A Convenient Synthetic Method of Certain Aromatic Polyiodo Compounds

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Aromatic polyiodo compounds are usually prepared from the corresponding amines by the lengthy, laborious procedures involving acetylation, nitration, diazotization and reduction. Nevertheless, the authors have found it possible to prepare certain types of polyiodo compounds directly from the readily available, simpler iodo compounds.

This method is based on the migration, in the presence of sulfuric acid, of iodine atoms present in the nucleous of aromatic iodo compound (Jacobsen reaction[1]). The procedure is quite simple and needs only to agitate the starting materials with suitable amount of sulfuric acid for some hours followed by chromatographic separation of the products on an alumina column. The products are sufficiently in high state of purity. Although the yields are, in some cases, not so high by the usual standards, the easy availability of starting materials and the simplicity of the procedure recommend this method over any others previously employed.

Present method is expecially attractive to the synthesis of symmetrically substituted or fully iodinated compounds.

Table I presents the compounds prepared by the authors with the aid of this method. Some examples will demonstrate the ease and mode of preparation.

Experimental

2, 5-Diiodo-*p*-xylene.—A mixture of 17.4 g. of 2-iodo-*p*-xylene and 30 g. of sulfuric acid was agitated vigorously with a magnetic stirrer while the temperature of the reaction mixture was held at 50~55°C for 4 hr. After cooling, the reaction mixture was poured into ice water, and the precipitated crystalline solid was filtered off. Recrystallization from petroleum benzine gave 4.2 g. of white needles, m. p. 103~104°C[2]. Mixed melting point with an authentic specimen showed no depression.

2,4-Diiodotoluene and 2,4,5-Triiodotoluene[3,4].—A mixture of 19.1 g. of *p*-iodotoluene and 35 g. of sulfuric acid was magnetically agitated and heated to 50~60°C for 6 hr. The reaction mixture was poured into ice water and the oily material was removed by ether extraction. The ethereal solution was evaporated and the residual oil was chromatographed on an alumina column with petroleum benzine (b. p. 65~70°C). Each 20 ml. fraction was collected and evaporated. 2, 4-Diiodotoluene and 2, 4, 5-triiodotoluene appeared, respectively, in the early and late fractions. 2, 4-Diiodotoluene weighed 4.9 g., b. p. 115~117°/1 mmHg. 2, 4, 5-Triiodotoluene, recrystallized from ethanol to separate as white needles, weighed 3.4 g. and melted at 119~120°C. Admixture with a sepecimen prepared from *m*-toluidine showed no depression.

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[1] L. I. Smith, "Organic Reactions", Vol. I, 370 (1942).

[2] P. S. Varma and K. S. V. Raman, *J. Indian Chem. Soc.*, **12**, 343 (1935).

[3] G. S. Neumann, *Ann.*, **241**, 33 (1887).

[4] H. L. Wheeler, *Am. Chem. J.*, **44**, 126, 493 (1910).

TABLE I

Iodo compounds	Sulfuric acid (moles per mole iodo compound)	Experimental condition	Product	M. p. or B. p. °C	Yield %	Iodine, % Found	Iodine, % Calcd.
Iodobenzene	4	6 hr. at 95~100°C	*p*-Diiodobenzene	128	11**	76.90	76.94
			1, 2, 4-Triiodobenzene	92	~ 5	83.37	83.53
p-Diiodobenzene	8	6 hr. at 120~130°C	1, 2, 4-Triiodobenzene[7]	92	15**	83.70	83.53
			1, 2, 4, 5-Tetraiodobenzene	253	26	87.51	87.27
o-Iodotoluene	4	6 hr. at 100~110°C	2, 4-Diiodotoluene	117/1 mmHg	14**		
			2, 4, 5-Triiodotoluene	120	26		
p-Iodotoluene	4	6 hr. at 50~60°C	**2, 4-Diiodotoluene*** **	117/1 mmHg	33**	73.79	73.79
			2, 4, 5-Triiodotoluene	120	25	81.07	81.04
p-Iodotoluene	4	6 hr. at 100~110°C	2, 4-Diiodotoluene	117/1 mmHg	11**		
			2, 4, 5-Triiodotoluene	120	28		
o-Iodoethylbenzene	4	6 hr. at 90~100°C	2, 4-Diiodoethylbenzene[8]	130/3 mmHg	~ 5**		
			2, 4, 5-Triiodoethylbenzene	74	24	78.72	78.68
p-Iodoethylbenzene	4	6 hr. at 50~55°C	2, 4-Diiodoethylbenzene	130/3 mmHg	53**	70.77	70.90
			2, 4, 5-Triiodoethylbenzene	74	~ 5		
p-Iodoethylbenzene	4	6 hr. at 90~100°C	2, 4-Diiodoethylbenzene	130/3 mmHg	~ 5**		
			2, 4, 5-Triiodoethylbenzene	74	15		
4-Iodo-*o*-xylene	4	4 hr. at 50~55°C	4, 5-Diiodo-*o*-xylene	90	38	70.77	70.90
4-Iodo-*m*-xylene	4	4 hr. at 70~80°C	4, 6-Diiodo-*m*-xylene	72	42	70.53	70.90
5-Iodo-*m*-xylene	4	4 hr. at 70~80°C	2, 5-Diiodo-*m*-xylene	75	39	70.92	70.90
2-Iodo-*p*-xylene	4	4 hr. at 50~55°C	**2, 5-Diiodo-*p*-xylene**	104	32	70.82	70.90
4, 5-Diiodo-*o*-xylene	10	4 hr. at 70~80°C	3, 4, 5, 6-Tetraiodo-*o*-xylene	129	72	81.13	83.25
4, 6-Diiodo-*m*-xylene	10	4 hr. at 70~80°C	**2, 4, 5, 6-Tetraiodo-*m*-xylene**	127	75	82.84	83.25
2, 5-Diiodo-*p*-xylene	10	4 hr. at 65~75°C	2, 3, 5, 6-Tetraiodo-*p*-xylene	247	59	83.33	83.25
5-Iodohemimellitene	4	4 hr. at 55~65°C	Diiodohemimellitene	114	27	68.24	68.23
Iodomesitylene	4	4 hr. at 60~65°C	Diiodomesitylene[9]	82	74	68.37	68.23
2, 4-Diiodotoluene	4	6 hr. at 90~100°C	2, 4, 5-Triiodotoluene	119	65		
2, 5-Diiodotoluene	4	6 hr. at 100~110°C	2, 4, 5-Triiodotoluene	119	42		
3, 4-Diiodotoluene	4	6 hr. at 100~110°C	2, 4, 5-Triiodotoluene	119	55		
3, 4, 5-Triiodotoluene	5	6 hr. at 90~100°C	2, 3, 5-Triiodotoluene	68	56	81.06	81.04
2, 3, 5-Triiodotoluene	15	6 hr. at 120~130°C	2, 3, 4, 5-Tetraiodotoluene[8]	189	74	85.42	85.21
2, 3, 6-Triiodotoluene	15	6 hr. at 120~130°C	2, 3, 4, 6-Tetraiodotoluene	171	42	85.45	85.21
o-Iodoanisol	2	6 hr. at 20~25°C	2, 4-Diiodoanisol	69	76	70.73	70.52
p-Iodoanisol	2	6 hr. at 20~25°C	**2, 4-Diiodoanisol**	69	75		
o-Iodophenol	2	6 hr. at 20~25°C	2, 4-Diiodophenol	72	59	73.51	73.39
p-Iodophenol	2	6 hr. at 20~25°C	2, 4-Diiodophenol	72	~40**		
p-Iodophenol	4	6 hr. at 20~25°C	2, 4, 6-Triiodophenol	158	~20	80.19	80.70

* Yields based on iodine are not necessarily the best obtainable.

** It is possible to obtain either one of products by proper choice of the experimental conditions.

*** Reaction products in gothic are given as examples in the experimental.

2, 4, 5, 6-Tetraiodo-*m*-xylene[5]. — A mixture of 3.6 g. of 4,6-diiodo-*m*-xylene and 10 g. of sulfuric acid was agitated and heated gradually to 70~80°C. The reaction mixture was kept at this temperature for 4 hr., and then poured over crushed ice. The solid material precipitated was filtered and dissolved in the minimum quantity of cold benzene. Chromatography through a short column packed with alumina gave 2.3 g. of fine, white needles melting at 126~127°C.

2, 4-Diiodoanisol[6].—A mixture of 11.7 g. of *p*-iodoanisol and 10 g. of sulfuric acid was stirred at room temperature for 6 hr. The resulting thick mixture was poured into excess water, and the precipitated dark oil was extracted with ether. The ethereal solution was evaporated and the residual oil was chromatographed on alumina. Elution with ether followed by recrystallization from hot petroleum benzine gave colorless large plates of 2,4-diiodoanisol in 70~75% yield, melting point alone or in admixture with an authentic specimen 68~69°C.

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5) A. Töhl and E. Bauch, *Ber.*, **26**, 1105 (1893).
6) P. Brenans, *Compt. rend.*, **132**, 831 (1901).
7) M. Boyle, *J. Chem. Soc.*, **95**, 1683 (1909).
8) H. Suzuki and R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 167, 284 (1963).
9) A. Töhl and R. Eckel, *Ber.*, **26**, 1099 (1893).