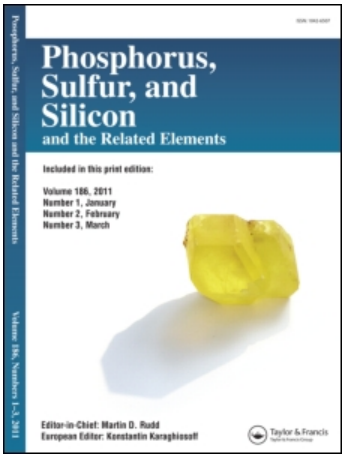

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NOVEL SYNTHESIS OF UNSATURATED ORGANOSELENIUM AND ORGANOTELLURIUM COMPOUNDS BASED ON ORGANIC DICHALCOGENIDES AND ELEMENTAL CHALCOGENS

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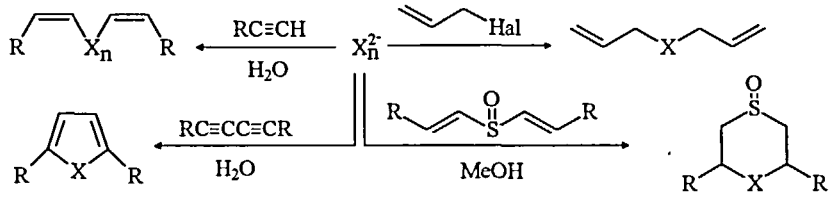
A number of synthetic approaches to unsaturated organoselenium and -tellurium compounds is discussed. The synthesis of unsymmetrical (Z)-1,2-bis(alkylseleno)ethenes from organic diselenides and acetylene as an example of one of these approaches is reported.

Keywords: acetylenes; diselenides; selenides; tellurides.

A number of synthetic approaches to unsaturated organoselenium and -tellurium compounds has been elaborated[1-20].

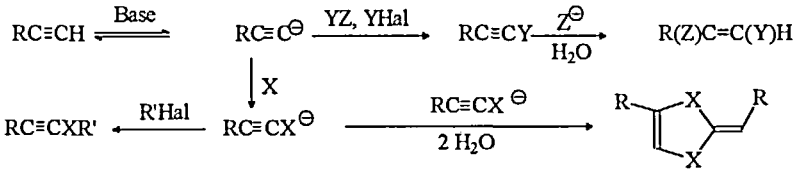
The approach to vinylic selenides and tellurides is based on the generation of chalcogenolate anions *in situ* from organic dichalcogenides in the reductive system $N_2H_4{\cdot}H_2O$/base/water/organic solvent followed by the nucleophilic addition of these anions to acetylenes[2-4].

In the systems reductant/base/water (and/or organic solvent) elemental selenium and tellurium can be used as a source of chalcogenide and dichalcogenide anions[5-9].



X = Se, Te; R = H, Alk, Ar, n = 1, 2

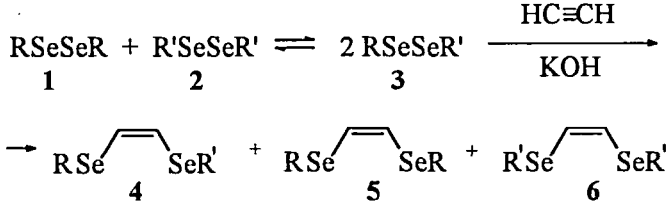
The approach to acetylenic chalcogenides is based on the generation of acetylide anions from acetylenes under phase transfer conditions or in aprotic bipolar solvents followed by the reaction of these acetylide anions with elemental chalcogens[10-14], dialkyl dichalcogenides[15-19] or selenenyl or tellurenyl halides[20].



X = Se, Te; Y, Z = AlkSe, AlkTe, ArSe, ArTe; R = H, Alk, Ar; R' = Alk

Using the latter approach we have recently elaborated the synthesis of (Z)-1,2-bis(alkylseleno)ethenes from organic diselenides and acetylene. We wish to report here the reaction of acetylene with an equilibrated mixture of the organic diselenides as an example of this approach.

The previously unknown unsymmetrical (Z)-1,2-bis(alkylseleno)-ethenes **4** has been obtained in 38-53% yield from acetylene and the equilibrated mixture of the organic diselenides **1**, **2**, and **3**.



R = Me, Et; R' = Bu, t-Bu, Am, Ph

Along with the target products **4**, symmetrical (Z)-1,2-bis-(organylseleno)ethenes **5** and **6** are formed in 18-28% yield. If the difference between organic moiety R and R' is 3 carbon atoms or more, the isolation of **4** from **5** and **6** can be easily performed by distillation.

The reaction is performed under phase transfer conditions in the system KOH/dibenzo-18-crown-6/benzene (toluene) at 90-100 °C The reaction path includes the generation of acetylide anion from acetylene and the rupture of the Se-Se bond by the acetylide anion, e. g.,

$$HC{\equiv}CH + KOH \rightleftharpoons HC{\equiv}CK + H_2O$$

$$HC{\equiv}CK + RSeSeR' \rightarrow RSeC{\equiv}CH + R'SeK \xrightarrow{H_2O} RSe\diagup\!\!=\!\!\diagdown SeR'$$

4

R = Me, Et; R' = Bu, t-Bu, Am, Ph

A simple mixing of two diselenides **1** and **2** in solution at room temperature produces unsymmetrical diselenides **3**[21]. The equilibrium constant of this reaction is close to 4, i. e., the ratio of **1/2/3** is approximately 1:1:2. A statistically expected ratio of **4/5/6** is 2:1:1. This is close to the experimental ratio of **4/5/6**.

This example is of interest since the method allows to obtain predominantly the target unsymmetrical compounds **4** from symmetrical diselenides **1** and **2** using statistical trends.

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