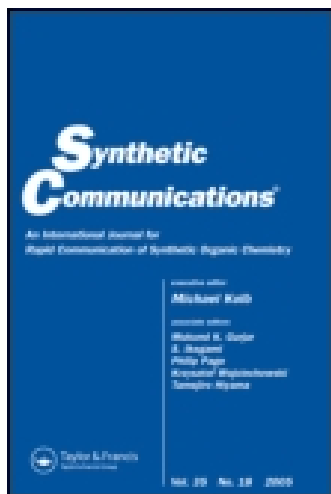


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Acid-Catalysed Selective Monoiodination of Electron-Rich Arenes by Alkali Metal Iodides

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Acid-Catalysed Selective Monoiodination of Electron-Rich Arenes by Alkali Metal Iodides

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ABSTRACT

The reaction of electron-rich arenes with alkali metal iodides such as sodium and potassium iodides in the presence of conc. H₂SO₄ gives *p*-iodoarenes in high yields.

Key Words: Iodination; Arenes; Sodium iodide; Potassium iodide; Conc. H₂SO₄.

INTRODUCTION

Iodination of organic compounds and the chemistry of organic iodides are of interest as major chemical fields. Their industrial application is wide.^[1]

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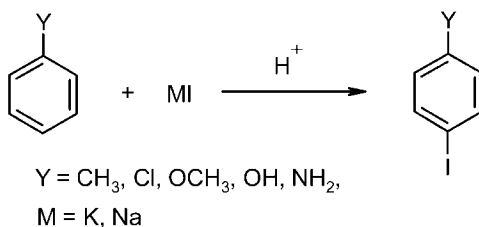
Iodination is one of the classical reactions of aromatic compounds and has been thoroughly investigated for both its theoretical and synthetic value. The iodination reactions of aromatic structures have generated a wealth of physico-organic data that define the structure–reactivity relationships and the steric and electronic factors that control this system.^[2] Aromatic iodo compounds are useful for the preparation of organometallic reagents and some are potential intermediates for the synthesis of pharmaceutical and bioactive materials. They are also useful in metal catalysed coupling reactions which are widely applied in the preparation of complex molecules.^[3]

Since the iodine molecule is the least reactive among the halogens toward an electrophilic substitution process, most of the synthetic effort has been placed in converting molecular iodine into a more active species.^[4] Aromatic compounds iodinated can be generally by iodine only in the presence of a Lewis acid, a hydrogen iodide trap, or most commonly in the presence of an oxidizing agent.^[5]

The reagents reported for iodination of aromatic compounds include use of *N*-iodosuccinimide (NIS),^[6] I_2/Ag_2SO_4 ,^[7] I_2/Cr_2O_3 ,^[8] $I_2/Pb(OAc)_2$,^[9] $I_2/TIOAc$,^[10] $I_2/KI/Hg(OAc)_2$,^[11] $NaOCl/NaI$ in aqueous alcohol medium,^[12] NaI /chloramine-T in methanol,^[13] and KI/HIO_4 in H_2SO_4 .^[14] Most of these reagents are complex, costly or involve toxic heavy metal catalysts with potential environmental problems due to the generation of hazardous waste. In this paper, we wish to report an efficient, new environmentally benign procedure for aromatic iodination.

Owing to the various synthetic utilities of aromatic halo compounds, an attempt has been made in our laboratory to synthesize *p*-haloarenes from tetraalkylammonium halides in the presence of conc. H_2SO_4 in high yields.^[15] To extend this reaction, we believe that alkali metal iodides can serve as iodinating agents. We carried out the reaction of aromatic hydrocarbons with alkali metal iodides such as sodium and potassium iodides in the presence of conc. H_2SO_4 and it was found that, iodination of arenes is possible with alkali metal iodides (Sch. 1).

The reaction of chlorobenzene and alkali metal iodides (NaI or KI) was carried out at different reaction temperatures ($25^\circ C$, $40^\circ C$, $60^\circ C$, $80^\circ C$,



Scheme 1.

100°C, and 120°C) in the presence of conc. H₂SO₄. The reaction goes to completion within 1.5 hr at 60°C and *p*-chloriodobenzene can be obtained in high yields.

To generalise the iodination reaction of arenes, different substituted aromatic hydrocarbons were chosen and the reaction was carried out under similar reaction conditions (Table 1). From the table it is clear that, except anisole, other arenes give iodination successfully in high yields.

Hot sulphuric acid is known to decompose sodium and potassium halides with evolution of halogen molecule as shown below.^[16] Iodine thus formed reacts with arenes to give rise to iodoarenes as shown in Sch. 2.

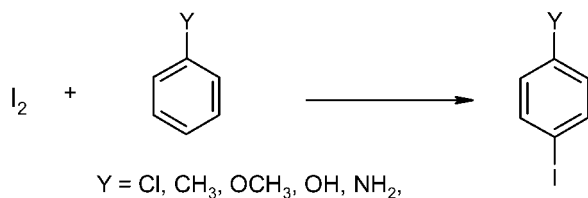
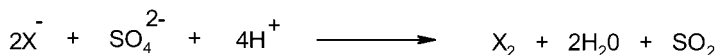
In summary, a novel approach to iodination of arenes using alkali metal iodides and conc. H₂SO₄ has been described.

EXPERIMENTAL

Nicolet 400D FT-IR spectrophotometer was used for IR spectral analysis and NMR spectra were recorded on a JEOL 90 FQ, Bruker AC 250 instrument. Yields refer to the isolated yields of the products.

Table 1. Reaction of different substituted arenes with alkali metal iodides in the presence of conc. H₂SO₄ at 60°C.

Entry	Substrate	Metal halide	Product	Yield (%)
1	Chlorobenzene	NaI	<i>p</i> -Chloriodobenzene	84
2	Chlorobenzene	KI	<i>p</i> -Chloriodobenzene	87
3	Toluene	NaI	<i>p</i> -Iodotoluene	76
4	Toluene	KI	<i>p</i> -Iodotoluene	78
5	Anisole	NaI	i) <i>p</i> -Iodoanisole ii) <i>p</i> -Iodophenol	59 19
6	Anisole	KI	i) <i>p</i> -Iodoanisole ii) <i>p</i> -Iodophenol	67 18
7	Phenol	NaI	<i>p</i> -Iodophenol	81
8	Phenol	KI	<i>p</i> -Iodophenol	79
9	Aniline	NaI	<i>p</i> -Iodoaniline	80
10	Aniline	KI	<i>p</i> -Iodoaniline	82
11	<i>o</i> -Cresol	NaI	4-Iodo-2-methylphenol	75
12	<i>o</i> -Cresol	KI	4-Iodo-2-methylphenol	77
13	Naphthalene	NaI	1-Iodonaphthalene	74
14	Naphthalene	KI	1-Iodonaphthalene	75
15	2-Naphthol	NaI	1-Iodo-2-naphthol	86
16	2-Naphthol	KI	1-Iodo-2-naphthol	83



Scheme 2.

Iodination of Arenes: General Procedure

Chlorobenzene (1.125 g, 10 mmol) and sodium iodide (3.0 g, 20 mmol) were added to conc. H₂SO₄ (1.96 g, 20 mmol) and then heated at 60°C. The reaction was monitored by TLC (light petroleum). After completion of the reaction (1.5 hr), water (10 mL) was added and extracted with ether (3 × 10 mL). The combined ethereal extract was washed with saturated sodium bicarbonate solution, water, and dried over anhydrous sodium sulphate. Solvent was removed, the residue purified on silica gel using pentane to give *p*-chloriodobenzene (1.72 g, 90%), m.p. 54°C (lit. m.p. 56°C^[17]).

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