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was confirmed by chemical-ionization mass spectra of the crude reaction mixtures (for example, the molecular ion $[PrSI+H]^+$ with $m/z \ 203$, $I_{rel} = 60 \%$).

Experimental

 31 P NMR spectra were recorded on a Bruker CXP-100 spectrometer (36.5 MHz) in benzene (with 85 % H₃PO₄ as the external standard). Mass spectra (CI, isobutane, 100 eV) were obtained with a Hitachi M80-B chromatomass spectrometer.

Tripropyl tetrathiophosphate (5a). Crystalline iodine (1.5 g, 5.9 mmol) was added portionwise with stirring at 20 °C to a solution of disulfide **2a** (6.4 g, 42.6 mmol) in 10 mL of benzene, followed by the addition of P_4S_{10} (2.7 g, 6.1 mmol). The mixture was stirred at 60 °C for 4 h. The precipitate was filtered off, and the filtrate was diluted with 30 mL of benzene and washed with a saturated aqueous solution of sodium thiosulfate and then with water. The benzene layer was separated and dried with MgSO₄. The dessicant was filtered off, and the filtrate was kept *in vacuo* (0.1 and 0.02 Torr). Distillation of the residue gave 1.7 g (25 %) of tetrathiophosphate **5a**, b.p. 126–128 °C (0.03 Torr), n_D^{20} 1.5890. ³¹P NMR, δ : 92.6. MS, m/z (I_{rel} (%)): 289 [M+H]⁺ (18) (cf. Ref. 7: b.p. 131–132 °C (0.5 Torr), n_D^{20} 1.5885; ³¹P NMR, δ : 92.5).

Triisopropyl tetrathiophosphate (5b). Analogously, 2.1 g (27 %) of tetrathiophosphate 5b were obtained from P_4S_{10}

(3.0 g, 6.8 mmol), disulfide **2b** (7.1 g, 47.3 mmol), and iodine (1.7 g, 6.7 mmol) (20 °C, 4 h), b.p. 110 °C (0.02 Torr), n_D^{20} 1.5663. ³¹P NMR, δ : 87.1. MS, m/z (I_{rel} (%)): 288 [M]⁺ (30) (cf. Ref. 2: yield 11 %; Ref. 7: b.p. 123–125 °C (0.3 Torr)).

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Isomerization processes in the synthesis of asymmetric allyl chalcogenides

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Allyl-propenyl rearrangement (prototropic isomerization) occurs in the synthesis of allyl organyl chalcogenides in a hydrazine hydrate—KOH system with a 6–10-fold molar excess of KOH. Specificities of the rearrangement that depend on the nature of the chalcogen were studied.

Key words: allyl chalcogenides, isomerization; hydrazine hydrate-KOH system.

Asymmetric dialkyl chalcogenides are obtained by the reduction of diorganyl dichalcogenides in a hydrazine hydrate—KOH system followed by alkylation of the thus formed chalcogenide anions with alkyl halides.¹

We have found that the allyl-propenyl rearrangement (Scheme 1) occurs in the course of the synthesis of asymmetric allyl chalcogenides from diorganyl dichalcogenides as the concentration of alkali in a hydrazine hydrate—KOH system (the molar ratio of R_2Y_2 : KOH = 1 : (6–10)) and the alkylation temperature increase (90–110 °C).

The ratio of isomers 1 and 2 formed depends on the nature of element Y; the degree of isomerization (2:1) decreases in the following order: S (95:5) > Se (53:47)

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> Te (3 : 97) (with all other factors being equal). The total yield of chalcogenides 1 and 2 is 80–90 %. When the R₂Y₂ : KOH ratio is 1 : (1–1.3), the reaction of diorganyl dichalcogenides with hydrazine hydrate and allyl bromide gives only allyl chalcogenides 1 (see Ref. 1).

The treatment of allyl chalcogenides with a hydrazine hydrate—KOH system at the alkylation temperature (90–110 °C) is not accompanied by the allylpropenyl rearrangement; we can conclude that the rearrangement occurs directly in the course of the synthesis, at the step of interaction of chalcogenide anion RY⁻ with allyl bromide. The substitution of the bromine atom in allyl bromide by the anion RY⁻ (Scheme 2) corresponds to the S_N2 mechanism.



In transition state 3 the carbon atom in the reactive center has a partial positive charge, which makes the hydrogen atoms bound with it more mobile. An excess of alkali is likely to favor deprotonation of the transition state, leading finally to rearrangement with simultaneous removal of a Br^- ion (Scheme 3).

Scheme 3



The degree of isomerization of allyl chalcogenides correlates with the value of charge δ^+ on the reaction center in the activated complex 3, which decreases in the following order: $\delta^+_{S} > \delta^+_{Se} > \delta^+_{Te}$.

Propenyl chalcogenides 2 are formed as mixtures of *cis*- and *trans*-isomers with the first isomer predominating (the *cis* : *trans* ratio = 3 : 1 for Y = S, and 5 : 4 for Y = Se); this is determined by the structure of the transition state **4**.

Allyl-propenyl rearrangement was also discovered in the synthesis of asymmetric sulfides from diallyl disulfide when an excess of KOH was used at the reduction step and the reaction was performed at 100-110 °C (Scheme 4).

Scheme 4

$$AII_2S_2 \xrightarrow{KOH, N_2H_4 \cdot H_2O} AIISK \xrightarrow{Mei} AIISMe + MeCH=CHSMe$$

The degree of isomerization does not depend on the duration of the reduction step. This indicates that the rearrangement occurs directly at the reduction step or prior to this step (Scheme 5), that was supported by the experiments.

Scheme 5

$$AII_{2}S_{2} \xrightarrow{+ OH^{-}} AIISS - \overline{C}H - CH = CH_{2} \longrightarrow$$
$$AIISS - CH = CH - \overline{C}H_{2} \xrightarrow{H^{+}} AIISS - CH = CH - Me$$

Thus, the allyl-propenyl rearrangement (prototropic isomerization) occurs in the synthesis of allyl organyl chalcogenides in a hydrazine hydrate—KOH system using a 6—10-fold molar excess of KOH. In this case the isomerization ability of the system hydrazine hydrate — KOH approximately corresponds to that of a 1.67 M solution of NaOEt in ethanol.² However, in the case considered the rearrangement proceeds only in the synthesis of asymmetric allyl chalcogenides.

Experimental

Analysis of the reaction products and determination of the ratio of isomers 1 and 2 was carried out on an LKhM-8MD-2 chromatograph (a 2-m column packed with 5 % XE-60 on Chromaton N-AW-HMDS, helium as carrier gas). The temperature was programmed linearly from 30 to 230 °C at a rate of 12 °C per min).

 1 H NMR spectra were recorded on a Tesla BS 567A instrument (100 MHz) in CDCl₃ with HMDS as the internal standard (Table 1).

Preparative GLC was performed on a PAKhV-07 (a 1000×10 mm stainless column packed with 15 % PEG-20000

RY	B.p./°C (<i>p</i> /Torr)	Yield (%) ^a	¹ H NMR, δ
PhS	75 (3) ^b	93	7.24 (m, 5 H, Ph); 6.19 (m, 2 H, =CH); 1.79 (m, 3 H, Me)
PhSe	77 (2) ^{c,d}	52	7.48, 7.21 (both m, 5 H, Ph); 6.15 (m, 2 H, =CH); 1.78 (m, 3 H, Me)
PhTe	100 (3) ^{c,e}	2.5	7.69, 7.18 (both m, 5 H, Ph); 6.18 (m, 2 H, =CH); 1.78 (m, 3 H, SMe)
MeS	85—90 (740) ^c	63	5.84 (m, =CH); 2.23, 2.19 (s, 3 H, Me, for <i>cis</i> - and <i>trans</i> -isomers, respectively); 1.67 (m, 3 H, CMe)

 Table 1. Characteristics of the propenyl chalcogenides synthesized

^{*a*} According to GLC data. ^{*b*} See Refs. 3 and 5.^{*c*} Boiling point of a mixture with the corresponding allyl derivative. ^{*d*} See Refs. 2 and 3. ^{*e*} See Ref. 3. ¹H NMR for allyl phenyl telluride, δ : 7.64 and 7.15 (both m, 5 H, Ph); 6.00 (m, 1 H, =CH); 4.72 (m, 2 H, =CH₂); 3.53 (d, 2 H, TeCH₂). ^{*f*} See Ref. 5.

on Chezasorb N-AW-HMDS (0.25-0.36), separation temperature 115 °C, carrier gas He).

Synthesis of allyl- and propenyl organyl chalcogenides (general procedure). In a four-necked flask fitted with a stirrer, reflux condenser, thermometer, and a system for introducing the reagents, KOH (0.2 mol) in 50 mL of hydrazine hydrate was placed; the reaction mixture was stirred until the KOH completely dissolved, and it was heated to 90–110 °C. At this temperature 0.02 mol of dichalcogenide was added (KOH : $R_2Y_2 = 10 : 1$),* the mixture was kept for an addi-

* At the ratio KOH : $Ph_2Y_2 = 6$: 1, the isomerizing effect decreases significantly (for Y = S the ratio of 2 : 1 is 10 : 90). At the ratio of KOH : $Ph_2Y_2 > 10$: 1, the degree of isomerization does not change.

tional 2 h, and allyl bromide (0.04 mol) was introduced. The organic layer was separated, dried with $CaCl_2$, and analyzed by GLC.

A nearly pure phenyl propenyl sulfide was isolated by vacuum distillation (see Table 1). Pure phenyl propenyl selenide was isolated using preparative GLC. Phenyl propenyl telluride and methyl propenyl sulfide were identified only in mixtures with the corresponding allyl derivatives.

Allyl phenyl chalcogenides were identified by comparison with the authentic samples obtained by alkylation of diphenyl dichalcogenides with allyl bromide at a KOH : Ph_2Y_2 ratio was 1.3 : 1.0 (see Ref. 3).

Heating All_2S_2 with an excess of KOH (1 : 10) in a solution of hydrazine hydrate (90–110 °C) followed by acidification and storage in air leads to the formation of a mixture of allyl disulfide with a small quantity of allyl propenyl disulfide (~5 % according to GLC).

Characteristics of propenyl chalcogalogenides RYCH=CHMe are given in Table 1. ¹H NMR spectra of only phenyl propenyl selenide are reported,² they are consistent with those obtained in the present work. The signals for protons of the propenyl moiety manifest themselves as multiplets (which are attributed to the presence of *cis*- and *trans*-isomers). In each of them ${}^{3}J_{CH_{3},H}$ and ${}^{4}J_{CH_{3},H}$ appear in addition to the coupling constants from the vicinal olefinic protons.

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