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Reactions of 2,3-Dichloro-1-propene with Sulfur and Tellurium in the System Hydrazine Hydrate–KOH

E. P. Levanova, V. A. Grabel'nykh, N. V. Russavskaya, L. V. Klyba, E. R. Zhanchipova, A. I. Albanov, O. A. Tarasova, and N. A. Korchevin

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: venk@irioch.irk.ru

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Abstract—2,3-Dichloro-1-propene reacts with sulfur dissolved in the system hydrazine hydrate–KOH (with formation of K_2S_2 or K_2S) to afford bis(2-chloro-1-propene-3-yl)sulfide as the main product in both cases. Under similar conditions tellurium induces β-elimination of both chlorine atoms resulting in the formation of allene and complete regeneration of tellurium metal.

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Reactions of organic dihalides with the alkali metal polychalcogenides M_2Y_n (M = Na, K; Y = S, Se, Te; n = 1–4) is a convenient preparative method for synthesis of the polychalcogenide oligomers and polymers. The so prepared polysulfide oligomers (Y = S) are widely used as hermetics and produced in industrial scale [1]. Selenium- and tellurium-containing oligomers attract the attention of researchers for the design of promising electrotechnical materials [2]. Low-molecular derivatives prepared from dihalides with participation of the alkali metal chalcogenolates RYM (M = Na, K; Y = S, Se, Te) are effective polydentate ligands for complex formation, in particular with the heavy metal ions [3].

As a rule, the reactions of nucleophilic substitution of halogen by chalcogenide function result in the target products in high yields and due to the softness of the reacting nucleophile are rarely followed by elimination of hydrogen halide. However, when using vicinal dihalides, especially for the selenium and tellurium derivatives, β-elimination of halogens and formation of the corresponding olefin is possible [4, 5]. For the sulfur-containing nucleophiles, only a few examples of such elimination are known. Debromination of vicinal dibromides under the action of $Na_2S{\cdot}9H_2O$ was observed in the DMF solution for dibromides in which both bromine atoms were attached to the sp^3-hybridized carbon atom as well as for 1,2-dibromo-1,2-diphenylethene in which the bromine atoms are attached to the double bond [6]. In the latter case, the formation of diphenylacetylene was observed. It is known [7] that halogen atoms at the C=C bond are hardly involved in the substitution or elimination reactions. Contrary to the previous data [4, 5], when studying the reactions of various dihaloalkanes with MeSeLi and PhSeLi in THF the products of substitution were obtained in good yields in all cases [8]. *cis*-1,2-Dichloroethene under similar conditions did not react with lithium methaneselenolate, although substitution of chlorine by the MeSe group occurred for this dichloride in ethanol when equimolar amount of sodium ethylate was added. The authors of [8] did not observe β-elimination neither for dichloro- nor dibromoderivatives. The synthesis of unsaturated selenacrown ethers was successfully performed by the use of Na_2Se (prepared in aqueous solution from selenium, NaOH and rongalite) and *cis*-1,2-dichloroethene in the presence of the phase transfer catalyst [9]. No elimination of chlorine from dichloroethene with the formation of acetylene was detected.

Thus, the course of the reaction of chalcogene-containing nucleophiles with vicinal dihalides is not unequivocal and depends on the nature of halogen, the structure of the dihalide (first of all on the character of hybridization of the carbon atoms the halogens are attached to) and on the nature of halogen in the nucleophilic reagent.

2,3-Dichloro-1-propene (**I**) may serve as an excellent model for investigation of the possibility of substitution and elimination of halogens bound with carbon atoms of different hybridization as a function of the nature of the attacking chalcogenide anion. First of all, we have studied the reactions of dihalide **I** with the sulfur and tellurium anions since for these very anions substantial differences in the course of the nucleophilic reactions were observed [5].

To transform sulfur and tellurium into the anionic form Y_n^{2-} we have used the system hydrazine hydrate–KOH [10]. Elemental sulfur and tellurium are reduced in this system with the formation of potassium polychalcogenides in which the value of *n* is determined by the molar ratio KOH : chalcogene [10].

$$2nY + 4\,KOH + N_2H_4\cdot H_2O \rightarrow 2\,K_2Y_n + N_2 + 5\,H_2O, \quad (1)$$
$$Y = S, Te.$$

At molar ratio KOH : Y = 1 : 1 the predominant formation of dichalcogenide anions S_2^{2-} and Te_2^{2-} (*n* = 2) is observed; in the case of sulfur, when the ratio increases to 2 : 1, the sulfide anions S^{2-} are formed rather selectively. The formation of potassium telluride requires a large excess of alkali (KOH : Y = 8 : 1) [10]. The solutions of K_2S_2, K_2S and K_2Te_2 thus obtained were introduced in the reaction with dichloride **I**.

Taking into account the possibility of the use of disulfides in the synthesis of thiols and other organosulfur compounds [11], we have first studied the reaction of dichloride **I** with sulfur reduced by Eq. (1) to the anions S_2^{2-}. In the result of the reaction, bis(2-chloro-1-propene-3-yl)sulfide (**II**) was obtained in 78% yield.

The data of elemental analysis and chromatomass spectrometry prove that it is sulfide **II** (rather than the anticipated disulfide) which is formed in reaction (2). Such a course of the reaction may be due to instability of disulfides having a halogen atom at the β-carbon atom. The addition of sulfur monochloride to (S_2Cl_2) to olefins is known to give, mainly, the corresponding sulfides [12].

$$2\,CH_2{=}\underset{\displaystyle Cl}{\overset{|}{C}}{-}CH_2Cl \xrightarrow[-2\,KCl\ -S]{K_2S_2} CH_2{=}\underset{\displaystyle Cl}{\overset{|}{C}}{-}CH_2{-}S{-}CH_2{-}\underset{\displaystyle Cl}{\overset{|}{C}}{=}CH_2. \quad (2)$$
I **II**

Apparently, by the same reason in the reaction of 1,2-dibromocyclohexane with sodium disulfide in the system aqueous hydrazine–alkali bis(2-bromocyclohexyl)sulfide (rather than disulfide) is formed [11].

Replacement of potassium disulfide by K_2S in reaction (2) (by using the ratio of KOH : S = 2 : 1 when dissolving sulfur in the system hydrazine hydrate–alkali) does not accelerate the process. The yield of sulfide **II** is even decreased (65%). In this case, a side reaction of alkylation of hydrazine by the starting dichloride **I** proceeds with the formation of (2-chloro-1-propen-3-yl)hydrazine (**III**) in 13% yield.

$$\mathbf{I} + N_2H_4 \xrightarrow[-HCl]{} CH_2{=}\underset{\displaystyle Cl}{\overset{|}{C}}{-}CH_2{-}NHNH_2. \quad (3)$$
III

^{1}H NMR spectrum of the obtained mixture of compounds **II** and **III** contains the signals of hydrazine **III** and sulfide **II**. The signals of the CH_2N or CH_2S protons appear as doublets due to long-range coupling with the olefinic proton in the *trans*-position (^4J = 0.8 Hz for hydrazine **III** and ^4J = 0.9 Hz for sulfide **II**). The signals of the olefinic protons in the *cis*-position to the CH_2N or CH_2S group appear as doublets (^2J = 1.5 Hz for hydrazine **III** and ^2J = 1.4 Hz for sulfide **II**) and those in the *trans*-position as doublets of triplets. It is interesting to note that in hydrazine **III** the olefinic proton in the *trans*-position resonates in a higher field as compared to the *cis*-proton (by 0.03 ppm) whereas in sulfide **II** vice versa, the *trans*-proton is deshielded relative to the *cis*-proton by the same value. The protons of the NH and NH_2 groups give one wide signal at 3.25 ppm.

The signals of both the ^{1}H (3.49 ppm) and ^{13}C (60.68 ppm) of the CH_2N group fall in the ranges corresponding to the signals of the OCH_2 groups [13]. In order to unambiguously prove that these signals correspond namely to the CH_2 group attached to the hydrazine fragment, that is, belong to compound **III**, we have recorded the 2D HETCOR HMBC (^{1}H–^{15}N) spectrum with the *Z*-gradient pulse. The protons of the methylene group give a cross-peak with the ^{15}N atom of the NH_2 group due to spin-spin coupling H_2C–NH–

$^{15}NH_2$ through three bonds [$\delta(_{15}N)$ = –316.8 ppm for $^{15}NH_2$].

With K_2S_2, hydrazine **III** is formed in reaction (2) in 3–5% yield only when excess dichloride **I** is used.

It should be mentioned that in the synthesis of chalcogenoorganic compounds in the hydrazine-containing systems practically no alkylation of the latter occurs [10]. It was shown by an independent experiment that hydrazine **III** is the main product (75% yield) in the reaction of 2,3-dichloro-1-propene **I** with the system hydrazine hydrate–KOH. From this reaction it can be isolated as an individual compound.

As evidenced by the results obtained, nucleophiles S_2^{2-}, S^{2-} and hydrazine in the reactions with dichloride **I** are capable of nucleophilic substitution of the chlorine atom only at the sp^3-hydridized carbon atom, the chlorine atom at the double bond in these reactions remains inert. Compounds **II** and **III** obtained in reactions (2) and (3) are polyfunctional synthons and can be used for preparation of practically valuable substances.

The reaction of potassium ditelluride (generated from tellurium in the system hydrazine hydrate–alkali) with dichloride **I** proceeds clearly and results in elimination of both chlorine atoms with the formation of allene **IV** (yield 78%) and recovery of elemental tellurium (yield 98%).

$$\mathbf{I} \xrightarrow[-2\,KCl;\ -Te]{K_2Te_2} \underset{\mathbf{IV}}{CH_2{=}C{=}CH_2}. \qquad (4)$$

In this reaction we have first followed the relative ability of chlorine atoms attached to carbon atoms of different hybridization, to elimination. This is redox reaction in which ditelluride anion acts as a reducing agent and organic dichloride **I** as an oxidant.

Reaction (4) may serve as a convenient synthetic method for preparation of allene, which is used for synthesis of a huge number of organic products [14]. Laboratory procedures for preparation of allene are based on dehalogenation of 2,3-dichloro- or -dibromo-1-propene with zinc metal, which during the course of the reaction is completely converted into its chloride or bromide and cannot be reused [15]. Quantitative recovery of tellurium in reaction (4) allows its multiple use for preparation of K_2Te_2 by Eq. (1) [16].

Therefore, in the reaction of anions generated from elemental sulfur and tellurium in the system hydrazine hydrate–KOH with 2,3-dichloro-1-propene (**I**) two different processes are observed: nucleophilic substitution of one chlorine atom in the 3 position in the case of sulfur, and elimination of both chlorine atoms in the case of tellurium. The course of the reaction with tellurium is not affected even by the fact that that one of the chlorine atoms is at the double bond and must be inert with respect to nucleophilic reagents. The reasons of different reactivity of the sulfur- and telluriumcontaining nucleophiles are determined both by different reductive ability of the corresponding anions (for tellurium it is much higher), and their size. It is evident, that an increase of the size of the attacking nucleophile in the presence of rather large adjacent group (in the present case, the chlorine atom) leads to steric hindrances to classical nucleophilic substitution.

EXPERIMENTAL

The reactions were monitored and the formed liquid products analyzed by GC using an LKhM 80-MD-2 (column 2000×3 mm, liquid phase DC-550, 5% on Chromaton N-AW-HMDS, linear temperature programming 12 deg min^{-1}, gas carrier helium). IR spectra were recorded in thin layer on a Bruker IFS-25 Fourier spectrometer. ^1H, ^{13}C and ^{15}N NMR spectra were registered on a Bruker DPX 400 spectrometer (working frequency 400.13, 100.62 and 40.55 MHz, respectively) in $CDCl_3$ solutions, internal standard for ^1H, ^{13}C are HMDS, for ^{15}N is CH_3NO_2. Electron impact (70 eV) mass spectra in the range 34–650 D were obtained on a Shimadzu GCMS-QP5050A chromatomass spectro-meter (column SPB-5, 60000×0.25 mm), stationary phase film thickness 0.25 μm; temperature of injector 200–250°C, gas carrier helium, flow rate 0.7 ml min^{-1}, temperature programming from 60 to 200°C, 10 deg min^{-1}, temperature of detector 200°C, quadrupole mass analyzer, temperature of ion source 190°C.

Bis(2-chloro-1-propene-3-yl)sulfide (II). *a.* To the solution of 2.8 g of KOH in 20 g of hydrazine hydrate at 80–85°C 1.6 g of powdered sulfur was added portionwise. The mixture was kept at this temperature during 2.5 h, cooled to room temperature, and 5.6 g of 2,3-dichloro-1-propene **I** was introduced dropwise and stirred for 10 h at 45–50°C. The reaction mixture was extracted with dichloromethane, ether, combined extract dried with $MgSO_4$. By the GC analysis, the residue after removal of solvents was compound **II** of ~90% purity (4.99 g, yield 78%), bp 78–79 °C (4 mm Hg).

IR spectrum, ν, cm^{-1}: 3107, 2972, 2918, 1789, 1627, 1408, 1382, 1209, 1113, 889, 841, 761, 683, 629, 521. ^1H NMR spectrum, δ, ppm: 3.36 d (2H, CH_2S, ^4J = 0.9 Hz), 5.33 d, 5.36 d.t (2H, CH_2=C, ^2J = 1.4 Hz). ^{13}C NMR spectrum, δ, ppm: 38.62 (CH_2S), 114.98 (CH_2=), 137.78 (=CCl). Mass spectrum, *m/z* (for Cl-containing ions, the peaks of ^{35}Cl are given) (*I,* % to total ion current): 147 (17.7) $[M - Cl]^+$, 111 (3.0) $[C_3H_5Cl_2]^+$, 107, 106 (14.1) $[C_3H_4SCl]^+$, $[C_3H_3SCl]^{+\times}$, 85 (2.5) $[C_4H_5S]^+$, 71 (11.1) $[C_3H_3S]^+$, 61 (2.9) $[C_2H_5S]^+$, 45 (29.0) $[CHS]^+$, 39 (19.3) $[C_3H_3]^+$. Found, %: C 39.49; H 4.67; Cl 40.11; S 16.82. $C_6H_8Cl_2S$. Calculated, %: C 39.34; H 4.37; Cl 39.34; S 17.49.

b. To the sulfur solution prepared under the conditions similar to those above in method *a* except for 0.8 g of sulfur was added (molar ratio KOH : S = 2 : 1), 5.6 g of dichloride **I** was introduced, the mixture was stirred for 12 h, cooled and extracted with CH_2Cl_2. After solvent removal the mixture of sulfide **II** and hydrazine **III** was obtained, which was analyzed by GC, GC–MS and ^1H, ^{13}C, ^{15}N NMR spectroscopy using the authentic samples of **II** and **III**.

(2-Chloro-1-propene-3-yl)hydrazine (III). To the solution of 3.0 g of KOH in 22 g of hydrazine hydrate at 35–50°C 4.5 g of dichloride **I** was added dropwise. The mixture was stirred for 10 h at 60–65°C, cooled, extracted with dichloromethane, the extract dried over $MgSO_4$. By the GC analysis, the residue after removal of solvent contained 3.24 g of hydrazine **III**. bp 66–67°C (19 mm Hg). IR spectrum, ν, cm^{-1}: 3407 (sh), 3298, 3189 (sh), 3107, 2973, 2916, 2851, 1789, 1634, 1426, 1385, 1328, 1284, 1254, 1167, 1111, 1061, 894, 804, 711, 632, 604, 409. ^1H NMR spectrum, δ, ppm: 3.25 br.s (3H, NH, NH_2), 3.49 d (2H, CH_2N, ^4J = 0.8 Hz), 5.40 d.t, 5.43 d (2H, =CH_2, ^2J = 1.5 Hz). ^{13}C NMR spectrum, δ, ppm: 60.70 (CH_2N), 115.31 (CH_2=), 138.65 (CCl). Mass spectrum, *m/z* (*I,* % to total ion current): 106 (9.6) $[M]^{+\cdot}$, 78 (3.8) $[M - N_2]^{+\cdot}$, 77 (4.9) $[M - HN_2]^+$, 76 (1.7) $[M - H_2N_2]^{+\cdot}$, 75 (1.0) $[M - H_3N_2]^+$, 71 (14.0) $[M - Cl]^+$, 61 (5.2) $[C_2H_2Cl]^+$, 45 (19.5) $[CH_3N_2]^+$, 39 (39.8) $[C_3H_3]^+$. Found, %: C 34.06; H 6.75; N 25.98; Cl 32.51. $C_3H_7N_2Cl$. Calculated, %: C 33.80; H 6.57; N 26.29; Cl 33.33.

Allene (IV). The reaction flask was charged with 2.8 g of KOH and 40 g of hydrazine hydrate. To the obtained solution heated to 85°C, 6.38 g of tellurium metal was introduced portionwise upon stirring with a magnetic stirrer, the mixture was stirred for 3 h at 85–90°C, cooled to 30°C, the reaction system was joined to two successively connected traps (the first was cooled to –35°C, the calibrated second trap to –70°C) and 2.78 g of dichloropropene **I** was added dropwise. During the course of the reaction the precipitation of tellurium was observed (6.3 g isolated) and the reaction mixture turned from dark-crimson to practically colorless. The formed allene **IV** was condensed in the second trap. The yield of allene **IV** was determined from the volume of the liquid in the trap (1.1 cm^3, d_4^{-70} 0.7064 [14]). Its spectral characteristics are given in our previous paper [16].

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