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REACTIONS OF SELENIUM AND TELLURIUM METALS WITH PHENYLACETYLENE IN THREE-PHASE CATALYTICAL SYSTEMS[1]

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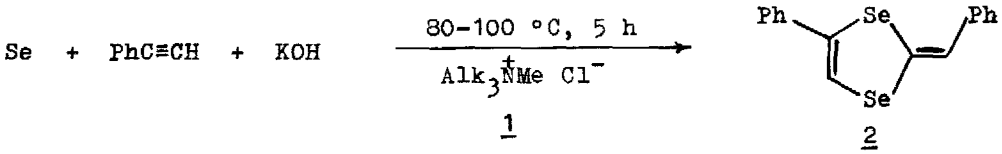
Summary: Compounds 2, 6a-d, 7, 8 were prepared in three-phase catalytical systems using selenium and tellurium metals as one phase. A radical anion chain mechanism is proposed in the reaction of tellurium metal with phenylacetylene.

Recently we focused our attention on the chalcogen-acetylene interaction in super base systems[2]. In this work we explore the reactions of selenium and tellurium metals with phenylacetylene under phase transfer conditions. As we know no study of the use of elemental chalcogens in organic synthesis by phase transfer technique has been done.

The interaction in the three-phase system selenium metal - aqueous base - phenylacetylene in the presence of 1 leads to Z-2-benzylidene-4-phenyl-1,3-diselenole (2) in 20% yield.



$\mathrm{Alk} = C_7H_{15}-C_9H_{19}$

The reaction pathway is suggested to include a cleavage of the selenium polymer chains by hydroxyl ions, a transfer of the species 3 to organic phase, an interaction of 3 with acetylide ion 4, and a dimerization of anions 5 as the last step (the formation of 2 by a dimerization of anions 5 is known[3]).

$$\boxed{SeSe_nSe} + HO^- \longrightarrow HO^-\ {}^+SeSe_nSe^-$$

3

$$PhC\equiv CH + HO^- \longrightarrow \underset{\underline{4}}{PhC\equiv C^-} \xrightarrow{\underline{3}} PhC\equiv CSeSe_nSe^- \xrightarrow{-Se_{n+1}} \underset{\underline{5}}{PhC\equiv CSe^-} \xrightarrow{H_2O} \underline{2}$$

Since the acetylide ion $\underline{4}$ in water should be protonated, there is little possibility that $\underline{4}$ is transferred from the organic phase to selenium to form $\underline{5}$ through the water phase (eqn. 2).

We extended these data to the synthesis of selenides $\underline{6}$a-d[4] trapping the intermediate anion $\underline{5}$ with alkyl halides.

$$Se + PhC\equiv CH + RX \xrightarrow[\underline{1},\ toluene]{80-100\ °C,\ 5\ h} \underset{6a-d}{PhC\equiv CSeR} \qquad (1)$$

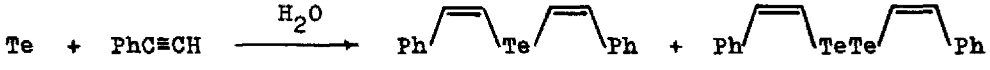
R = Me (a), Et (b), i-Pr (c), Bu (d), X = Cl, Br, I

Primary and secondary alkyl bromides and iodides provide selenides $\underline{6}$a-d in 40-50% yield; in the case of alkyl chlorides the results are about twice less. We failed to prepare the corresponding selenide with t-BuBr. Without $\underline{1}$ the yields of $\underline{2}$ and of $\underline{6}$a-d are negligible.

The anion $\underline{5}$ can also be generated at ambient temperature in the system selenium metal - solid KOH - phenylacetylene solution in toluene with dibenzo-18-crown-6 as a catalyst. In this case the acetylide ion $\underline{4}$ is believed to react directly with metal to produce the intermediate $\underline{5}$ that was trapped with BuBr furnishing selenide $\underline{6}$d in 36% yield (not optimized).

$$\underset{\underline{4}}{PhC\equiv C^-} + \overline{\lfloor -SeSe_nSe- \rfloor} \longrightarrow PhC\equiv CSeSe_nSe^- \xrightarrow{-Se_{n+1}} \underset{\underline{5}}{PhC\equiv CSe^-} \xrightarrow{BuBr} 6d \qquad (2)$$

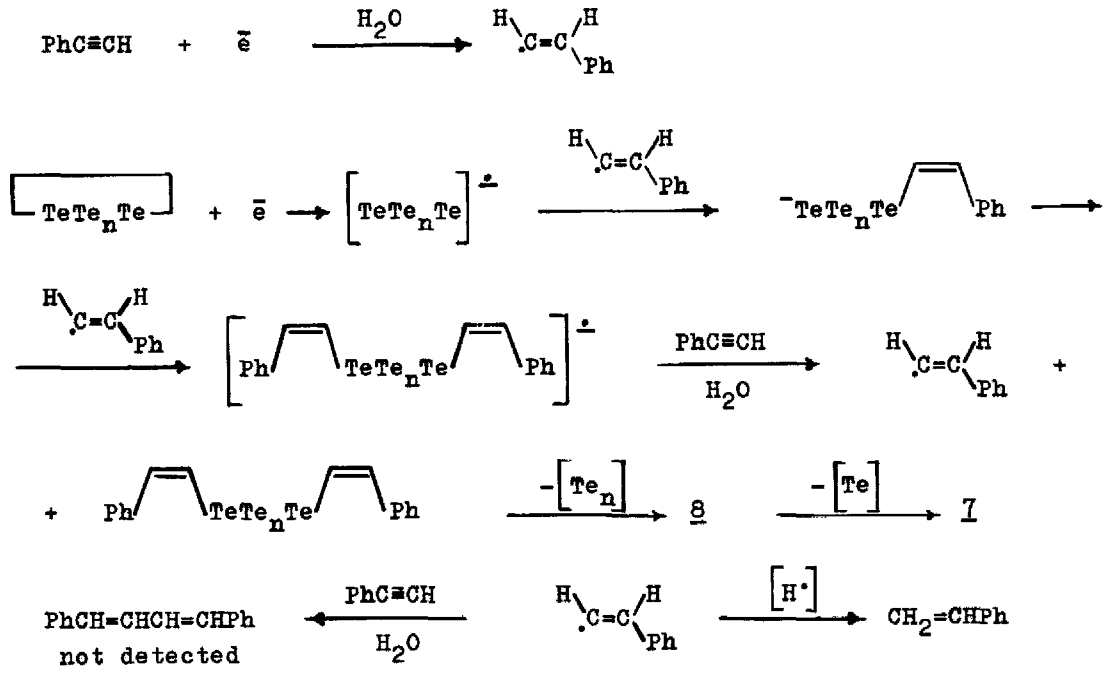
Under the same experimental conditions as above there is no reaction of tellurium metal with phenylacetylene. But this reaction can be initiated by the addition of reducing agents ($SnCl_2$, $N_2H_4 \cdot HCl$, $N_2H_4 \cdot H_2O$) affording telluride $\underline{7}$[5] and ditelluride $\underline{8}$[6] in 15% and 10% yield.



$\underline{7}$ $\underline{8}$

Without $\underline{1}$ only $\underline{8}$ is formed in 2% yield. The addition of hydroquinone inhibits the formation of compounds $\underline{7}$, $\underline{8}$ sharply. An attempt to obtain $\underline{7}$ from Na_2Te and phenylacetylene under similar conditions was unsuccessful.

These results can be rationalized by assuming a radical anion chain mechanism of the nucleophilic addition initiated by the electron transfer from a reducing agent.



According to this scheme styrol and diphenyl butadiene can be formed as by-products. We failed to find diphenyl butadiene in the reaction mixture, but an appreciable amount of styrol was really indicated by GLC analysis (up to 8% of consumed phenylacetylene converted into styrol). That can be considered as an evidence of the radical anion species formation in the reaction.

The sequence of the steps in the above scheme may be different; thus, the tellurium atom elimination from the polytelluride species can occur in any steps. The trans-addition of electron and proton to a triple bond is in accordance with known data[7]. The conversion of ditelluride 8 into telluride 7 in the reaction conditions was proved by experiment.

The use of hydrazine hydrate medium as one phase instead of the water solution allows the yields of compounds 7, 8 to be elevated to 50% and 18%, respectively. The most favourable conditions for the synthesis of telluride 7 include a 10-14-fold mole excess of potassium hydroxide to tellurium and a 1-2-fold excess of KOH for the ditelluride 8 synthesis.

The additives of the reducing agents in the reaction (1) initiate a process of a nucleophilic addition of selenium species to phenylacetylene. In this case along with acetylenic selenides 6a-d Z-alkyl styryl selenides[8] were obtained but with low yields.

Z,Z-Distyryl telluride (7). A mixture of Te (12.8 g), phenylacetylene (20.4 g), KOH (84 g), $N_2H_4 \cdot H_2O$ (120 ml), H_2O (24 ml), toluene (40 ml), and $Alk_3\overset{+}{N}Me\ Cl^-$ (1 g) was heated (100-110 °C) with a stirring of 6 h. The mixture was diluted with water and extracted with benzene. The organic layer was washed with water, dried over K_2CO_3, and evaporated. The residue was dissolved in ether, the ether solution was poured into ethanol and put into refrigerator. After several days yellow crystals of 7 (16.7 g, 50% yield) were separated and dried.

References and Notes

1. Partly presented on the First International Conference on Heteroatom Chemistry, Kobe, Japan, 1987. Abstracts Book, p. 178.
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4. Besides our work[2] the synthesis of selenides 6a, 6b was reported: V.Z.Laishev, M.L.Petrov, A.A.Petrov, Zh. Org. Khim, 18, 514 (1982); J.V.Comasseto, V.Catani, J.T.B.Ferreira, A.L.Braga, J. Chem. Soc., Chem. Commun., 1067 (1986).
5. Earlier telluride 7 was obtained in HMPA medium from tellurium metal and phenylacetylene in 45% yield based on tellurium consumed (9% yield based on taken tellurium, 20% conversion of the metal): V.A.Potapov, N.K.Gusarova, S.V.Amosova, A.A.Tatarinova, L.M. Sinegovskaya, B.A.Trofimov, Zh. Org. Khim., 22, 220 (1986).
6. Ditelluride 8, m.p. 82 °C, IR, cm^{-1}: 3050, 3035, 3000, 2960, 1575, 1465, 1425, 1300, 1280, 740, 485, 460. ^1H-NMR (δ, $CDCl_3$): 7.71 d, 7.31 m, 7.02 d, J = 10.3 Hz. MS (rel. int.): 466 (13), 336 (10), 233 (20), 206 (47), 103 (100).
   Distyryl ditelluride of an unknown configuration was prepared as red oil in the work: M.J.Dabdoub, V.B.Dabdoub, J.V.Comasseto, N.Petragnani, J. Organomet. Chem., 308, 211 (1986).
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8. Z-Alkyl styryl selenides are formed in high yield from dialkyl diselenides and phenylacetylene in the presence of hydrazine hydrate and KOH (the results are to be published).

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