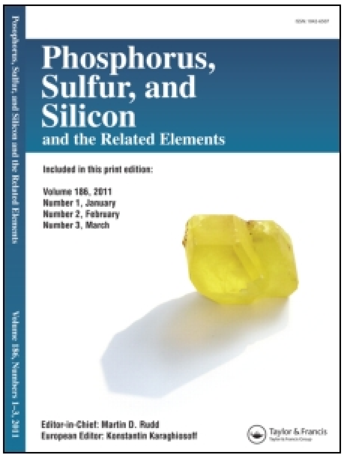

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Vladimir A. Potapov; Svetlana V. Amosova; Boris V. Petrov

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SYNTHESIS BASED ON ELECTROPHILIC SELENIUM REAGENTS AND ACETYLENES

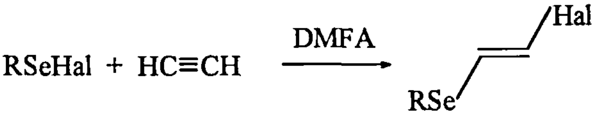
VLADIMIR A. POTAPOV, SVETLANA V. AMOSOVA,
and BORIS V. PETROV
Institute of Chemistry, Siberian Division of
the Russian Academy of Sciences, RUS-664033 Irkutsk, Russia

Reactions of dicyanodiselenide, selenenyl chlorides and bromides with acetylenes and some further transformations of obtained products have been studied.

Keywords: acetylenes, dicyanodiselenide, ethynyl selenides, 2-halovinyl selenides, selenenyl halides.

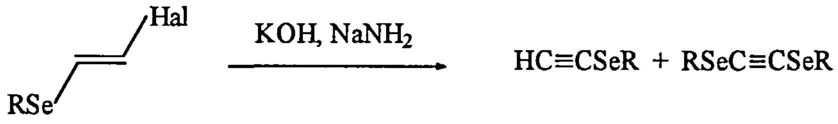
Data concerning selenenyl halides relate to aromatic compounds and little is known about alkaneselenenyl halides[1,2].

We have studied the electrophilic addition of alkaneselenenyl chlorides and bromides to acetylene. The reaction proceeds in a stereospecific manner to afford previously unknown (E)-alkyl 2-halovinyl selenides in high yield.



R = Me, Et, i-Pr, t-Bu; Hal = Cl, Br

The dehydrohalogenation of (E)-alkyl 2-halovinyl selenides leads to alkyl ethynyl selenides and bis(alkylseleno)acetylenes. Depending on the concentration of a base the reaction can be directed either to the predominant formation of alkyl ethynyl selenides (70-85% yield) or exclusively to bis(alkylseleno)acetylenes (up to quantitative yield).



R = Me, Et, i-Pr, t-Bu, Hal = Cl, Br

It has been found that the formation of bis(alkylseleno)acetylenes proceeds *via* alkyl ethynyl selenides under the reaction conditions. Alkyl ethynyl selenides suffer deprotonation under the action of the base and alkylselenoacetylide anion substitutes ethynyl moiety in alkyl ethynyl selenide to form bis(alkylseleno)acetylenes.

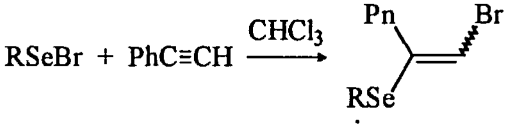
$$\mathrm{RSeC{\equiv}CH} \xrightarrow{\mathrm{NaNH_2}} \mathrm{RSeC{\equiv}CNa}$$

$$\mathrm{RSeC{\equiv}CNa} + \mathrm{RSeC{\equiv}CH} \longrightarrow \mathrm{RSeC{\equiv}CSeR} + \mathrm{HC{\equiv}CNa}$$

R = Me, Et, i-Pr, t-Bu

Alkaneselenenyl halides react with phenylacetylene to give different products depending on the reaction conditions.

Simple mixing of the reagents at room temperature leads to the products of electrophilic addition of alkaneselenenyl chlorides and bromides to phenylacetylene.



R = Me, Et, i-Pr

The structure of (E)- and (Z)-1-alkylseleno-2-bromo-1-phenylethenes has been determined using ^{77}Se NMR and coupling constants $J_{Se\text{-}H}$, which have been shown to be stereospecific[3].

The slow dropwise addition of alkaneselenenyl halides to the mixture phenylacetylene/toluene/KOH/dibenzo-18-crown-6 provides organyl phenylethynyl selenides in 90-98% yield.

$$\mathrm{RSeBr + PhC{\equiv}CH \xrightarrow{KOH/dibenzo\text{-}18\text{-}crown\text{-}6} PhC{\equiv}CSeR}$$

R = Me, Et, i-Pr, t-Bu, Ph

The reaction pathway is suggested to include the generation of phenylacetylide anion from phenylacetylene under the action of the system KOH/dibenzo-18-crown-6 and the nucleophilic substitution of halogen in selenenyl halides by the phenylacetylide anion.

$$\mathrm{PhC{\equiv}CH \xrightarrow{KOH} PhC{\equiv}CK}$$

$$\mathrm{PhC{\equiv}CK + RSeHal \longrightarrow PhC{\equiv}CSeR + KHal}$$

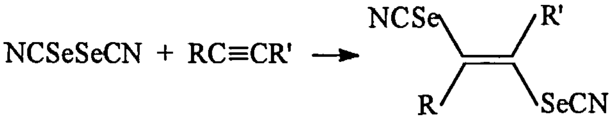
R = Me, Et, i-Pr, t-Bu, Ph

Tellurenyl halides react with phenylacetylene under the phase transfer conditions in similar manner to afford organyl phenylethynyl tellurides in 83-96% yield.

$$\mathrm{RTeBr + PhC{\equiv}CH \xrightarrow{KOH/dibenzo\text{-}18\text{-}crown\text{-}6} PhC{\equiv}CTeR}$$

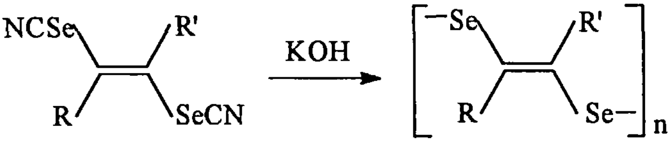
R = Me, Et, i-Pr, Ph

The reaction of dicyanodiselenide with acetylenes proceeds in a stereoselective manner as the electrophilic *anti* addition to furnish (E)-1,2-bis(selenocyanato)ethenes in 78-93% yield.



R = H, R' = H; R = H, R' = Ph; R = Ph, R' = Ph

Under the action of potassium hydroxide (E)-1,2-bis(selenocyanato)-ethenes are converted into polymers containing a diselenide unit between the double bonds.



R = H, R' = H; R = H, R' = Ph; R = Ph, R' = Ph

These polymers are prospective as precursors of conductive materials.

Acknowledgements

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[2.] T. G. Back, in *Organoselenium Chemistry,* edited by D. Liotta (John Wiley & Sons, New York, 1987), Chap. 1, p. 1.

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