Pergamon

Tetrahedron Letters, Vol. 37, No. 25, pp. 4361-4362, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00866-0

PHOTOSTIMULATED TELLUROMETHYLATION

Thomas Junk*

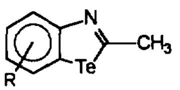
Hazardous Waste Research Center, Louisiana State University, Baton Rouge, LA 70803

Frank R. Fronczek

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

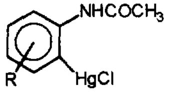
Abstract: Photostimulated reaction of bromo– and iodoarenes with potassium tellurocyanate in dimethylsulfoxide produces aryl methyl tellurides in moderate yields. This method offers facile access to aryltellurium compounds which are difficult to prepare by other methods. Copyright © 1996 Elsevier Science Ltd

Functionalized aryltellurium compounds commonly are prepared from arylmagnesium, aryllithium, or arylmercury compounds.[1] Reactivities of these organometallic intermediates impose restrictions on the presence of substitutents. Specifically, aryltellurium compounds carrying nitrogen–containing moieties, which serve as starting materials for organotellurium compounds of ongoing interest (e.g., tellurazoles[2] and tellurium containing polymethine dyes[3]) remain relatively inaccessible. Only two methods currently are available for the regiospecific preparation of precursors to arenotellurazoles **1**, namely mercury displacement in 2-acetamidoarylmercuric chlorides **2** with tellurium tetrachloride[4] and treatment of 2-nitroaryldiazonium tetrafluoroborates **3** with dialkyl ditellurides under phase transfer conditions.[5]

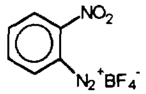


R = H, Cl, CH_3, $C(CH_3)_3$

1



2



3

Photostimulated aromatic nucleophilic substitution, or $S_{RN}1$, has been reported to afford diaryl ditellurides in yields below 20%, starting with haloarenes and disodium ditelluride in liquid ammonia.[6] This method has not found widespread use. Attempts to extend the synthesis of aryl chalcogenacyanates from haloarenes and alkali metal chalcogenacyanates by $S_{RN}1$ reaction[7] to the preparation of tellurocyanates resulted in an unexpected formation of aryl methyl tellurides in yields ranging from 9% (for 2–acetamidophenyl methyltelluride) to 33.8% (for 2–naphthyl methyltelluride, Scheme 1). Dimethylsulfoxide (DMSO), which was chosen as solvent for this reaction because it solubilizes alkali tellurocyanates without decomposition, also served as methyl source.

In a typical experiment, a mixture of 5.0 g (24.1 mmol) 2-bromonaphthalene and potassium tellurocyanate, generated from 3.68 g (29 mmol) tellurium powder and 2.4 g (37 mol) potassium cyanide in 200 mL dry DMSO was purged with nitrogen and irradiated in a quartz reactor with unfiltered light from a 450W

Hanovia high pressure mercury vapor UV lamp for 10 hrs. **CAUTION: formation of extremely malodorous volatile sulfur and tellurium compounds.** The reaction mixture was subsequently diluted with water, the product extracted with 3 × 100 mL diethyl ether, and precipitated as dibromide by addition of excess bromine. The crude dibromide was reduced with sodium sulfide and purified by chromatography (silica gel–hexane). Yield: 2.2 g (33.8%), mp 60–1°. The material was identical to an authentic sample, prepared by methylation of sodium 2-naphthyl-tellurolurolate[8] with iodomethane.

$$\mathrm{R{-}X} \quad + \quad \mathrm{TeCN^-} \quad \xrightarrow[\mathrm{DMSO}]{h\nu} \quad \mathrm{R{-}TeCH_3}$$

R = phenyl, 1-naphthyl, 2-naphthyl, 2-acetamidophenyl
X = I, Br

Scheme 1. Formation of aryl methyl tellurides by photostimulated telluromethylation of haloarenes

Product formation was monitored by removal of samples during photolysis and analysis by GC–MS. Several byproducts were tentatively identified (dimethyl sulfide, dimethyl disulfide, diaryl tellurides, and respective arenes resulting from dehalogenation). Intermediate aryl tellurocyanates presumably react with methyl radicals formed by DMSO reduction and subsequent photolysis of resultant dimethyl sulfide,[9] to produce the observed products. The molecular geometry of 2-acetamidophenyl methyl telluride was determined by x–ray crystallography.[10]

Acknowledgment: We thank Dr. W. James Catallo for his ongoing interest in this project.

REFERENCES

1. Irgolic, K. J. *Methoden der organischen Chemie*, **1990**, *E12b*, Georg ThiemeVerlag Stuttgart – New York, Dieter Klamann, ed.
2. U.S. 4607000 (August 19, 1986), Eastman Kodak Co., W. H. H. Guenther and R. Lok, C. A. 105, **1986**, 235722.
3. U.S. 4575483 (March 11, 1986), Eastman Kodak Co., W.H. H. Guenther, J. D. Mee; C.A. 104, **1986**, 216429.
4. Junk. T.; Irgolic, K. J. *Phosphorus Sulfur* **1988**, *38*, 121–35.
5. Luxen, A.; Christianes, L. *Tetrahedron Letts.* **1982**, *23(38)*, 3905–8.
6. Rossi, R. A.; Penenori, A. B. *J. Org. Chem.* **1981**, *46*, 4580–1.
7. El'tsov, A. V.; Kul'bitskaya, O. V.; Frolov, A. N. *Zh. Org. Khim.* **1972**, *3(1)*, 76–84.
8. Gardner, S. A.; Gysling, H. J. *J. Organomet Chem.* **1980**, *197(1)*, 111–21.
9. Rao, P. M.; Knight, A. R. *J. Can. Chem.* **1971**, *50*, 844–52.
10. Crystallographic Data for n: $C_9H_{11}TeNO$, FW=276.8, colorless lath fragment, monoclinic space group $P2_1/n$, with a=9.3327(9) Å, b=8.6130(7) Å, c=25.899(2) Å, β=94.212(8)°, V= 2076.2(6) $Å^3$, Z=8, Dc=1.771 g cm^{-3}, $\mu(MoK\alpha)$=28.3 cm^{-1} at T=297K. Absorption corrections by ψ scans; 4756 unique data with $1<\Theta<27.5°$; 3357 data with $I>1\sigma(I)$ used in the refinement; R=0.043. Two independent molecules exist in the asymmetric unit. Coordinates and geometric data have been deposited with the Cambridge Crystallographic Data Centre.

(*Received in USA* 22 *March* 1996; *accepted* 23 *April* 1996)