CHEMISTRY LETTERS, pp. 1115-1116, 1981.

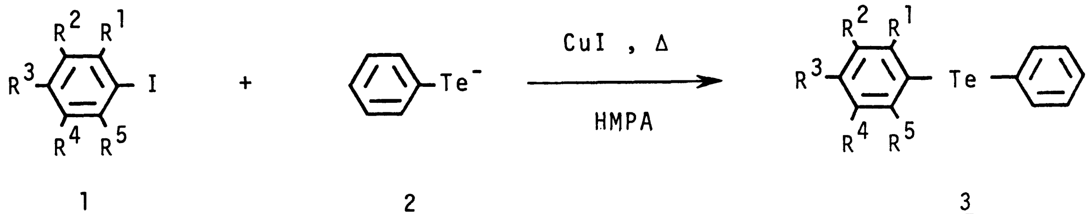
DIARYL TELLURIDES FROM THE REACTION OF MODERATELY ACTIVATED IODOARENES WITH BENZENETELLUROLATE ION IN HEXAMETHYLPHOSPHORIC TRIAMIDE

Hitomi SUZUKI,* Hisako ABE, Nobuko OHMASA, and Atsuhiro OSUKA
Department of Chemistry, Faculty of Science,
Ehime University, Bunkyo-cho, Matsuyama 790

When heated in hexamethylphosphoric triamide at 80-90°C, preferably in the presence of copper(I) iodide, moderately activated iodoarenes undergo nucleophilic attack by benzenetellurolate ion, giving the corresponding unsymmetrical diaryl tellurides in fair to good yields.

Aromatic tellurides constitute a group of substances of increasing attention owing to their potentials as synthetic intermediates as well as photoimaging compounds. Practical methods for the synthesis of the tellurides involve the reduction of diaryltellurium dihalides, reaction of tellurium tetrachloride with aryllithium or Grignard reagent, pyrolysis of diaryl ditellurides, reaction of elemental tellurium with diaryl mercury or Grignard reagent, and action of alkali telluride on arenediazonium salts.[1] A more direct route based on the reaction of haloarenes with arenetellurolates has not been feasible, since the arenetellurolate ions are poor nucleophile; unlike thiolate and selenolate ions they fail to react.

We have recently shown that nonactivated iodoarenes can react with various nucleophiles in hexamethylphosphoric triamide (HMPA) in the presence of copper(I) iodide, giving the corresponding substutution products in modest to good yields.[2-4] The reaction has now been extended to include arenetellurolate as nucleophile. We have found that diaryl tellurides 3 can be obtained in fair to good yields in one step when moderately activated iodoarenes, such as iodonitrobenzenes 1a - 1e, are treated with benzenetellurolate ion 2 in HMPA at 80-90°C, preferably in the presence of copper(I) iodide. To our knowledge, the literature so far contains no report of the $\mathrm{S_NAr}$ reaction employing arenetellurolate ion as nucleophile.[5] The tellurides 3a - 3e are easily isolated and purified through alumina chromatography; the yields are listed in the Table.



1 2 3

Table Reaction of Iodoarenes with Benzenetellurolate Ion in Hexamethylphosphoric Triamide

Aryl telluride	R^1	R^2	R^3	R^4	R^5	Mp (°C)	Yield (%)[a]
3a	NO_2	H	H	H	H	93-94	95
3b	H	NO_2	H	H	H	119-121	53
3c	H	H	NO_2	H	H	110-112	65
3d	CH_3	CH_3	NO_2	H	H	115-117	55
3e	NO_2	CH_3	H	CH_3	CH_3	95-97	58

a Yields refer to the compounds isolated and are not optimized.

Use of other aprotic solvents such as DMF and DMSO is not effective. Iodoarenes bearing no activating substituents are unreactive with tellurolate ion 3 under experimental conditions similar to those used for reactions with thiolate[3] and selenolate ions.[4] Although the scope of the reaction seems to be limited, the synthetic method described herein is considered to be complementary to the existing ones in terms of ready accessibility of starting materials, simplicity of manipulation, and mild reaction conditions.

In a representative procedure, sodium borohydride (0.70 mmol) is added to a stirred solution of diphenyl ditelluride (0.73 mmol) in HMPA (5 ml) at 70-80 °C under an atmosphere of nitrogen. After 0.5 h copper(I) iodide (0.73 mmol) is added. The mixture turns black. Iodoarene (1d; 0.73 mmol) is then introduced and the mixture is maintained at 80-90 °C with good stirring for 1.5 h. The progress of the reaction is monitored by TLC. After cooling, the mixture is diluted with water and the product is extracted with ether, washed with brine, and dried over sodium sulfate. The solvent is removed *in vacuo* and a residue is chromatographed on a short column of alumina using hexane as eluant. Unchanged iodoarene and ditelluride formed during workup elute first, then follows telluride 3d which is recrystallized from ethanol to give red plates, mp 115-117 °C. Yield, 55%.

REFERENCES

1. For recent reviews of organic tellurides, see: K.J. Irgolic, "The Organic Chemistry of Tellurium," Gordon and Breach, London (1974); J. Organomet. Chem., 189, 65 (1980).
2. H. Suzuki, K. Miyoshi, and M. Shinoda, Bull. Chem. Soc. Jpn., 53, 1765 (1980).
3. H. Suzuki, H. Abe, and A. Osuka, Chem. Lett., 1980, 1358.
4. H. Suzuki, H. Abe, and A. Osuka, Chem. Lett., 1981, 151.
5. Photoinduced $S_{RN}1$ reaction of haloarenes with tellurolate ion in liquid ammonia has recently been reported.[6] In the present case, however, no reversible coupling of aromatic moieties is observed.
6. A.B. Pierini and A. Rossi, J. Org. Chem., 44, 4667 (1979).

(Received May 19, 1981)