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A synthesis of 1-thia-4-chalcogenacyclohexane-1-oxides and 1,1-dioxides

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Abstract

The addition of selenide and tellurides anions to divinyl sulfoxide and sulfone affords the heterocycles **1**–**4**.

Keywords: Divinyl sulfoxide; Divinyl sulfone; Selenide; Telluride

1. Introduction

Selenide and telluride anions are powerful nucleophiles, which have found application in organic synthesis and for the preparation of organoselenium and tellurium compounds [1–5]. The addition of the selenide and telluride anions to a triple bond affords vinylic selenides and tellurides, which serve as precursors to a variety of useful products [6–8]. The addition of the selenide anion to a carbon–carbon double bond usually proceeds only in the presence of electron-withdrawing substituents, which activate a double bond. However, there are examples of the addition of sodium hydrogen telluride to inactivated double bonds proceeding presumably via a hydrogen atom transfer [9].

Addition reactions involving selenide and telluride anions can be applied for the preparation not only of linear products but of heterocycles as well. The addition of the selenide and telluride anions to 1,3-butadienes provides selenophene, tellurophene and their 2,5-substituted derivatives [10–13]. The reaction of sodium selenide and telluride with diethynyl sulfides gives thiaselenins and thiatellurins [14,15]. The addition of sodium selenide and telluride to ethynyl vinyl sulfoxides and sulfones affords corresponding six-membered heterocycles [16].

2. Results and discussion

Here we report a synthesis of previously unknown 1-thia-4-chalcogenacyclohexane-1-oxides (**1**, **2**) and 1,1-dioxides (**3**, **4**) by the addition of selenide and telluride anions to divinyl sulfoxides and sulfones (Scheme 1).

Previously we have extended a method for generation of selenium and tellurium anions from the elemental chalcogens using tin dichloride and hydrazine hydrate as reducing agents. The systems $SnCl_2(N_2H_4 \cdot H_2O)$–KOH–$H_2O$, $SnCl_2(N_2H_4 \cdot H_2O)$–KOH–aprotic dipolar solvent–H_2O, and $SnCl_2$–KOH–H_2O–solvent–phase transfer catalyst have been applied for the preparation of a variety of organoselenium and tellurium compounds [17–25] including the synthesis of selenophenes and tellurophenes [24,25] by nucleophilic addition of selenide and telluride anions to diacetylenes. However, the attempted preparation of the compounds **1**–**4** in the above systems from the elemental chalcogens and divinyl sulfoxide or sulfone failed probably due to the high sensitivity of divinyl sulfoxide and sulfone to hydrolysis in the presence of potassium hydroxide.

We succeeded in the preparation of the heterocycles **1**–**4** by addition of sodium selenide and telluride to divinyl sulfoxide and sulfone in methanol. The sodium selenide and telluride were prepared by reduction of the elemental selenium and tellurium with sodium in liquid ammonia followed by the evaporation and the addition of methanol. The method of the preparation of alkali metal chalcogenides from the elemental chalcogens and

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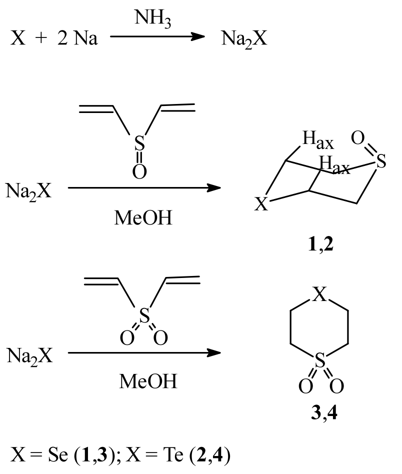

Scheme 1.

sodium in liquid ammonia provides sodium selenide and telluride in almost quantitative yield and with high purity [26].

In spite of the high reactivity of the selenide and telluride anions the yield of **1**–**4** is not too high. A possible reason for the decreased yield is a concurrent addition reaction of selenide and telluride anions to divinyl sulfoxides and sulfones to produce linear oligomers rather than heterocycles **1**–**4**. In general, the dilution of the reaction mixture (i.e. increasing of the methanol amount) favors the formation of heterocycles **1**–**4** and reduces the oligomerization.

It is worthy to note the pronounced difference between the ^{1}H-NMR spectra of the sulfoxides **1**, **2** and the sulfones **3**, **4**. The protons of a methylene group in the sulfoxides **1**, **2** exhibit two signals with considerable chemical shift difference (>1 ppm) between them. It is known that the sulfoxide group in a heterocyclic ring provides an interesting example for studies of the competitive requirements of an oxygen atom vs. an electron pair [27–29]. The axial preference exhibited by the sulfoxide oxygen in six-membered rings is well established [27–29]. The deshielding effect of the sulfoxide group on axial β-hydrogen atoms has been used for assignment of stereochemistry to six-membered ring sulfoxide [27,28]. Drawing a parallel with known data the above mentioned signals have been ascribed to axial and equatorial hydrogen atoms of the fragment CH_2XCH_2 (X = Se, Te). The low-field band has been assigned to axial hydrogen atoms and high-field band has been attributed to equatorial hydrogen atoms. We suppose that the pronounced deshielding of a β-hydrogen, which is *syn* to the S=O bond, is attributed to a proximity effect (Scheme 1).

The oxygen-free analogs of the compounds **1**–**4**, 1,4-thiaselenane and 1,4-thiatellurane, are available compounds [30]. However, it is hardly possible to prepare the compounds **1**–**4** by the action of oxidizing agents on 1,4-thiaselenane and 1,4-thiatellurane since in this case the oxidation of the selenium or tellurium atoms prevails over that of the sulfur atom.

3. Experimental

3.1. General

Divinyl sulfoxide was prepared by oxidation of divinyl sulfide [31] with hydrogen peroxide by known methods [32]. Divinyl sulfone was purchased from Merck.

^{1}H-NMR spectra (400 MHz) were recorded in $CDCl_3$ on a Bruker DPX-400 spectrometer. The chemical shifts are reported in parts per million relative to $SiMe_4$. Mass spectra were obtained on a HP 5971A spectrometer (70 eV).

3.2. Typical procedure for the preparation of the compounds (*1*–*4*)

To a solution of sodium (4.6 g, 0.2 mol) in liquid ammonia (200 ml) the selenium powder was added portionwise until a blue color of the solution had disappeared (7.5 g or 0.095 mol of selenium was consumed). After the evaporation of liquid ammonia the residue was dissolved and cooled to −20 °C in methanol (400 ml) under nitrogen. A solution of divinyl sulfoxide (10.2 g, 0.1 mol) in methanol (150 ml) was added dropwise for 30 min and the mixture was stirred for 3 h at room temperature. The mixture was diluted with ice water and extracted with chloroform. The organic phase was washed with water, dried over K_2CO_3 and the chloroform evaporated. Recrystallization of the residue from ether gave 1-thia-4-selenacyclohexane-1-oxide (**1**). Yield: 11.3 g (65%), m.p.: 133–134 °C. ^{1}H-NMR: δ 3.64 (m, 2H, $CH_{ax}SeCH_{ax}$); 3.20 (m, 4H, CH_2SOCH_2); 2.51 (m, 2H, $CH_{eq}SeCH_{eq}$). MS, *m/z*: 184 [$M^{+\bullet}$]. Anal. Found: C, 26.13; H, 4.63. Calc. for C_4H_8OSSe: C, 26.24; H, 4.40.

1-Thia-4-telluracyclohexane-1-oxide (**2**), m.p.: 143–144 °C. Yield: 60%. ^{1}H-NMR: δ 3.73 (m, 2H, $CH_{ax}TeCH_{ax}$); 3.30 (m, 4H, $CH_2SO_2CH_2$); 2.47 (m, 2H, $CH_{eq}TeCH_{eq}$). MS, *m/z*: 234 [$M^{+\bullet}$]. Anal. Found: C, 20.73; H, 3.48. Calc. for C_4H_8OSTe: C, 20.95; H, 3.59.

1-Thia-4-selenacyclohexane-1,1-dioxide (**3**), m.p.: 214–216 °C. Yield: 62%. ^{1}H-NMR: δ 3.36 (m, 4H, $CH_2SO_2CH_2$); 3.17 (m, 4H, CH_2SeCH_2). MS, *m/z*: 200 [$M^{+\bullet}$]. Anal. Found: C, 24.52; H, 4.12. Calc. for $C_4H_8O_2SSe$: C, 24.13; H, 4.05.

1-Thia-4-telluracyclohexane-1,1-dioxide (**4**), m.p. 232–234 °C (decomp.). Yield: 52%. ^{1}H-NMR: δ 3.45 (m, 4H, ($CH_2SO_2CH_2$); 3.22 (m, 4H, CH_2TeCH_2). MS, *m/z*: 250 [$M^{+\bullet}$]. Anal. Found: C, 19.22; H, 3.31. Calc. for $C_4H_8O_2STe$: C, 19.39; H, 3.25.

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