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# SYNTHESIS OF UNSYMMETRICAL TELLURIDES AND SELENADITELLURIDES

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## Summary

Unsymmetrical tellurides may be prepared by the reaction of arenetellurenyl halides, generated in situ, with Grignard reagents. Selenaditellurides, RTeSeR, are prepared from the reaction of arenetellurenyl halides with ArSeMgBr.

## Introduction

Unsymmetrical diorganotellurides are well-known compounds [1]. The most useful and general method of preparation involves the reaction of an aryltellurium trichloride with an aryl- or alkyl-mercuric chloride followed by reduction

$$ArTeX_3 + RHgCl \rightarrow ArRTeCl_2 + HgCl_2 \qquad (1a)$$

$$ArRTeCl_2 \xrightarrow{Red.} ArTeR \qquad (1b)$$

of the resulting diorganotellurium dichloride (eqns. 1a and b) [2,3]. Diaryl ditellurides can also be used as starting materials, giving unsymmetric diaryl tellurides on treatment with Grignard reagents (eqn. 2) [4]. The reaction of aromatic ditellurides with dialkylmercury compounds yields aryl alkyl tellurides (eqn. 3) [5].

$$ArTeTeAr + Ar'MgX \rightarrow ArTeAr' + ArTeMgX \qquad (2)$$

$$Ar_2Te_2 + R_2Hg \rightarrow 2ArTeR + Hg \qquad (3)$$

Recently, Piette and Renson [6-8] have synthesized unsymmetric tellurides by use of lithium or sodium aryl tellurides (eqns. 4a-c):

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$$\begin{tikzcd}[column sep=large] & & \mathrm{ArTeR_2^+X^-} \arrow[r, "\mathrm{py}"] & \mathrm{ArTeR + pyR^+X^-} \quad (4a) \\ \mathrm{ArLi} \arrow[r, "\mathrm{Te}"] & \mathrm{ArTeLi} \arrow[ur, "\mathrm{RX\ (excess)}"] \arrow[dr, "\mathrm{n\text{-}BuBr}"'] & & \\ & & \mathrm{ArTeBu} & \quad (4b) \end{tikzcd}$$

$$\mathrm{Ar_2Te_2} \xrightarrow{\mathrm{NaBH_4}} \mathrm{2ArTeNa} \xrightarrow{\mathrm{2RX}} \mathrm{2ArTeR} \qquad (4c)$$

Our discovery that arenetellurenyl halides could be prepared in situ (and converted to dihaloraryltellurates [9]) led us to examine their utility in the synthesis of organotellurium compounds. In this paper we report the use of arenetellurenyl halides in the preparation of unsymmetrical tellurides and selenaditellurides.

## Results and discussion

Arenetellurenyl halides generated in situ react with Grignard reagents (eqn. 5) and yield the unsymmetrical tellurides listed in Table 1. Some of the

$$\mathrm{ArTeTeAr} \xrightarrow{\mathrm{X_2}} \mathrm{2ArTeX} \xrightarrow{\mathrm{RMgX}} \mathrm{ArTeR + MgX_2} \qquad (5)$$

tellurides were isolated and identified as dichlorides or dibromides. The reaction provides a convenient, general method for the preparation of unsymmetric tellurides in high yields. Aromatic, aliphatic, cycloaliphatic, and acetylenic Grignard reagents can be used employing simple techniques and mild experimental conditions. Unlike the method described by eqn. 2, the present method

TABLE 1

DIORGANOTELLURIDES AND DIORGANOTELLURIUM DIHALIDES

| | Compound[a] | M.p or b p. (°C/Torr) | Appearance | Te. found (calcd.) (%) |
|---|---|---|---|---|
| I | $(p\text{-}CH_3OC_6H_4)(C_6H_5)Te$ | 60-61[b] | yellow needles[c] | — |
| IIa | $(p\text{-}C_2H_5OC_6H_4)(C_6H_5)Te$ | 113-115/$10^{-1}$ | yellow oil | 39.40(39.17) |
| IIb | $(p\text{-}C_2H_5OC_6H_4)(C_6H_5)Te$ | 148-151 | yellow crystals[d] | 26.23(26.26) |
| IIIa | $(p\text{-}CH_3C_6H_4)(C_6H_5)Te$ | 88-90/$10^{-1}$ | yellow oil | 43.01(43.14) |
| IIIb | $(p\text{-}CH_3C_6H_4)(C_6H_5)TeBr_2$ | 180-182 | yellow crystals[d] | 28.20(28.00) |
| IV | $(p\text{-}C_2H_5C_6H_4)(C_4H_9)Te$ | 90-92/$10^{-2}$ | pale yellow oil | 41.67(41.70) |
| V | $(p\text{-}CH_3C_6H_4)(C_4H_9)Te$ | 75-76/$10^{-1}$ | pale yellow oil | 46.54(46.25) |
| VI | $(C_6H_5)(C_4H_9)Te$ | 71-72/$10^{-2}$ | pale yellow oil | 48.90(48.73) |
| VIIa | $(p\text{-}C_2H_5OC_6H_4)(C_6H_{11})Te$ | 110-111/$10^{-2}$ | pale yellow oil | 38.18(38.46) |
| VIIb | $(p\text{-}C_2H_5OC_6H_4)(C_6H_{11})TeCl_2$ | 112-114 | colorless crystals[d] | 31.51(31.68) |
| VIIIa | $(p\text{-}CH_3C_6H_4)(C_6H_{11})Te$ | 100-101/5 × $10^{-3}$ | pale yellow oil | 42.16(42.27) |
| VIIIb | $(p\text{-}CH_3C_6H_4)(C_6H_{11})TeCl_2$ | 84-85 | colorless crystals[d] | 34.38(34.23) |
| IXa | $(C_6H_5)(C_6H_{11})Te$ | 93-94/$10^{-2}$ | pale yellow oil | 44.48(44.33) |
| IXb | $(C_6H_5)(C_6H_{11})TeCl_2$ | 61-62 | colorless crystals[c] | 35.42(35.57) |
| X | $(p\text{-}C_2H_5OC_6H_4)(C_6H_5C{\equiv}C)Te$ | 67-68 | pale orange crystals[b] | 36.28(36.46) |
| XI | $(p\text{-}CH_3C_6H_4)(C_6H_5C{\equiv}C)Te$ | 74-76 | colorless crystals[c] | 39.84(39.90) |
| XII | $(C_6H_5)(C_6H_5C{\equiv}C)Te$ | 115-116/5 × $10^{-3}$ | red oil | 41.96(41.72) |

[a] Yields were routinely 90% or greater. [b] Agrees with literature (ref. 2). [c] Recrystallized from methanol. [d] Recrystallized from benzene/petroleum ether.

TABLE 2

SELENADITELLURIDES

| Compound | Yield (%) | M.p. or b.p. (°C/Torr) | Appearance | % Te + Se found (calcd.) |
|---|---|---|---|---|
| XIII $C_6H_5TeSeC_6H_5$ | 63 | 47-48 | reddish needles[a] | 57.77(57.27) |
| XIV $p$-$CH_3C_6H_4TeSeC_6H_5$ | 42 | | reddish oil | 55.51(55.10) |
| XV $p$ $CH_3OC_6H_4TeSe$-$p$-$CH_3OC_6H_4$ | 87 | 155-158/$10^{-2}$ | reddish oil | 49.56(49.08) |

[a] Recrystallized from petroleum ether.

does not require a large excess of a Grignard reagent and all of the ArTe moieties are converted to ArTeR.

In situ generated arenetellurenyl halides can be used to synthesize selenaditellurides via reaction with ArSeMgX (eqn. 6). The compounds prepared in this manner may be found in Table 2. This class of compound was unknown until recently when the first example was prepared by Piette et al. [10]. Selenaditellurides are stable compounds, similar in chemical behavior to ditellurides and diselenides. The Te—Se bond is cleaved by bromine, giving a mixture of aryltellurium tribromide and areneselenenyl bromide (eqn. 7). The two bromides are easily separated by their differential solubility in organic solvents.

$$\mathrm{ArSeH} \xrightarrow[-C_2H_6]{\mathrm{EtMgBr}} \mathrm{ArSeMgBr} \xrightarrow{\mathrm{ArTeX}} \mathrm{ArTeSeAr'} \qquad (6)$$

$$\mathrm{ArTeSeAr} + 2\mathrm{Br}_2 \rightarrow \mathrm{ArTeBr}_3 + \mathrm{ArSeBr} \qquad (7)$$

## Experimental

Di-$p$-ethoxyphenyl ditelluride [12], di-$p$-methoxyphenyl ditelluride [12], di-$p$-tolyl ditelluride [13], diphenyl ditelluride [13], selenophenol [14], and $p$-methoxyselenophenol [15] were prepared according to published procedures.

*Grignard reagents.* Ethereal solutions of phenylmagnesium bromide, butylmagnesium bromide, cyclohexylmagnesium bromide and ethylmagnesium bromide were prepared as usual utilizing distilled commercial halides. The concentrations of the Grignard solutions were determined by titration with standard HCl. Phenylacetylenylmagnesium bromide was prepared by treating phenylacetylene in THF with $C_2H_5MgBr$ and refluxing the mixture for 6 h [16].

*Tellurides.* A solution of the diaryl ditelluride (0.002 mol) in 30 ml THF (distilled from $LiAlH_4$) was treated dropwise at 0°C in a $N_2$ atmosphere with bromine (0.32 g, 0.002 mol) in 4 ml benzene. The Grignard reagent was then added dropwise by means of a hypodermic syringe. Gradual disappearance of the dark color of the solution was observed. The solution finally became almost colorless after addition of 10% excess Grignard reagent. After stirring for 30 min at room temperature, the solution was diluted with 40 ml low-boiling petroleum ether, and treated with aqueous $NH_4Cl$ and saturated aqueous NaCl. The organic layer was dried with anhydrous $MgSO_4$ and the solvent evaporated.

Compounds I, X, and XI were obtained as solids. Compounds IV-VI and XII were distilled in vacuo.

Compounds IIa and IIIa in 15 ml benzene were each treated with 0.64 g (0.004 mol) bromine in 8 ml benzene. On concentration and addition of petroleum ether (30-50°C) the dibromides separated as yellow crystals (compounds IIb and IIIb). Compounds VIIa, VIIIa and IXa in 15 ml benzene were treated at 0°C with freshly distilled $SO_2Cl_2$ (0.54 g, 0.004 mol). On concentration and addition of petroleum ether, the corresponding dichlorides (VIIb, VIIIb and IXb) separated as colorless crystals. The dichlorides and dibromides were reduced to the desired tellurides by treatment with a fifteen-fold excess of $Na_2S \cdot 9H_2O$ at 100°C for 15 min. The mixtures were diluted with water and extracted with petroleum ether. The petroleum ether layer was washed with water and saturated aqueous NaCl, dried with $MgSO_4$ and evaporated. The resulting tellurides (compounds IIa, IIIa, VIIa, VIIIa and IXa) were distilled in vacuo.

*Selenaditellurides.* A solution of a selenol (0.005 mol) in 15 ml THF was treated with EtMgBr (2*M*, 2.6 ml, 0.0052 mol) in a $N_2$ atmosphere, and the mixture was refluxed for 2 h. After cooling to 0°C, the tellurenyl bromide solution, prepared from diaryl ditelluride (0.0025 mol) and bromine (0.40 g 0.0025 mol) in THF/benzene, was added dropwise. The mixture was stirred for 30 min at room temperature. The product was worked up as described for the tellurides.

Compound XIII was purified by chromatographing the crude product (1.38 g) on silica gel G (120 g). Petroleum ether elution gave pure XIII ($R_F$, 0.60) as a reddish solid. The same chromatographic procedure gave pure XIV as a red oil ($R_F$, 0.50). This compound decomposed on attempted distillation in vacuo. An analytically pure sample was obtained by preparative thin layer chromatography on silica gel G. Compound XV was obtained by distillation in vacuo.

*Reaction of $C_6H_5TeSeC_6H_5$ with bromine.* Compound XIII (0.52 g 0.0014 mol) in 10 ml $CCl_4$ was treated with bromine (0.45 g 0.0028 mol) in 5 ml $CCl_4$ at 0°C. Yellow-orange phenyltellurium tribromide (0.58 g, 94%) was collected by filtration, and recrystallized from benzene (m.p. 245-246°C (dec.) [17]). Evaporation of the dark red filtrate gave benzeneselenenyl bromide, (0.27 g 82%) which was recrystallized from petroleum ether (m.p. 60°C [18]).

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