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PREPARATION OF AROMATIC IODIDES FROM BROMIDES
VIA THE REVERSE HALOGEN EXCHANGE

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Aromatic bromides undergo halogen exchange reaction with iodide ion in the presence of copper(I) iodide in hot hexamethylphosphoric triamide, to give the corresponding iodides in good to moderate yields.

Although the halogen exchange reactions are widely used for the preparation of aliphatic iodides from the corresponding chlorides and bromides, the aromatic counterparts have seldom been synthesized for practical purposes from aryl chlorides and bromides, due to the inertness of the latter toward the nucleophilic attack of iodide ion. Unless being activated by electron-withdrawing substituents, aryl halides do not undergo halogen exchange even after prolonged heating in aprotic dipolar solvents at high temperatures. Copper(I) chloride and bromide have been long known as efficient reagents to effect halogen exchange of aromatic halides.^{1,2)} With these copper(I) reagents, however, the direction of feasible halogen exchange is from iodides to bromides to chlorides, and the reaction does not proceed in the opposite direction. Thus copper(I) iodide is ineffective for such a purpose. The photo-stimulated halogen exchange reactions also follow the same order of reactivity.³⁻⁵⁾

During the course of our studies on the copper(I)-promoted nucleophilic aromatic substitutions, we have found that a combination of potassium iodide, copper(I) iodide and hexamethylphosphoric triamide (HMPA) can bring about halogen exchange of nonactivated aromatic halides in the reverse sense. Thus, when aryl bromides 1 is heated with excess of potassium iodide and copper(I) iodide in HMPA at 150-160 °C for appropriate hours, bromine atom is replaced by iodine atom to give the corresponding aryl iodides 2 in 60-80% yields (Table 1). Use of large excess of potassium iodide and copper(I) salt is indispensable to accomplish high conversion. The reaction proceeds cleanly, with no appreciable amounts of side-products being formed. Steric crowding around the reaction site does not seem to work unfavorably toward the displacement of bromine atom. Without copper(I) catalyst, no halogen

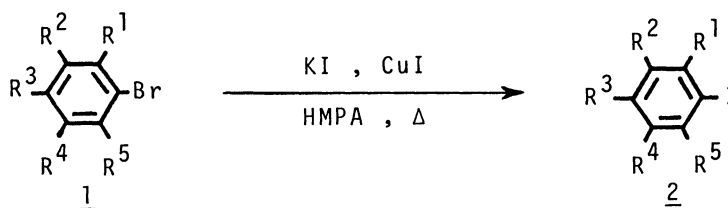


Table 1. Aryl iodides obtained from the halogen exchange of bromides with iodide ion in the presence of copper(I) iodide

R ¹	Aryl bromide <u>1</u>				Reaction time/h	Aryl iodide <u>2</u> ^{a)} Yield/%
	R ²	R ³	R ⁴	R ⁵		
H	H	CH ₃	H	H	6	60
CH ₃	CH ₃	CH ₃	H	CH ₃	15	84
CH ₃ O	H	H	H	H	5	61
H	H	CH ₃ O	H	H	5	80
H	-OCH ₂ O-		H	H	5	71
H	H	CH ₃ CO	H	H	5	60
H	H	C ₆ H ₅	H	H	5	80
H	-(CH=CH) ₂ -		H	H	6	85
-CH=CHCH=CBr-	H		H	H	7	75 ^{b)}

a) Products were identified by mass, IR, and ¹H NMR spectra as well as by direct comparison with authentic specimens. All compounds are known. Yields refer to the isolated compounds and are not optimized.

b) Double amount of the reagents was used to obtain diiodination product.

exchange takes place. Since the reaction occurs under non-aqueous neutral conditions, it would be compatible with many sensitive functional groups.

A general procedure is illustrated below: A mixture of aryl bromide 1 (1 mmol), potassium iodide (15 mmol), copper(I) iodide (5 mmol), and HMPA (3 ml) is agitated at 150-160 °C for appropriate hours under nitrogen. The heterogeneous mixture gradually turns light brown. The progress of exchange is monitored by GLC. When 80-90% conversion is reached, the reaction is quenched by the addition of dilute hydrochloric acid followed by ether, and the mixture is freed from insoluble copper(I) salt by filtration. The organic phase is separated, washed with aqueous sodium sulfite and water, dried, and evaporated to leave iodide 2 as a light yellow oil or pasty solid, which is purified by chromatography or Kugelrohr distillation or fractional crystallization.

The present method provides a convenient direct way to obtain less easily accessible aromatic iodides from readily available bromides, and is characterized by its simple manipulation and inexpensiveness. Unfortunately, it is not applicable to aromatic chlorides.

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