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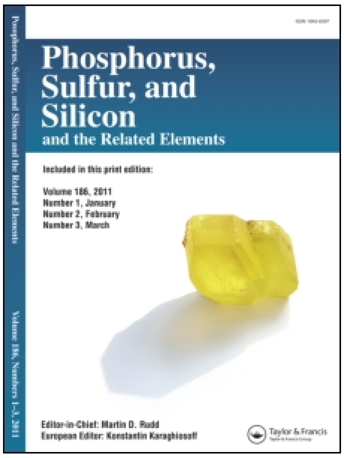

Phosphorus, Sulfur, and Silicon and the Related Elements

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ORGANIC DISELENIDES AND DITELLURIDES: DISPROPORTIONATIONS, SYNTHESIS OF STANNYL SELENIDES, REACTIONS WITH ACETYLENES

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The disproportionation reaction of organic diselenides 1 and ditellurides 2, the synthesis of stannyl selenides 4, and the addition reaction (palladium-catalyzed, thermal) of dialkyl diselenides to acetylenes are discussed.

Keywords: acetylenes, diselenides, ditellurides, stannyl selenides.

Reactions of organic diselenides and ditellurides are the field of our permanent interest[1-5]. Recently we have studied the disproportionation of organic diselenides and ditelluride, the synthesis of stannyl selenides based on diselenides, and the reactions of diselenides and ditellurides with acetylenes.

It is known that homolitic dissotiation of diselenides and ditellurides takes place under irradiation and thermotreatment because of the low energy of the Se-Se and Te-Te bonds. We have shown that the mixture of different diselenides gains the equilibrium with the rate depending on irradiation or temperature. The same is true for the mixture of diselenides and ditellurides. These trends exhibit that the reaction proceeds *via* recombination of the radicals.

Examples of the synthesis of compounds containing the selenium-tellurium bond are very scarce in the literature[5-7]. We have found that tellurenyl selenides **3** in solution at room temperature exist in equilibrium with **1** and **2**. A simple mixing of **1** and **2** in solution leads to the formation of **3**. The process can be monitored by NMR. The isolation of **3** by usual methods is hardly possible due to the reversible exchange reaction.

$$\underset{\mathbf{1}}{\mathrm{RSeSeR}} + \underset{\mathbf{2}}{\mathrm{R'TeTeR'}} \rightleftarrows \underset{\mathbf{3}}{\mathrm{2RSeTeR'}}$$

R = Me, Et, i-Pr, t-Bu, Ph; R' = Me, Et, i-Pr, t-Bu, Ph, 4-MeC_6H_4

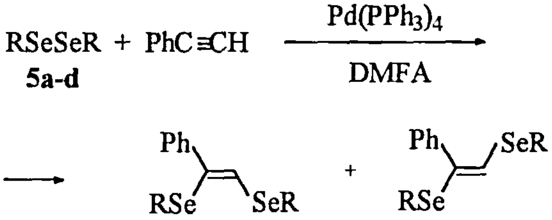
Known stannyl selenides are generally related to compounds containing arylseleno groups, and there are little data concerning stannyl alkyl selenides[8]. We have elaborated the synthesis of stannyl alkyl selenides **4** in 80-90% yield from dialkyl diselenides and chlorostannanes in reductive system $DMSO/N_2H_4{\cdot}H_2O/KOH$. It consists in the reduction of the diselenides to selenolate anions followed by the nucleophilic substitution of chlorine in chlorostannanes by selenolate anions.

$$\mathrm{RSeSeR} \xrightarrow{\mathrm{DMSO/N_2H_4{\cdot}H_2O/KOH}} 2\,\mathrm{RSe^-} \xrightarrow{2\,\mathrm{R'_3SnCl}} \underset{\mathbf{4}}{2\,\mathrm{RSeSnR'_3}}$$

R = Me, Et, i-Pr; R' = Me, Et, Pr, Bu

The reactions of organic diselenides and ditellurides with acetylenes can proceed *via* different mechanisms[1-4,9,10]. The base-catalyzed reaction of organic diselenides with phenylacetylene leads to alkyl phenylethynyl selenides[2]. Organic ditellurides react with acetylenes in the presence of electrophilic reagent (alkyl halides, Lewis acids) in the system KOH/dibenzo-18-crown-6/toluene (benzene) to afford organyl phenylethynyl tellurides (in the case of phenylacetylene[3]) and ethynyl organyl tellurides and bis(organyltelluro)acetylenes (in the case of acetylene[4]).

It is known that the palladium-catalyzed addition reaction of diaryl diselenides to acetylenes proceeds in a *syn* manner[9]. We have studied the reaction of dialkyl diselenides **5a-d** with acetylene, phenylacetylene and 1-hexyne under similar conditions. It has been found that the reaction leads to addition products preferentially of (Z)-stereochemistry, *e.g.*, in the case of phenylacetylene **6a-d** are predominantly formed.



5a-d

6a-d

7a-d

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

The tertiary alkyl diselenide **5d** gives only traces of the adducts with phenylacetylene. A mechanistic proposal includes three steps: oxidative addition of diselenides to Pd(O), the insertion of acetylenes into the Pd-Se bond of a complex thus formed, and reductive elimination of the product. We suggest that the reason why **5d** can not be involved in the reaction is low reactivity of the corresponding tertiary alkyl species (probably due to sterical hindrance) either on the first step or on the second step.

The formation of (Z)-isomers **6a-c** is believed to be the result of the palladium-catalyzed *syn* addition. The (E)-isomers **7a-c** is suggested to form *via* a radical mechanism. In order to estimate a contribution of the radical addition into the yield **6a-d** and **7a-d**, the thermal reaction under the same conditions but in the absence of $Pd(PPh_3)_4$ has been performed. The obtained data corroborated the assumption that (E)-isomers **7a-c** are derived from the radical addition:

Conditions	Yield of 6a-c and 7a-c, %		
	6a/7a	6b/7b	6c/7c
$Pd(PPh_3)_4$, 70-80 °C	55/18	43/12	28/10
70-80 °C	4/16	2.3/11	1.6/10
140 °C	21/75	15/77	10/68

The (E)-isomers **7a-d** considerably predominate over the (Z)-isomers **6a-c** in the thermal reaction. When the thermal reaction is performed at 140 °C (heating of neat **5a-c** and phenylacetylene in a sealed tube), the total yield of **6a-c** and **7a-c** is 78-96%. The reactivity of **5a-d** in the thermal reaction with phenylacetylene decreases in the range: MeSeSeMe > EtSeSeEt > i-PrSeSePr-i >> t-BuSeSeBu-t.

Thus, depending on the reaction conditions either **6a-c** or **7a-c** can be obtained predominantly. In the palladium-catalyzed addition the (Z)-isomers **6a-c** prevail while in the thermal addition the (E)-isomers **7a-c** are predominant.

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