

Synthesis of Organochalcogen Compounds Based on Diorganyl Dichalcogenides

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A number of approaches to organochalcogen compounds have been elaborated based on diorganyl dichalcogenides.

Novel efficient methods for the preparation of acetylenic selenides and tellurides have been worked out. The reaction of diorganyl diselenides with acetylenes proceeds under phase transfer conditions at room temperature to afford acetylenic selenides in high yield. The reaction pathway includes the generation of the acetylide anion and its interaction with diorganyl diselenides involving a rupture of the Se-Se bond.

Under the same conditions diorganyl ditellurides do not react with acetylenes. We have proposed a new approach to the intensification of the nucleophilic substitution at tellurium atom consisting in the performance of the reaction in the presence of electrophilic reagents. Based on this approach the syntheses of organyl phenylethynyl tellurides (98% yield), organyl ethynyl tellurides (70% yield) and 1,2-di(organyltelluro)acetylenes (96% yield) from diorganyl ditellurides, acetylenes and iodomethane have been developed.

Organic selenenyl and tellurenyl halides, which are available by halogenolysis of diorganyl dichalcogenides, have been used for the preparation of acetylenic selenides and tellurides.

The electrophilic addition of alkaneselenenyl chlorides and bromides to acetylene has been performed for the first time. The reaction proceeds in a stereoselective manner to afford (E)-alkyl 2-halovinyl selenides in high yield. The dehydrohalogenation of (E)-alkyl 2-halovinyl selenides leads to alkyl ethynyl selenides and bis(alkylseleno)acetylenes. The reaction can be directed either to the preferable formation of alkyl ethynyl selenides (70-85% yield) or exclusively to bis(alkylseleno)acetylenes (up to quantitative yield).

The efficient synthesis of organyl phenylethynyl selenides and tellurides in 90-98% yield by the reaction of phenylacetylene with selenenyl and -tellurenyl halides under phase transfer conditions has been worked out.

A number of methods for the preparation of the compounds containing the chalcogen-heteroatom bond have been elaborated. The synthesis of stannyl chalcogenides by the reaction of triorganotin chlorides with organylchalcogenolate anions generated *in situ* from organic dichalcogenides has been developed. The novel method for the preparation of stannyl selenides, which consists in the interaction of organic diselenides with triorganotin chlorides in the presence of hydrazine hydrate, has been found.

The synthesis of diorganyl dichalcogenides containing different chalcogens in one molecule has been worked out. The disproportionation reaction of the mixed diorganyl dichalcogenides has been studied. It has been found that the ease of this reaction generally rises with increasing atomic number of the chalcogen and with decreasing bulk of the organic moiety.

These results will be presented and discussed in detail.

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