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FACILE SUBSTITUTION REACTION BETWEEN NONACTIVATED ARYL IODIDES AND ARENETHIOLATES IN THE PRESENCE OF COPPER(I) IODIDE

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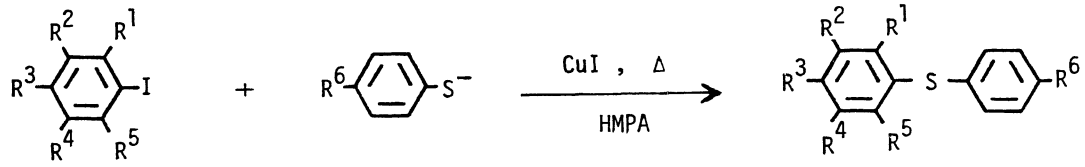
In hexamethylphosphoric triamide containing copper(I) iodide, nonactivated aryl iodides undergo a facile nucleophilic attack by arenethiolate ions to give the corresponding aryl sulfides in good yields.

The relative reactivity of aryl halides toward nucleophile decreases in the order: ArF $\gg$ ArCl $>$ ArBr $>$ ArI. Unlike alkyl iodides, aryl iodides are the least reactive, since the carbon-halogen bond strength is not an important factor in bimolecular nucleophilic aromatic substitutions. Thus, the reaction of aryl iodides with thiolate ions can take place only if activating groups are present in the nucleus. When polymethylated, aryl iodides are quite inert to thiolate ions; they do not react even in polar aprotic solvents heated at high temperatures.

We now wish to report that arenethiolate ions can readily react with various nonactivated aryl iodides in hexamethylphosphoric triamide (HMPA) containing copper(I) iodide, giving the corresponding aryl sulfides in good yields. The reaction seems to provide a new route to some unsymmetrical aryl sulfides, which are otherwise difficult to prepare.



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The procedure involves simply heating a mixture of an aryl iodide 1, an alkali metal arenethiolate 2, copper(I) iodide, and HMPA at 70-80°C for 1-2 h. The results are summarized in the Table. Noteworthy is that no detectable substitution reaction occurs in the absence of copper(I) iodide. Attempts to extend this procedure to alkanethiolates and arylalkanethiolates have so far failed. With these thiolates, complicated side-reactions become important and aryl iodides are often recovered unchanged.

Table. Copper(I) Iodide-assisted Reaction of Aryl Iodides with Arenethiolates in HMPA

Aryl sulfide	R^1	R^2	R^3	R^4	R^5	R^6	Mp (°C)	Yield[a] (%)
3a	Me	Me	H	Me	Me	H	63-64	69
3b	Me	Me	Me	Me	Me	H	105-106	65
3c	Me	Me	H	Me	Me	Cl	106-109	71
3d	Me	Me	Me	Me	Me	Cl	125-126	75
3e	Me	Me	Me	Cl	Me	H	102-103	60
3f	NO_2	H	H	H	H	H	80-82	77

a The yields refer to the isolated ones and are not optimized.

Aryl iodides react readily with thiolate ions in liquid ammonia under irradiation, for which the $S_{RN}1$ mechanism is proposed.[1] In our case the sulfide formation is suppressed considerably, but not completely, by the presence of m-dinitrobenzene which is known to interrupt the chain cycle of the $S_{RN}1$ reaction. Quenching of the reaction mixture at low conversion with hydroxylic solvents does not reveal the formation of parent hydrocarbon, ruling out a possible intervention of organocopper species as intermediate. Thus, the present reaction may proceed via copper(I) arenethiolate formed in situ from copper(I) iodide and arenethiolate ion.[2]

Work is in progress to extend the scope of this copper(I) iodide-assisted reaction with respect to nucleophiles and aromatic substrates.

The typical procedure is illustrated below for the preparation of 4'-chloro-2,3,5,6-tetramethyldiphenyl sulfide 3c.

Sodium hydride (0.103 g, 4.29 mmol) is added to a warm solution of 4-chlorobenzenethiol (0.619 g, 4.28 mmol) in HMPA (6 ml) under nitrogen atmosphere. Copper(I) iodide (0.678 g, 3.56 mmol) is then introduced and the mixture is stirred for a while until a black solution results, to which 2,3,5,6-tetramethyliodobenzene (0.929 g, 3.57 mmol) is added. After being kept at 70-80°C for 1 h, the mixture is poured into water and the product is extracted with ether. The extract is washed with brine, dried over anhydrous sodium sulfate, and evaporated to give sulfide 3c as an oily residue, which is purified by chromatography over alumina using hexane as solvent. White needles from ethanol, mp 106-109°C. Yield, 0.69 g (71%).

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2. R. Adams and A. Ferretti, J. Am. Chem. Soc., 81, 4927 (1959); R.G.R. Bacon and H.A.O. Hill, J. Chem. Soc., 1964, 1097; for a review of copper-promoted aromatic substitution reactions, see: R.G.R. Bacon and H.A.O. Hill, Quart. Rev., 19, 95 (1965).

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