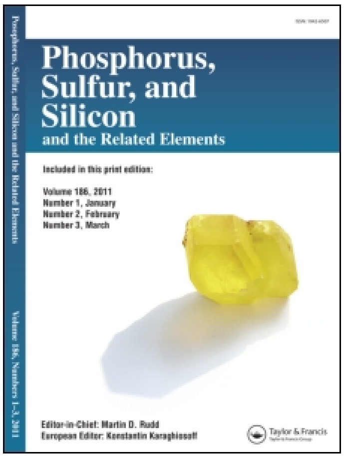

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SYNTHESIS OF ACETYLENIC TELLURIDES BY THE IODOMETHANE-INDUCED REACTION OF DIALKYL DITELLURIDES WITH PHENYLACETYLENE

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SYNTHESIS OF ACETYLENIC TELLURIDES BY THE IODOMETHANE-INDUCED REACTION OF DIALKYL DITELLURIDES WITH PHENYLACETYLENE[1]

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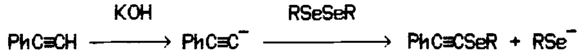
Interaction of dialkyl ditellurides with phenylacetylene under phase transfer conditions occurs only in the presence of iodomethane giving rise to alkyl phenylethynyl tellurides in high yield. These compounds can also be obtained from alkyltellurenyl iodides and phenylacetylene under the same conditions.

Key words: Alkyl phenylethynyl tellurides, dialkyl ditellurides, iodomethane, phenylacetylene, alkyltellurenyl iodides.

INTRODUCTION

Recently we described the synthesis of alkyl phenylethynyl selenides in high yield by an interaction of dialkyl diselenides with phenylacetylene in the system solid KOH/benzene/dibenzo-18-crown-6 under phase transfer conditions.[2] The reaction pathway is suggested to include a generation of phenylacetylide anion and a cleavage of the diselenide bond by this anion.



$$PhC{\equiv}CH \xrightarrow{KOH} PhC{\equiv}C^- \xrightarrow{RSeSeR} PhC{\equiv}CSeR + RSe^-$$

RESULTS AND DISCUSSION

Being involved under the same conditions dialkyl ditellurides (**1**) do not undergo rupture of the Te—Te bond and generally remain unconverted in the reaction. To activate the Te—Te bond we tested an addition of iodomethane (**2**) to the reaction mixture having in mind formation of the salt **5** which should be easily cleaved. Addition of **2** allowed us to obtain acetylenic tellurides (**3**) in 83–98% yield. Another product of this reaction is alkyl methyl telluride (**4**).

To understand the reaction pathway we studied the interaction between **1** and **2**. There were no data on this subject except the work[3] which described the reaction of (p-MeOC$_6$H$_4$Te)$_2$ with an excess of **2** leading to the formation of p-MeOC$_6$H$_4$(Me)TeI$_2$ and p-MeOC$_6$H$_4$$\overset{+}{\text{Te}}Me_2I^-$.

When we mixed equimolar quantities of **1** and **2** in benzene, precipitation was observed after several hours. The precipitate was examined by ^{1}H-NMR and el-

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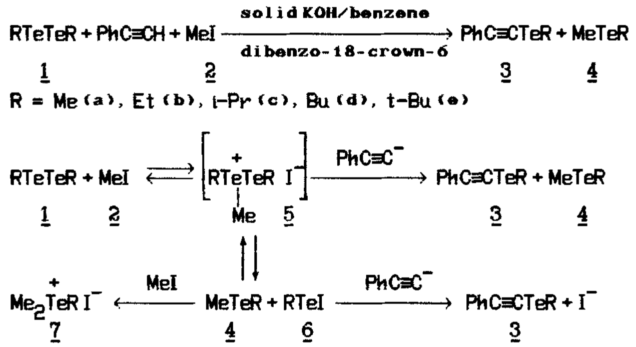

emental analysis and found to be alkyl dimethyl telluronium iodide **7**. The ease of formation of **7** increases in the order:

$$t\text{-}Bu_2Te_2 < i\text{-}Pr_2Te_2 < Et_2Te_2 < Me_2Te_2.$$

The interaction between **1** and **2** can be monitored by ^{1}H-NMR. During 1–2 hours after mixing equimolar quantities of **1** and **2** in $CDCl_3$ additional signals arose with a concomitant decrease of the intensity of the **1** and **2** signals. We found that the additional signals can be attributed to **7** and alkyltellurenyl iodides (**6**). For example, a mixture of **1c** with **2** revealed the following signals (δ, ppm): 1.65 d, 2.45 s, 3.80 m (attributed to **7c**), 1.86 d, 3.95 m (attributed to **6c**). The former group of signals coincides with a ^{1}H-NMR spectrum of the precipitate which was obtained from **1c** and **2** in benzene, as well as with the spectrum of **7c** which was prepared from **4c** and **2**. The latter group of the signals coincides with the spectrum of **6c** which was formed by an interaction of **1c** with iodine.

Expecting the reaction pathway to be realized via **6** we performed the reaction under the same conditions but adding iodine instead of **2**. We obtained **3c** in 18% yield only. Then we found that the formation of **6** from **1** and iodine proceeds very slowly and in order to obtain **6** in good yield stirring of **1** with iodine at room temperature for several hours is necessary. When we used a benzene solution of **6c** prepared in this manner in the reaction, **3c** was obtained in 90% yield.

$$i\text{-}PrTeI + PhC{\equiv}CH + KOH \rightarrow i\text{-}PrTeC{\equiv}CPh + KI + H_2O$$

Therefore, the reaction pathway via **6** is proved by the experiment. But it is hardly reasonable to exclude a possibility of a reaction pathway via the intermediate **5** at the very moment of the formation of **5**.

An interesting observation was made when the reaction was monitored by GLC. In a short time period after mixing **1c** and **2** the conversion of **1c**, **2** was seen to stop or to proceed very slowly. But with the addition of phenylacetylene into the reaction mixture we observed a quick disappearance of **1c**, **2** by GLC with a concomitant emergence of **3c**, **4c**. To explain this fact a reversibility of the formation of **4c**, **6c** from **1c**, **2** (possibly via **5c**) is expected.

The compounds **3a–d** are described earlier.[4,5] The tertiary telluride **3e** was synthesized for the first time.

EXPERIMENTAL

Usually a disappearance of the dark red colour of **1** indicates the reaction to be near to the end. The colour disappearance occurs when 1–1.2 mole of **2** is added per mole of **1**. A little excess of **2** is thought to be necessary due to a partial alkylation of **4** with **2**.

To a stirred mixture of powdered KOH (50 g, 0.75 mol), dibenzo-18-crown-6 (0.2 g, 0.56 mmol), phenylacetylene (10 g, 0.1 mol), benzene or toluene (50 ml), and ditelluride **1** (0.02 mol) **2** is added dropwise at room temperature until the dark red colour of **1** disappeared (10–20 min, 0.02–0.024 mol of **2** is consumed). The mixture is stirred for 2 h, washed with water and dried over K_2CO_3. The solvent is evaporated and the residue is distilled in vacuum to give the pure telluride **3**.

Under the same conditions but using *i*-PrTeI solution in benzene instead of **1c** and **2** we obtained **3c** in 90% yield.

tert-Butyl phenylethynyl telluride (**3e**), b.p. 141/1 mm Hg. IR (cm^{-1}): 2130 ($C\equiv C$). ^1H-NMR (δ, ppm): 1.76 s, 7.35 m. MS, m/z (rel. int., %): 288 (2), 231 (4), 102 (31), 101 (19), 57 (100).

REFERENCES

1. Preliminary letter: V. A. Potapov, S. V. Amosova and A. V. Khangurov, *Metalloorg. Khim.*, **4**, 948 (1991).
2. V. A. Potapov, S. V. Amosova and A. V. Khangurov, *Zh. Org. Khim.*, **26**, 2635 (1990).
3. G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 2307 (1925).
4. M. J. Dabdoub and J. V. Comasseto, *Organometallics*, **7**, 84 (1988).
5. Yu. A. Boiko, B. S. Kupin and A. A. Petrov, *Zh. Org. Khim.*, **4**, 1355 (1968).