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COPPER(I) IODIDE-FACILITATED NUCLEOPHILIC SUBSTITUTIONS OF NONACTIVATED ARYL IODIDES WITH ARENESELENOLATES

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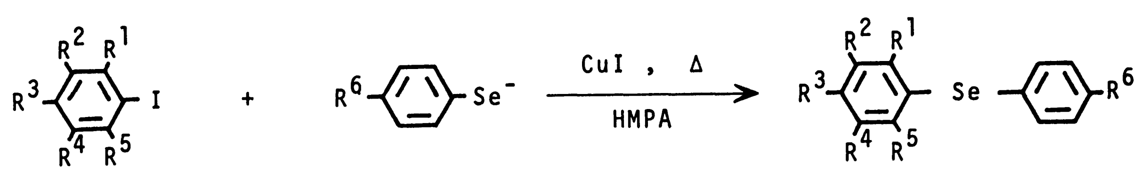
Nonactivated aryl iodides readily react with areneselenolates, in the presence of copper(I) iodide, in hexamethylphosphoric triamide to produce the corresponding diaryl selenides in good yields.

Standard methods for the preparation of diaryl selenides involve the reaction of arenediazonium salt with alkali metal selenide, pyrolysis of diaryl sulfone or diaryl mercury in the presence of elemental selenium, action of aryllithium on aryl selenocyanate, and cleavage of diaryl diselenide with arylmagnesium halide.[1] However, synthetic utility of these methods greatly depends upon the availability of specific starting materials. The modified Williamson synthesis is widely used for the preparation of aliphatic selenides,[1] but it can not be applicable to aromatic analogues, since nucleophilic substitutions of aryl halides generally proceed too slowly for this process to be used for practical purpose.

We wish to report that nonactivated aryl iodides undergo a facile nucleophilic attack by areneselenolate ions in hexamethylphosphoric triamide (HMPA) containing copper(I) iodide, giving the corresponding diaryl selenides in good yields. The reaction seems to provide a new route to some unsymmetrical diaryl selenides, which otherwise require laborious steps to obtain.

The procedure involves simply heating a mixture of aryl iodide 1, alkali metal areneselenolate 2, copper(I) iodide, and HMPA at 80-90 °C for 1-2 h. The reaction proceeds smoothly and affords satisfactory yields of products, as shown by results summarized in the Table. In contrast to the well established order of reactivity of aryl halides toward nucleophile: ArF ≫ ArCl > ArBr > ArI, aryl iodide is found to be most reactive in our case. Thus, when mixed aryl halides 1d-1f are treated with areneselenolates, the products obtained are those arising from the preferential replacement of iodine atom. Noteworthy is that no detectable substitution



1 2 3

Table. Copper(I) Iodide-facilitated Reaction of Aryl Iodides with Areneselenolates in HMPA[a]

Aryl selenide	R^1	R^2	R^3	R^4	R^5	R^6	Mp (°C)	Yield[b] (%)
3a	Me	Me	Me	Me	Me	H	100-102	60
3b	Me	Me	Me	Me	Me	Cl	91-93	50
3c	Me	Me	H	Me	Me	H	65-66	56
3d	Me	Me	Me	Cl	Me	H	86-87	43
3e	Me	Me	Cl	Me	Me	H	84-86	52
3f	Me	Me	Me	Me	Br	H	105-107	54
3g	NO_2	H	H	H	H	H	90-92	76

[a] All aryl iodides are easily obtained by direct iodination of arenes with iodine/periodic acid.[4]

[b] The yields refer to the compounds isolated and are not optimized.

reaction takes place without copper(I) catalyst.[2] The mechanism of this facile selenolation is not clear at present, although we may expect a possible role of the in situ-formed copper(I) areneselenolate.[3] Work is in progress to extend the scope of the present reaction with respect to nucleophile and substrates.

In a representative procedure, sodium hydride (0.033 g, 1.37 mmol) is added to a stirred solution of benzeneselenol (0.214 g, 1.36 mmol) in HMPA (4 ml) maintained at 80-90 °C under nitrogen. When hydrogen evolution has ceased, copper(I) iodide (0.171 g, 0.90 mmol) is added. The solution gradually turns black, to which is added iododurene (1c; 0.234 g, 0.90 mmol). The mixture is heated with stirring for 1.5 h and then diluted by the addition of water. The product is extracted with ether, washed with brine, and dried over sodium sulfate. The solvent is removed in vacuo to leave a solid residue, which is chromatographed on alumina using hexane as eluent. Unchanged 1c is eluted first, then follows 3c which is recrystallized from ethanol as colorless prisms, mp 65-66 °C. Yield, 0.146 g (56%).

REFERENCES

1. For a review of organic selenides, see: L.-B. Agenäs, in D.L. Klayman and W.H.H. Günther, "Organic selenium compounds: their chemistry and biology," John Wiley, London (1973).
2. Use of the other dipolar aprotic solvent systems instead of HMPA largely suppresses the reaction. A combination of aryl chloride and copper(I) chloride gives poor results.
3. For a review of copper(I)-promoted aromatic substitutions, see: R.G.R. Bacon and H.A.O. Hill, Quart. Rev., 19, 95 (1965).
4. H. Suzuki, Org. Synth., 51, 94 (1971).

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