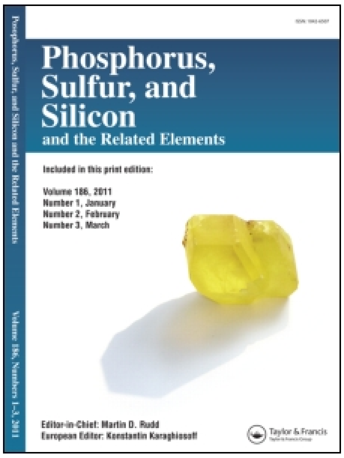

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SYNTHESIS OF VINYLIC SELENIDES AND TELLURIDES BY THE ADDITION OF ALKANESELENOLATE AND -TELLUROLATE ANIONS TO ACETYLENES

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Alkaneselenolate and -tellurolate anions, which are generated from dialkyl dichalcogenides in the system potassium hydroxide-hydrazine hydrate-dimethyl sulfoxide-water, add to acetylene and phenylacetylene to give alkyl vinyl chalcogenides and (*Z*)-alkyl styryl chalcogenides in high yield.

Key words: Vinylic selenides and tellurides, alkaneselenolate and -tellurolate anions, dialkyl diselenides and ditellurides, acetylene, phenylacetylene.

INTRODUCTION

The vinylic selenides and tellurides are of great synthetic potential.[1–3] The addition of selenium- and tellurium-centered nucleophiles to a triple bond is mainly related to the synthesis of aryl vinyl selenides and tellurides.[1–3]

Little is known about the nucleophilic addition of alkaneselenolate and -tellurolate anions to acetylene and phenylacetylene. The only general route[4–6] to unsubstituted alkyl vinyl selenides (**3**) and tellurides (**4**) (30–70% yield) consists of the interaction of the chalcogen, acetylene and alkyl halides in an autoclave under a 12–15 atm pressure.

Along with **3**, **4**, divinyl and dialkyl selenides and tellurides are formed. The drawbacks of this approach are difficulties concerning the use of a high-pressure equipment and the isolation of **3**, **4** (usually preparative GLC is necessary), and the low average yields of **3**, **4**.

RESULTS AND DISCUSSION

We have developed[7,8] a new synthesis of **3** and **4** with 90–100% yields by the interaction of dialkyl dichalcogenides **1**, **2** with acetylene under atmospheric pressure at 20–80°C. Because alkaneselenolate (**5**) and especially -tellurolate (**6**) anions are exceptionally oxidizable species we used the reductive system $KOH\text{-}N_2H_4\cdot H_2O\text{-}DMSO\text{-}H_2O$ which allowed the generation of these species from **1**, **2** under the reaction conditions.

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$$\underset{1,2}{RXXR} + HC\equiv CH \xrightarrow[20\text{-}80\ ^{\circ}C]{KOH/N_2H_4\cdot H_2O/DMSO/H_2O} \underset{3,4}{2\,RXCH{=}CH_2}$$

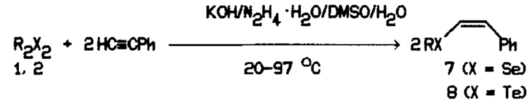
$$\underset{1,2}{RXXR} \underset{O_2}{\overset{KOH/N_2H_4\cdot H_2O}{\rightleftarrows}} \underset{5,6}{2\,RX^-} \xrightarrow[H_2O]{HC\equiv CH} \underset{3,4}{2\,RXCH{=}CH_2}$$

X = Se (1, 3, 5), Te (2, 4, 6), R = Me, Et, Pr, i-Pr, Bu

The system consists of two phases. The lower phase is generally an aqueous solution of potassium hydroxide and hydrazine hydrate. The other role of water is as proton donor to a carbanion which is formed by the addition of **5**, **6** to acetylene. We think that the activation of the nucleophilic process in this system resembles phase transfer catalysis.

We studied the addition of **5**, **6** to phenylacetylene under similar conditions and found the reaction to proceed in a regio- and stereoselective manner giving rise to (*Z*)-alkyl styryl selenides (**7**) and tellurides (**8**) in good yields (see Table I).

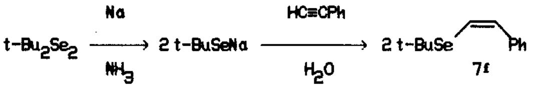
A concurrent reaction is a dealkylation[9] of **7**, **8** by the corresponding **5**, **6**. The dealkylation is thought to decrease the yields of **7**, **8** especially in the case of the methyl derivatives **7a**, **8a**.



R = Me (a), Et (b), i-Pr (c), Pr (d), Bu (e)

The reaction of ditellurides **2** usually needs a higher temperature in comparison with diselenides **1** in order to obtain **4**, **8** in good yields. We believe that this effect is not attributed to the nucleophilicity of the anions **5**, **6**. We think that in order to reduce **2** into **6** more severe conditions are necessary.

Di-*tert*-butyl diselenide did not react under these conditions but we obtained *tert*-butyl vinyl selenide[10] and *tert*-butyl styryl selenide (**7f**) by the addition of sodium *tert*-butyl selenide to acetylene and phenylacetylene in the system KOH-$N_2H_4\cdot H_2O$-DMSO-H_2O at 95–97°C. The sodium *tert*-butyl selenide was prepared by the interaction of di-*tert*-butyl diselenide with sodium in liquid ammonia.



With the method of concurrent reactions we estimated the relative nucleophilicity of **5** in the addition reaction with phenylacetylene and in the nucleophilic substitution with benzyl chloride. For this investigation we prepared an equimolar mixture of different sodium alkaneselenolates from **1** and sodium in liquid ammonia. The reactions were performed under the same conditions in the system KOH-$N_2H_4\cdot H_2O$-DMSO-H_2O and monitored by GLC. Alkyl benzyl selenides and **7** were identified by GLC with authentic samples. Based on the yields of alkyl benzyl selenides and **7** the nucleophilicity of **5** decreases in the following order:

$$MeSe^- > EtSe^- > i\text{-}PrSe^- > t\text{-}BuSe^-.$$

TABLE I

(Z)-Alkyl styryl selenides (**7a–f**) and -tellurides (**8a–c**)

Product	Yield, %	B.p./1 mm Hg, °C	^{1}H-NMR ($CDCl_3$, δ, ppm, J, Hz)
MeSeCh=CHPh (**7a**)	40	111–112	1.85 s, 6.52 d (J = 10.3), 6.86 d (J = 10.3), 7.30 m
EtSeCH=CHPh (**7b**)	82	115–116	1.45 t, 2.75 q, 6.58 d (J = 10.3), 6.86 d (J = 10.3), 7.32 m
i-PrSeCH=CHPh (**7c**)	80	119–120	1.45 d, 3.22 m, 6.65 d (J = 10.8), 6.90 d (J = 10.8), 7.31 m
PrSeCH=CHPh (**7d**)	90	121–122	0.98 t, 1.75 m, 2.73 t, 6.56 d (J = 10.8), 6.86 d (J = 10.8), 7.30 m
BuSeCH=CHPh (**7e**)	85	128–130	0.85 t, 1.34 m, 1.64 m, 2.62 t, 6.40 d (J = 10.5), 6.73 d (J = 10.5), 7.31 m
t-BuSeCH=CHPh (**7f**)	60	124–126	1.50 s, 6.72 d (J = 10.8), 6.91 d (J = 10.8), 7.31 m
MeTeCH=CHPh (**8a**)	44	123–125	1.98 s, 6.93 d (J = 10.8), 7.27 m, 7.36 d (J = 10.8)
EtTeCH=CHPh (**8b**)	85	131–133	1.66 t, 2.68 q, 6.97 d (J = 10.8), 7.27 m, 7.40 d (J = 10.8)
i-PrTeCH=CHPh (**8c**)	83	129–120	1.62 d, 3.34 m, 7.04 d (J = 10.8), 7.27 m, 7.42 d (J = 10.8)

We also estimated a tendency of **5** to be oxidized by air into **1** with the method of concurrent reactions. Based on the yields of **1** the ease of the oxidation of **5** by air increases in the order:

$$\mathrm{MeSe^-} < \mathrm{EtSe^-} < \mathrm{i\text{-}PrSe^-} < \mathrm{t\text{-}BuSe^-}.$$

EXPERIMENTAL

Typical Procedure. To a mixture of KOH (40 g, 0.61 mol), water (20 ml), hydrazine hydrate (13 g, 0.26 mol), and DMSO (20 ml) a solution of **1d** (5.1 g, 0.021 mol) in DMSO (10 ml) is added dropwise for 10 min at 95–97°C. Then a solution of phenylacetylene (8 g, 0.079 mol) in DMSO (30 ml) is added during 2 h, the mixture is stirred at 95–97°C for 2 h, diluted with water and extracted with pentane. After evaporation of pentane the residue is distilled in vacuum to give **7d** (8.5 g, 90% yield). *tert*-Butyl styryl selenide (**7f**). To sodium *tert*-butyl selenide, which has been obtained in liquid ammonia from di-*tert*-butyl diselenide (3.05 g, 0.011 mol) and sodium, a mixture of phenylacetylene (5 g, 0.049 mol), hydrazine hydrate (5 g, 0.1 mol), KOH (15 g, 0.23 mol), water (10 ml), and DMSO (20 ml) is added with stirring at 0°C. Then the mixture is stirred at 95–97°C for 5 h, diluted with water and extracted with ether. The organic layer is washed with water, dried over K_2CO_3 and the ether is evaporated. The residue is distilled in vacuum to give **7f** (3.5 g, 65% yield).

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