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STUDIES ON THE IODINATION OF AROMATIC COMPOUNDS BY A MIXTURE OF PEROXYACETIC ACID AND IODINE

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Abstract—The iodination of aromatic compounds by a mixture of peroxyacetic acid and iodine in an acetic acid solution has been studied with a special interest concerning effects of acidity, temperature and the nature of peroxy acid. The addition of sulfuric acid catalyst to the reaction system increased the yield of the corresponding iodinated compound with benzene, halobenzene and benzoic acid, while it decreased the yield with alkylbenzenes. The benzenes having electron-releasing groups and naphthalene are iodinated more satisfactorily with lower temperature and without sulphuric acid catalyst. The use of peroxybenzoic acid instead of peroxyacetic acid gives an unsatisfactory result, which suggests that acetyl hypoiodite is an attacking species.

IT HAS previously been reported that the iodination of aromatic compounds is possible in an homogeneous system by the introduction of an acetic acid solution of peroxyacetic acid to a solution of iodine and aromatic compounds.[1] The over-all rate of the reaction was found to be determined by the rate of reaction of iodine with peroxyacetic acid and to be independent of the concentration of benzene or the acidity of solution.[1] The attacking species may be hypoiodous acid or acetyl hypoiodite. The present study was undertaken to obtain more information on the attacking species, to examine the effect of acidity on the iodination and also to improve the yield.

RESULTS AND DISCUSSION

Although the rate of the consumption of peroxyacetic acid in the mixture of benzene and iodine was independent of the acidity of the solution,[1] the yield of the iodobenzene was increased by the addition of sulfuric acid to the reaction mixture. The data are listed in Table 1. Therefore, the iodinating species may be protonated.

TABLE 1. IODINATION OF BENZENE BY THE ADDITION OF SULPHURIC ACID AT 70°

Benzene mole	Iodine mole	Peroxyacetic acid mole	Sulphuric acid mole	$[H_2SO_4]/[I_2]$ molar ratio	Reaction time min	Yield %
1·36	0·106	0·196	—	0	230	60·9
1·29	0·106	0·175	0·050	0·48	230	75·0
1·29	0·0787	0·168	0·097	1·23	160	77·3

For the examination of the effect of acetic acid, peroxybenzoic acid was employed instead of peroxyacetic acid, and the solvent was changed to chloroform in place of acetic acid. The attempted iodination of benzene by this reaction mixture at 60° for 270 min was unsuccessful (Table 2). The main product was iodic acid accompanied

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[1] Y. Ogata and K. Nakajima, *Tetrahedron* **20,** 43 (1964).

by a trace of iodobenzene (1–5 %) which was confirmed by gas chromatography. The addition of acetic acid to the reaction mixture of peroxybenzoic acid increased the yield, e.g., the yield was 0·88 % with molar ratio of acetic acid vs. iodine of 1·4, while the yield increased to 5 % with the molar ratio of 11. Therefore, peroxyacetic acid seems to play an important role in the present reaction owing to the formation of acetyl hypoiodite.

TABLE 2. IODINATION OF BENZENE BY A CHLOROFORM SOLUTION OF PEROXYBENZOIC ACID AT 60° FOR 270 MIN

Benzene mole	Iodine mole	Peroxybenzoic acid mole	Acetic acid mole	$[CH_3CO_2H]/[I_2]$ molar ratio	Yield %
0·641	0·0473	0·104	—	0	1·3
0·641	0·0473	0·0891	0·067	1·4	0·88
0·641	0·0473	0·0972	0·25	5·3	2·1
0·641	0·0473	0·107	0·50	11	5·0

The increase in yield of iodobenzene by the addition of mineral acid implies a mechanism involving protonated acetyl hypoiodite as an attacking species.

$$I_2 + CH_3CO_3H + H_2O \xrightarrow{\text{slow}} 2HIO + CH_3CO_2H$$
$$HIO + CH_3CO_2H + H^+ \underset{}{\overset{\text{fast}}{\rightleftarrows}} (CH_3CO_2HI)^+ + H_2O$$
$$(CH_3CO_2HI)^+ + ArH \xrightarrow{\text{fast}} ArI + CH_3CO_2H + H^+$$
$$HIO + 2CH_3CO_3H \longrightarrow HIO_3 + 2CH_3CO_2H$$

The formation of a trace of iodobenzene with an anhydrous solution of peroxybenzoic acid suggests that iodine oxide (I_2O) is another probable but weak attacking species.

The similar procedure may be applied to a number of aromatic compounds (Table 3). The compounds having electron-attracting groups, e.g., benzoic acid, gave poor yield by the previously reported method,[1] but the addition of sulfuric acid to the system increased the yield. On the other hand, aromatic compounds having electron-releasing groups, on addition of sulfuric acid, gave less satisfactory results probably because of the further reaction of the product; hence, it is recommended that the reaction of these active compounds is carried out under milder and less acidic conditions.

TABLE 3. IODINATION OF AROMATIC COMPOUNDS WITH A MIXTURE OF PEROXYACETIC ACID AND IODINE

Substrate	(mole)	Iodine mole	Peroxyacetic acid mole	Sulphuric acid mole	Temp °C	Time min	Yield %	Product
Toluene	(1·09)	0·0787	0·102	0·0485	70	87	65·6	*o*-and *p*-Iodotoluenes
	(1·10)	0·0865	0·143	—	60	120	84·6[1]	
m-Xylene	(0·940)	0·0787	0·143	0·0485	70	120	54·4	4-Iodo-*m*-xylene
	(0·255)	0·0393	0·0560	—	60	75	74·4	
Cumene	(0·841)	0·0787	0·187	—	60	169	59·5	*p*-Iodocumene
Anisole	(0·237)	0·0393	0·0649	—	50	105	74·5	*p*-Iodoanisole
Naphthalene	(0·117)	0·0393	0·212	—	70	330	56·1	1-Iodonaphthalene
	(0·195)	0·0393	0·0750	—	60	185	59·0	
Chlorobenzene	(0·955)	0·0787	0·116	0·0485	70	96	40·9	*p*-Chloroiodobenzene
Bromobenzene	(0·318)	0·0787	0·178	0·0485	80	205	35·5	*p*-Bromoidobenzene
Benzoic acid	(0·165)	0·0393	0·292	0·0485	80	205	35·5	*m*-Iodobenzoic acid
	(0·262)	0·0985	0·262	—	90	240	0[1]	

An attempt for the identification of acetyl hypoiodite at room temperature by spectrophotometry failed, since a solvent, acetic acid, had a strong absorption below 250 mμ. Although the measurement was undertaken by means of a 9 mm cell spacer, no new absorption of the attacking species could be observed.

EXPERIMENTAL

Materials. The peroxyacetic acid used (1·3–1·5 M) was prepared by the reaction of 30% H_2O_2aq (40 g) containing conc. H_2SO_4 (1–2 g) with acetic anhydride (180 g) and stored in a refrigerator. The content of peroxyacetic acid was determined iodometrically before use. The other materials were commercial and purified by fractional distillation or recrystallization and their b.ps for liquids or m.ps for solids agreed with those given in the literature. Benzene (b.p. 80·1°), toluene (b.p. 110·5°), *m*-xylene (b.p. 138–139°), cumene (b.p. 152°), anisole (b.p. 156°), naphthalene (m.p. 80·5°), chlorobenzene (b.p. 132°), bromobenzene (b.p. 156°), and benzoic acid (m.p. 122·5°).

Iodination of benzene. An acetic acid solution of 1·40 M peroxyacetic acid (122 ml, 0·168 mole) was added dropwise with stirring to a mixture of iodine (20·0 g, 0·0187 mole), benzene (100 g, 1·29 mole) and 98% H_2SO_4 (10 g, 0·097 mole) at 70° for 160 min. After the reaction, the colourless solution was diluted to 1 l. with water. The oily layer was separated, washed with an aqueous solution containing KI and $Na_2S_2O_3$ dried with $CaCl_2$ and distilled. Iodobenzene (24·9 g; 77·3%), b.p. 182–185°, n_D^{25} 1·6165 was obtained and identified by nitration and the mixed m.p. determination with *p*-nitroiodobenzene (m.p. and m.m.p. 176°).

Attempted iodination of benzene with a mixture of peroxybenzoic acid and iodine was listed in Table 2. The product, after the similar work-up, was concentrated as a choroform solution and analysed by a Yanagimoto Model GCG-220 gas chromatograph operated with a 2 m column packed with firebrick (40–60 mesh) containing 5% PEG # 4000, or operated with 1·3 m. column packed with celite 545 (80–90 mesh) containing silicone DC 703 using a flow rate of 35 ml He per min at 140°. The quantitative determinations were made using bromobenzene as an internal standard.

Iodination of toluene. The iodination of toluene without H_2SO_4 at lower temp gave a higher yield of iodotoluenes (84·6%). The IR spectrum of the product, b.p. 203–210°, showed characteristic absorption of *p*-iodotoluene (790 cm^{-1}) and *o*-iodotoluene (745 cm^{-1}), but no absorption corresponding to *m*-iodotoluene and benzyl iodide. On cooling the product with a dry ice–ethanol solution *p*-iodotoluene, m.p. 33·8° (lit.[2] m.p. 35°) was obtained. Distillation of the mother liquor gave *o*-iodotoluene, b.p. 204–205° (lit.[3] b.p. 204°).

Iodination of m-*xylene*. *m*-Xylene gave on iodination at 60° without acid catalyst 29·0 g (74·4%) 1,3-dimethyl-4-iodobenzene, b.p. 111–112° (13·5 mm), lit.[4] b.p. 111° (14 mm). The IR spectrum showed characteristic maxima at 800 cm^{-1} in the out-of-plane vibration region of C—H bond and at 1010, 1030, 1140, 1170, 1230 and 1270 cm^{-1} in the in-plane vibration region of C—H bond. These maxima and the absorption pattern in the range from 1900 to 1700 cm^{-1} suggests 1,2,4-substitution in a benzene ring.

Iodination of cumene. Cumene on iodination at 60° without acid catalyst gave 23·1 g (59·5%) *p*-iodocumene, b.p. 113–114° (13·5 mm), lit.[5] 112–113° (13 mm). The IR spectrum showed strong maxima at 3000, 1490, 1010 and 810 cm^{-1}. The maximum at 810 cm^{-1} in the out-of-plane vibration region of C—H bond and the absorption pattern in the range from 1900 to 1700 cm^{-1} may suggest 1,4-substitution of benzene ring.

Iodination of anisole. The iodination of anisole at 50° without acid catalyst gave 13·7 g (74·5%) *p*-iodoanisole, m.p. 49·5–50·0° (lit.[5] m.p. 51–52°). The IR spectrum (nujol) showed principal bands at 1490, 1040, 1030, 1000 and 820 cm^{-1} for benzene ring and C—H bond, and also at 1290, 1250 and 1170 cm^{-1} for C—O—C bond. The maximum at 820 cm^{-1} suggests 1,4-substitution in a benzene ring.

Iodination of naphthalene. The iodination of naphthalene at 60° without acid catalyst in a CCl_4 gave 1-iodonaphthalene, b.p. 160–162° (15 mm), lit.[6] b.p. 161–162° (15 mm). The IR spectra showed sharp maxima at 3100, 1660, 1560, 1500, 1250, 1200, 1130, 1020, 940, 780 and 750 cm^{-1}. The very

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[3] R. Elbs and A. Jaroslawzew, *J. Prakt. Chem.* [2] **88**, 92 (1913).

[4] K. v. Auwers, *Liebig's Ann.* **422**, 161 (1921).

[5] H. O. Wirth, O. Königstein and W. Kern, *Liebig's Ann.* **634**, 84 (1960).

[6] F. Krollpfeiffer, *Liebig's Ann.* **430**, 198 (1923).

strong maxima at 780 and 750 cm^{-1} indicate adjacent three and four hydrogen atoms of C—H bonds, which correspond to 1-substitution in a naphthalene ring.

Iodination of halobenzenes. Chloroiodobenzene, m.p. 54·5° (lit.[6] m.p. 55–55·5°). The IR spectrum (nujol) showed a simple pattern having maxima at 1090, 1060, 1010 and 810 cm^{-1}. These maxima suggest 1,4-substitution in a benzene ring.

Similarly, bromobenzene gave *p*-bromoiodobenzene, m.p. 90·0° (lit.[5] m.p. 91°). The IR spectrum (nujol) showed a similar pattern having maxima at 1100, 1090, 1070, 1000 and 800 cm^{-1}. These maxima suggest 1,4-substitution in a benzene ring.

Iodination of benzoic acid. The iodination of benzoic acid in acetic acid gave *m*-iodobenzoic acid, m.p. 186–187° (lit.[7] m.p. 185–186°). The UV absorption spectrum in methanol showed a maximum at 286 mμ ($\log \varepsilon = 3{\cdot}96$) (lit.[8] 284 m$\mu$, $\log \varepsilon = 3{\cdot}98$) in ethanol.

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[8] W. F. Forbes and M. B. Sheratte, *Canad. J. Chem.* **33**, 1829 (1955).