The Iodination of Aromatic Compounds with Iodine in 20% Oleum

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PREVIOUS reports[1] of the iodination of aromatic compounds with iodine in oleum have been concerned with iodine in 50—65% oleum in which the electrophile is probably[2] the cation I_2^+. This reagent will polyiodinate benzene derivatives containing two deactivating groups but partial iodination under controlled conditions is difficult, as the reaction mixture has to be heated to remove much of the sulphur trioxide before dilution and isolation.

We have found iodine in 20% oleum at room temperature, in which the major electrophilic species has been shown[3] to be the cation I_3^+, to be a convenient reagent for the iodination of benzene derivatives containing a single deactivating substituent, as it generally produces a single product in reasonable yield. Benzene derivatives with two deactivating substituents are not iodinated.

The experimental procedure for both the preparation and the isolation is straightforward and the method can yield otherwise difficultly accessible compounds in a single step. In a typical experiment the aromatic compound (1 equivalent) was added to a solution (0·4 molal) of iodine (3 equivalents) in 20% oleum and the mixture was stirred at room temperature in a closed system for 24 hr. The mixture was poured on to crushed ice, the excess of iodine was removed by passing sulphur dioxide, and the crude iodo-compound was purified.

Our results are summarised in the Table. In cases 1—6 the melting points of the products and of suitable derivatives agree with those previously reported. In cases 7—10 the structures assigned are consistent with the analytical evidence, with the infrared and proton magnetic resonance spectra, and with theories of chemical reactivity. These structures are at present being confirmed by suitable chemical transformations.

TABLE

	Starting material	Product	Yield %	m.p.
1.	Nitrobenzene	*m*-Iodonitrobenzene	52	37—38°
2.	Benzoic acid	*m*-Iodobenzoic acid	76	183—184
3.	Benzaldehyde	*m*-Iodobenzaldehyde	44	55—56
4.	Benzamide	*m*-Iodobenzamide	73	185—186
5.	*p*-Nitrotoluene	2,6-Di-iodo-4-nitrotoluene	47	117—118
6.	*m*-Nitrotoluene	2,3-Di-iodo-5-nitrotoluene	28	144—145
7.	*o*-Nitrotoluene	4,6-Di-iodo-2-nitrotoluene	43	66— 67
8.	*p*-Toluic acid	3,5-Di-iodo-4-methylbenzoic acid	70	334—335
9.	*m*-Toluic acid	4,5-Di-iodo-3-methylbenzoic acid	85	238—240
10.	*o*-Toluic acid	3,5-Di-iodo-2-methylbenzoic acid	43	223—225

m-Dinitrobenzene, *m*-nitrobenzoic acid, isophthalic acid, and 2,4-dinitrotoluene did not react and were recovered in high yield.

The products obtained by heating these reaction mixtures are also under investigation.

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[1] For pertinent references see A. Roedig "Houben-Weyl, Methoden der Organischen Chemie", George Thieme Verlag, Stuttgart, Fourth edition, 1960, Vol. 5/4, p. 574.

[2] R. J. Gillespie and J. B. Milne, *Chem. Comm.*, 1966, 158.

[3] M. C. R. Symons, *J. Chem. Soc.*, 1957, 2186; J. Arotsky, H. C. Mishra, and M. C. R. Symons, *ibid.*, 1961, 12.