinated as aromatic hydrocarbons or phenols or amines. Most of the bromo- and iodo-derivatives of the aromatic acids have been obtained either by the oxidation of the side-chain of the corresponding homologues of benzene or by the replacement of amino-groups in aromatic acid derivatives by bromine or iodine atoms through diazotisation (Richter, *Ber.*, 1871, 4, 465; Hübner, Ohly and Phillip, *Annalen*, 1867, 143, 247; Wroblewski, *Annalen*, 1873, 168, 200; Graebe, *Annalen*, 1893, 276, 56). *m*-Bromobenzoic acid alone has been obtained by direct bromination by heating benzoic acid with water and bromine for several days in a sealed tube at 100° or at 130°-160° (Hübner, Ohly and Phillip, *Annalen*, 1867, 143, 233; Hübner, Petermann, *Annalen*, 1894, 281, 246; Augerstein, *Annalen*, 1871, 158, 4). It is difficult to obtain iodo-benzoic acid by direct iodination (Peltzer, *Annalen*, 1865, 136, 201; Birnbaum and Reinherz, *Ber.*, 1882, 15, 456).

It has been possible to obtain a good yield of *m*-bromobenzoic acid by carrying on bromination in presence of a mixture of fuming nitric acid and nitrosulphonic acid. In presence of sodium nitrite and fuming sulphuric acid also *m*-bromobenzoic acid is obtained. *m*-Iodobenzoic acid is similarly obtained in good yield. With *p*- and *o*-toluic acids monobromo-, and moniodo-derivatives have been obtained. *m*-Toluic acid is, however not brominated or iodinated by the same reagent. Anisic acid gives bromo- and iodo-derivatives whilst phthalic, isophthalic and terephthalic acids are unaffected. Substituted benzoic acids, such as *p*-nitro-, *p*-chloro-, and *o*-bromobenzoic acids are also not halogenated.

EXPERIMENTAL.

The aromatic acid (5 g.), and iodine or bromine (5 g.) (with or without any solvent) are heated on a water-bath under reflux. The mixture of fuming nitric acid and nitrosulphonic acid (10 c.c.), obtained by passing sulphur dioxide through the fuming nitric acid till a mixture containing about 50 per cent. of nitrosulphonic acid is obtained, then dropped from the top of the condenser tube in quantities of 1 c.c. at a time in course of half an hour. Then the

whole of the acid mixture is heated on the water-bath for a further period of four hours. The product is cooled and poured into cold water (200 c.c.). The unchanged iodine or bromine is removed by washing with a dilute solution of sodium bisulphite and the solid thus separated is then filtered at the pump, washed thoroughly with cold water and then recrystallised from dilute acetic acid. The product thus obtained is found to melt sharply.

When sodium nitrite and fuming sulphuric acid are used in place of the nitrosulphonic acid mixture, the sodium nitrite is placed in the flask along with benzoic acid and bromine or iodine and the fuming sulphuric acid dropped through the condenser tube. The product is then worked up exactly as before. In the experiments in which bromine is used, the unchanged bromine is removed by heating the reaction product on a water-bath in a fume cupboard. The results obtained with different substances are summarised below.

TABLE I.

Substance.	Halogen.	Solvent.	Halogenating agent.	Product and yield.
Benzoic acid (5 g.)	Iodine (5 g.)	Carbon tetra-chloride (10 c.c.)	Nitrosulphonic acid mixture (10 c.c.), NaNO_2 (10 g.) and fuming H_2SO_4 (10 c.c.)	<i>m</i> -Iodobenzoic acid (5.7 g.; m.p. 186°). <i>m</i> -Iodobenzoic acid (5.2 g.; m.p. 186°).
"	"	"	"	<i>Nil</i> .
"	"	No solvent	Fuming HNO_3	<i>m</i> -Iodobenzoic acid (2.5 g.; m.p. 186°)
"	"	Carbon tetra-chloride (10 c.c.)	Fuming H_2SO_4	<i>Nil</i> .
Calcium benzoate (5 g.)	"	"	NaNO_2 (10 g.) and fuming H_2SO_4 (10 c.c.)	<i>m</i> -Iodobenzoic acid (2.0 g.; m.p. 186°).
Benzoic acid (5 g.)	Bromine (5 g.)	"	NaNO_2 (10 g.) and fuming H_2SO_4 (10 c.c.)	<i>m</i> -Bromobenzoic acid (4 g. m.p. 155°).
"	"	"	Nitrosulphonic acid mixture (10 c.c.)	<i>m</i> -Bromobenzoic acid (6.8 g.; m.p. 155°).
"	"	No solvent.	NaNO_2 (10 g.) and fuming H_2SO_4 (10 c.c.)	<i>m</i> -Bromobenzoic acid (2.5 g.; m.p. 155°).
<i>p</i> -Toluic acid (5 g.)	"	Carbon tetra-chloride (10 c.c.)	"	8-Bromo-4-methyl benzoic acid (3.0 g.; m.p. 204°).
"	Iodine (5 g.)	"	"	8-Iodo-4-methylbenzoic acid (3.0 g.; m.p. 206°).
<i>o</i> -Toluic acid (5 g.)	"	"	"	5-Iodo-2-methylbenzoic acid (1.7 g.; m.p. 178°).
"	Bromine (5 g.)	"	"	5-Bromo-2-methylbenzoic acid (2.5 g.; m.p. 167°).
Anisic acid (5 g.)	"	Glacial acetic acid	"	3-Bromoanisic acid (3.0 g.; m.p. 215°).
"	Iodine (5 g.)	"	"	3-Iodoanisic acid (2.5 g.; m.p. 192°).