33. *Examples of the Direct Iodination of Aromatic Compounds.*

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Examples are given of the direct iodination of aromatic liquids by treatment with iodine in the presence of silver sulphate dissolved in concentrated sulphuric acid. For the iodination of benzene the conditions for attaining optimum yields are indicated. Iodination of naphthalene has been effected by using its solutions in *cyclo*hexane, but when high concentrations of sulphuric acid are used αα′-dinaphthyl is also formed.

Derbyshire and Waters (*J.*, 1950, 3694) have recently indicated the practicability of iodinating aromatic compounds by means of iodine and silver sulphate in the presence of sulphuric acid, and exemplified their procedure by describing the direct *m*-iodination of benzoic acid. We now report the successful iodination of several aromatic liquids by the same method. The concentration of sulphuric acid used is of prime importance in determining the percentage yield of the iodinated product. As the sulphuric acid is diluted the yield drops, probably on account of increasing hydrolysis of the iodine to a

mixture of iodide and iodate, though to some extent the diminished solubility of the aromatic compound in the aqueous phase may be a contributory factor.

Conversely, if the sulphuric acid concentration is too high, then the yield of iodo-compound may be impaired owing to concurrent sulphonation or other side reactions. These factors have been made evident by a study of the iodination of benzene and of toluene. Chlorobenzene and iodobenzene, which are somewhat less reactive, are both iodinated in high yield without difficulty.

As already indicated, the iodination process is satisfactory for some *meta*-substituting compounds. It is successful with benzaldehyde, nitrobenzene, and *p*-nitrotoluene, but it fails with *m*-dinitrobenzene and 2 : 4-dinitrotoluene, even at 100°, though both the latter compounds can be brominated successfully by the analogous procedure (Derbyshire and Waters, *J.*, 1950, 564). This result can be expected since the iodine cation should be a less potent electrophilic substituting agent than the bromine cation.

When attempts were made to extend the method to the direct iodinations of solid aromatic compounds insoluble in water, it was found that acetic acid, which had been used for the bromination of benzoic acid, was not always a practicable co-solvent, since on warming it reacted itself with the iodinating reagent. For the direct iodination of naphthalene a two-phase system comprising a solution of silver sulphate in sulphuric acid and a solution of naphthalene in *cyclo*hexane has been used with some success. With such mixtures, best yields of α-iodonaphthalene were obtained by use of 50—60% sulphuric acid; for when the concentration of sulphuric acid was raised to 75—85%, αα′-dinaphthyl formed the main product, and with over 85% acid sulphonation of the naphthalene occurred extensively.

This may be due to oxidation by the silver salt since αα′-dinaphthyl can be obtained in small yield by stirring a *cyclo*hexane solution of naphthalene with 85% sulphuric acid and silver sulphate, though the addition of α-iodonaphthalene considerably increases the yield. In the absence of silver sulphate naphthalene is removed from *cyclo*hexane solution by 85% sulphuric acid on account of sulphonation without any concurrent formation of dinaphthyl.

From the preparative standpoint, the utility of this method of iodination should be assessed on the assumption that complete recovery of the silver salt is achieved, and fortunately the quantitative collection of silver in the form of silver halides presents no difficulty. Our work indicates, however, that predictable factors, such as solubilities in sulphuric acid and liability to hydrolysis and/or sulphonation, severely limit the applicability of this method of iodination to further aromatic compounds and consequently it is of much less general value than the corresponding bromination method.

Experimental

Iodination of Benzene.—In a 1-l. 3-necked flask, fitted with a thermometer and a water-sealed stirrer, benzene (23 g., 0·3 mole) was rapidly stirred into an emulsion with a solution of silver sulphate (31 g., 0·1 mole) in a mixture of concentrated sulphuric acid (200 c.c.) and water (20 c.c.). Finely powdered iodine (56 g., 0·22 mole) was added in portions during 2 hours. After a further hour's stirring the mixture was diluted with water (600 c.c.) and decanted through a filter from the solid residue of silver iodide and free iodine. This residue was stirred for some time with an excess of sodium sulphite solution and again separated. The solid and the liquid portion of the reaction product were then extracted separately with ether, and after drying and removal of free iodine (Na_2SO_3) the organic product was fractionated. The yield of iodobenzene, b. p. 188°, which was collected under reduced pressure, was 32 g. (78% calc. on the silver sulphate, 98% of which was directly recovered as silver iodide and the small remainder precipitated as the chloride).

Yields obtained under other conditions were as follows :

H_2SO_4, concn. by vol., %	95	90	50	25	2N-HNO_3
C_6H_5I, calc. on Ag_2SO_4, %	75	80	40	0	0

Iodination of Toluene.—Toluene (14 g., 0·15 mole) was stirred with a solution of silver sulphate (15·6 g., 0·05 mole) in sulphuric acid (100 c.c.) and water (20 c.c.), and iodine (28 g.,

0·11 mole) was added during 1½ hours. On working up as described above, 12 g. (55%) of yellow oil, b. p. 205—215°, were obtained, consisting of mixed *o*- and *p*-iodotoluene. From this, by oxidation with aqueous potassium permanganate, there was obtained *p*-iodobenzoic acid, m. p. 266° (Whitmore and Woodward, *Org. Synth.*, 1927, **7**, 58, give 266—267°).

A similar yield of iodotoluenes was obtained by using 60% sulphuric acid by volume, but acids of over 80% concentration gave little product since sulphonation was too rapid.

Iodination of Chlorobenzene.—This was carried out similarly on the 0·05-mole scale by using 80% sulphuric acid by volume and gave 72% of crude iodination products from which was separated, by crystallisation from alcohol, 60% of *p*-chloroiodobenzene of m. p. 54—55° (the m. p. being unchanged after admixture with an authentic specimen prepared from *p*-chloroaniline), together with a little oil, b. p. 233°, which was probably the *o*-isomer.

Iodination of Iodobenzene.—Procedure identical with that used for chlorobenzene yielded 75% of crude iodination products which on crystallisation gave 60% of *p*-di-iodobenzene, m. p. 130—131° (Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 293, give 129·4°), and a residual oil, b. p. 280°, containing the *o*-isomer.

Iodination of Benzaldehyde.—Freshly distilled benzaldehyde (25 g., 0·25 mole) was stirred rapidly with a solution of silver sulphate (0·05 mole) dissolved in 80% sulphuric acid (100 c.c. of concentrated acid plus 20 c.c. of water) in a flask immersed in a water-bath kept at 65—70°. Iodine powder (27 g., 0·105 mole) was added during 1½ hours and thereafter the stirring was continued for a further 1½ hours. From time to time the reaction vessel was shaken vigorously to dislodge iodine which had sublimed above the liquid. On working up as usual, 10·4 g. (45%) of crude solid product was obtained which after repeated crystallisation gave 7 g. of *m*-iodobenzaldehyde of m. p. 58° (Patterson, *J.*, 1896, **89**, 1002, gives 57°), from which were prepared the semicarbazone, m. p. 226° (Willgerodt and Rieke, *Ber.*, 1905, **38**, 1479, give 225—226°), and the phenylhydrazone, m. p. 156° (Patterson, *loc. cit.*, gives 155°).

Iodination of Nitrobenzene.—Nitrobenzene (18·5 g., 0·15 mole) was stirred at 100° with a solution of silver sulphate (0·05 mole) in a mixture of concentrated sulphuric acid (110 c.c.) and water (15 c.c.), and iodine powder (0·105 mole) was added gradually during an hour. After a further hour's heating with stirring and occasional vigorous shaking (see above), the mixture was cooled and diluted with water. The organic layer was separated and, after removal of the excess of nitrobenzene by distillation under reduced pressure, yielded 15 g. (60%) of an oil which remained solid after freezing. After crystallisation from alcohol it had m. p. 34—39°; subsequent chromatographic separation on alumina, with benzene–light petroleum as the eluent, gave pure *m*-iodonitrobenzene (14 g., 55%), m. p. 38—39° unchanged by admixture with an authentic specimen prepared from *m*-nitroaniline.

The reaction occurred more slowly at 80°, but the yield (13·9 g.) was almost the same; at 60° very little iodination occurred.

Iodination of p-*Nitrotoluene.*—This was carried out at 80° on the 0·05-mole scale by the method used for nitrobenzene. The solid product was steam-distilled to remove unchanged *p*-nitrotoluene, and the residue (yield 60%), m. p. 45—54°, was repeatedly crystallised from methanol, whereupon pure 2-iodo-4-nitrotoluene, m. p. 53—54°, was obtained (Found: I, 48·1, 48·2. Calc. for $C_7H_6O_2NI$: I, 48·2%) (Willgerodt and Kok, *Ber.*, 1908, **41**, 2077, give m. p. 58°).

Similar iodinations were attempted on a boiling water-bath with both *m*-dinitrobenzene and 2 : 4-dinitrotoluene, but in neither case did any reaction occur.

Iodination of Naphthalene.—(a) *With* 85% *sulphuric acid.* A solution of naphthalene (12·8 g., 0·1 mole) in *cyclo*hexane (130 c.c.) was stirred at room temperature with a solution of silver sulphate (0·05 mole) in a mixture of concentrated sulphuric acid (130 c.c.) and water (25 c.c.). Iodine powder (0·105 mole) was added during an hour and stirring was continued for a further hour. The reaction mixture was worked up as usual, and the organic portion on fractionation under reduced pressure gave, besides unchanged naphthalene, 1·7 g. of an oil, b. p. *ca.* 300°/1 atm., and 4 g. of a solid residue which could be sublimed. 1·1 G. of this residue were dissolved in light petroleum and chromatographed on alumina with benzene–light petroleum mixtures. It yielded 1·1 g. of pure αα′-dinaphthyl, m. p. (and mixed m. p. with an authentic specimen) 157—158° (Willgerodt and Schlosser, *Ber.*, 1900, **33**, 698, give 158·5°). Similar material was obtained by sublimation. The oil when treated in alcohol with picric acid yielded the solid yellow picrate, m. p. 127·5°, of α-iodonaphthalene (Roux, *Bull. Soc. chim.*, 1886, **45**, 517, gives 127°).

(b) *With* 50% *sulphuric acid.* A reaction carried out on the above scale, but with 250 c.c. each of concentrated sulphuric acid and water, gave 8·6 g. (34%) of α-iodonaphthalene and

only 0·8 g. of tarry residue which after crystallisation from alcohol had m. p. 98—104° and contained iodine. Other mixtures gave the following yields :

H_2SO_4, % by vol.	85	75	60	50
α-Iodonaphthalene, %	6·7	3·1	32	34
αα′-Dinaphthyl, %	34·5	33·5	0	0

Reaction between Naphthalene and α-Iodonaphthalene.—Silver sulphate (4·5 g.) dissolved in a mixture of sulphuric acid (85 c.c.) and water (15 c.c.) was stirred for 1½ hours with a solution of naphthalene (10 g.) and α-iodonaphthalene (6·4 g.) in *cyclo*hexane (80 c.c.), during which time it gradually became black. The organic material was then separated and steam-distilled to remove the excess of naphthalene, and the residue was fractionated under reduced pressure. There were obtained 1·4 g. of a dark solid which on chromatographic purification yielded 1·09 g. of αα′-dinaphthyl, m. p. and mixed m. p. 157—158°.

In a similar experiment in which a solution of 10 g. of naphthalene in 100 c.c. of *cyclo*hexane was stirred with a solution of 8 g. of silver sulphate in 85 c.c. of sulphuric acid and 15 c.c. of water there was obtained 0·37 g. of αα′-dinaphthyl. When no silver sulphate was present an identical reaction mixture, after 1½ hours' stirring, contained only 5·5 g. of naphthalene and left no residue after steam-distillation. When a mixture of 90 c.c. of sulphuric acid and 10 c.c. of water was used as the solvent, the whole of the naphthalene originally present in a similar *cyclo*hexane solution was removed during 2 hours' stirring at room temperature, forming sulphonic acids which dissolved in the aqueous layer.

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