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SHORT COMMUNICATIONS

Reactions of 1,1-Dichloroethene with Elemental Chalcogens in the System Hydrazine Hydrate–Alkali

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1,1-Dichloroethene (**1**, vinylidene chloride) is an important monomer for the manufacture of chlorine-containing polymers and copolymers [1]. Nucleophilic substitution of the chlorine atoms linked to *sp*^{2}-carbon atom of vinylidene chloride is generally difficult to accomplish; therefore, there are almost no published data on the synthesis of organochalcogen compounds from vinylidene chloride and even from its derivatives. Nevertheless, transformations of **1** into unsaturated chalcogenides may be quite promising from the viewpoint of the design of novel reagents for organochalcogen synthesis, monomers, ligands for complexation with metals, and biologically active compounds.

Elemental selenium and tellurium, as well as sulfur (in most cases), are fairly inert toward many organic compounds. On the other hand, these elements become efficient nucleophiles after preliminary redox activation to the Y_n^{2-} state (Y = S, Se, Te; *n* = 1–4) [2]. Elemental chalcogens are readily activated with the system hydrazine hydrate–alkali [2] (Scheme 1).

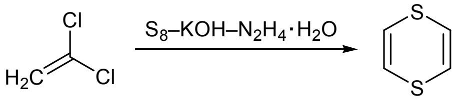
Scheme 1.

$$2Y + N_2H_4 \cdot H_2O + 4KOH \longrightarrow 2K_2Y + N_2 + 5H_2O$$

Selective formation of monochalcogenide ions (Y^{2-}) requires excess alkali (Y–KOH ratio 1:2.5 to 1:8). The resulting chalcogenides can be used in further syntheses without isolation.

Vinylidene chloride reacts with all these chalcogens in the system hydrazine hydrate–KOH under fairly mild conditions (25°C, 3 h), but the products of these reactions were essentially different. In the reaction of **1** with sulfur (as K_2S) we isolated 1,4-dithiine (**2**) as the only product (yield 27%, unoptimized; Scheme 2).

Scheme 2.



1 **2**

Compound **2** is a fairly rare sulfur-containing heterocycle with two sulfur atoms. Sun and Yang [3] previously reported the reaction of **1** with sodium sulfide nonahydrate in acetonitrile in the presence of 15-crown-5, which afforded a mixture of **2** (~15%) and macrocyclic thiacrown ethers (39%). 1,4-Dithiine (**2**) was also obtained in 68% yield from difficultly accessible diethynyl sulfide and Na_2S (prepared from sulfur and sodium metal in liquid ammonia) [4] and in 82% yield from 1,4-dithiane-2,5-diol and thionyl chloride in anhydrous DMF [5]. The procedure for the synthesis of **2** proposed by us is advantageous due to high selectivity, accessibility of the initial compounds, and experimental simplicity.

In the reactions of **1** with selenium and tellurium we isolated diethyl selenide (**3a**, 29%) and diethyl telluride (**3b**, 22%; Scheme 3). The yields of **2** and **3** were calculated with respect to the initial chalcogen.

Scheme 3.

$$\mathbf{1} \xrightarrow{Y\text{–}KOH\text{–}N_2H_4 \cdot H_2O} Et_2Y$$

3a, **3b**

Y = Se, Te.

Thus, sulfide ion reacts with **1** via nucleophilic substitution of the chlorine atoms, whereas the reactions of **1** with selenium and tellurium are accompanied by profound reduction. Reductive substitution of a halogen atom by hydrogen by the action of tellurium nucleophiles has been reported fairly frequently [6]; however, only hydrogenation of double bond in the system hydrazine hydrate–alkali [7] and reduction of activated benzyl halides with RSe^- ions (R = Me, Et, Ph) [8] is known for selenium nucleophiles.

Reductive activation of chalcogens with the system hydrazine hydrate–KOH was achieved according to the procedure described in [2], the Y/KOH ratios being 1:4, 1:5, and 1:8 for sulfur, selenium, and tellurium, respectively. Excess vinylidene chloride (Y/**1** 1:3) was then added to the resulting chalcogenide-containing solution at 25°C, and the product was isolated by extraction with Et_2O. Removal of the solvent from the extract gave almost pure compound **2**, **3a**, or **3b**.

1,4-Dithiine (2). Red liquid, bp 78°C (20.5 mm); published data [9]: bp 77–79°C (15 mm). ^1H NMR spectrum: δ 6.19 ppm, s. ^{13}C NMR spectrum: δ_C 121.20 ppm (cf. [3–5]). Mass spectrum: *m*/*z* 116 $[M]^+$. Found, %: C 41.17; H 3.50; S 54.72. $C_4H_4S_2$. Calculated, %: C 41.35; H 3.47; S 55.18.

Diethyl selenide (3a) and diethyl telluride (3b) were identified by comparing their NMR spectra (^1H, ^{13}C, ^{77}Se, ^{125}Te) with those of authentic samples.

The ^1N, ^{13}C, ^{77}Se, and ^{125}Te NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13, 100.62, 76.31, and 126.2 MHz, respectively, using $CDCl_3$ as solvent and TMS (^1H, ^{13}C), Me_2Se (^{77}Se), or Me_2Te (^{125}Te) as internal standard. The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP5050A instrument (SPB-5 column, 60000×0.25 mm; quadrupole mass analyzer, ion source temperature 190°C, a.m.u. range 34–650).

The main results were obtained using the facilities of the Baikal Joint Analytical Center, Siberian Branch, Russian Academy of Sciences.

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