the column was eluted with AcOEt. ^{1}H NMR, δ: 5.85 (d, 1 H, H_β-*cis*, J = 9.3 Hz); 6.15 (d, 1 H, H_β-*trans*, J = 16.3 Hz); 6.62 (dd, 1 H, H_α); 7.50 (m, 5 H) (Ref. 15: ^{1}H NMR ($CHCl_3$), δ: 5.63—6.17 (m, 2 H); 6.44—6.87 (m, 1 H); 7.10—7.55 (m, 5 H)).

***p*-Chlorophenyl vinyl sulfoxide** (**2c**) was isolated by analogy with compound **2a** without repeated separation, but with subsequent distillation *in vacuo*. B.p. 140 °C (0.05 Torr). ^{1}H NMR, δ: 5.89 (d, 1 H, H_β-*cis*, J = 9 Hz); 6.15 (d, 1 H, H_β-*trans*, J = 17 Hz); 6.60 (dd, 1 H, H_α); 7.50 (q, AB system, 4 H).

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A mechanism of the hydrogenation of the double bond in the synthesis of allyl chalcogenides in the hydrazine hydrate—potassium hydroxide system

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Allyl halides react with elemental selenium in the $N_2H_4 \cdot H_2O$—KOH system to give diallyl chalcogenides and allyl propyl chalcogenides. The latter form only in the presence of oxygen when unsaturated intermediates CH_2=$CHCH_2YK$ (Y = S and Se), which are soluble in hydrazine hydrate, are hydrogenated with diimide.

Key words: allyl chalcogenides, synthesis; hydrogenation, mechanism.

Symmetrical diorganyl chalcogenides R_2Y (Y = S, Se, or Te) can be readily synthesized by reaction of elemental chalcogens Y with the $N_2H_4 \cdot H_2O$—KOH system followed by alkylation of chalcogenide anions obtained with organyl halides.[1,2] Unsymmetrical organyl chalcogenides RYR' are formed as a result of generation of organyl chalcogenide anions from diorganyl dichalcogenides R_2Y_2 in the same system with subsequent alkylation with organyl halides.[3–5]

In some cases, reaction of allyl chloride with the Se—$N_2H_4 \cdot H_2O$—KOH system affords not only diallyl selenide but also allyl propyl selenide, the yield of which can be as large as 38%.[6] The authors of Ref. 6 have explained the formation of the latter by hydrogenation

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of one of the double bonds of diallyl selenide with diimide that is generated from hydrazine hydrate. However, since diimide is extremely unstable (its lifetime does not exceed a few seconds[7]), it is unlikely that it was present in the reaction mixture after complete dissolution of selenium and heating of the mixture at 60 °C for 2 h. We established with a great number of examples that diallyl selenide is formed under similar conditions in high yield, giving no admixture of products of hydrogenation of the double bonds.[1–5]

In our opinion, the only reason for allyl propyl selenide to be formed in the synthesis of diallyl selenide[6] is the presence of atmospheric oxygen in the system. Oxygen is involved in the generation of diimide already in the stage of formation of potassium allyl selenide $CH_2=CHCH_2SeK$, which is dissolved in hydrazine hydrate and hydrogenated with diimide to form $MeCH_2CH_2SeK$. The latter reacts with allyl chloride to give unsymmetrical selenide. This assumption was confirmed by us experimentally.

Diallyl selenide was synthesized according to the known procedures[2,6] with introduction of atmospheric oxygen into the reaction mixture and the use of various alkylating agents $CH_2=CHCH_2X$.

$$2\,Se + N_2H_4\cdot H_2O + 4\,KOH \longrightarrow 2\,K_2Se + N_2 + 5\,H_2O$$

$$K_2Se + \underset{\mathbf{1}}{CH_2=CHCH_2X} \xrightarrow{k_1} \underset{\mathbf{2}}{CH_2=CHCH_2SeK} + KX$$

$$\mathbf{1} + \mathbf{2} \xrightarrow{k_2} (CH_2=CHCH_2)_2Se + KX$$

X = Cl, Br, I

Note that at X = Cl, the yield of diallyl selenide amounts to 35% and the main reaction product is allyl propyl selenide (yield 65%), while at X = Br or I, the yield of the latter is not higher than 3—5%. In our opinion, these results are due to the fact that the double bonds of the substrate in the $O_2—N_2H_4\cdot H_2O—KOH$ system are hydrogenated as the substrate and hydrazine hydrate are in the same phase. The selenide **2** that forms is soluble in hydrazine hydrate, and it is selenide **2** that is hydrogenated by diimide generated from hydrazine and atmospheric oxygen.

$$2\,N_2H_4 + O_2 \longrightarrow 2\,N_2H_2 + 2\,H_2O$$

$$\mathbf{2} + N_2H_2 \longrightarrow \underset{\mathbf{3}}{MeCH_2CH_2SeK} + N_2$$

$$\mathbf{3} + \mathbf{1} \longrightarrow CH_2=CHCH_2SeCH_2CH_2Me + KX$$

Under the conditions of continuous generation of diimide in the system, the yield of allyl propyl selenide is determined by the lifetime of potassium allyl selenide **2** in solution, *i.e.*, by the ratio of the rate constant of its formation to that of its transformation into diallyl selenide (k_1 and k_2, respectively).

In many cases, alkyl chlorides in the $N_2H_4\cdot H_2O—KOH$ system react with the Se^{2-} anions faster than bromides do.[2] Apparently, allyl chloride reacts with the Se^{2-} anions quite rapidly, and the more stable potassium allyl selenides **2** that are formed react further with allyl chloride slowly (for X = Cl $k_1 > k_2$). In the presence of diimide, the double bond of selenide **2** has enough time to be hydrogenated. At X = Br or I, an opposite picture is observed, *viz.*, $k_1 < k_2$, and diimide has no time to hydrogenate the double bond of selenolate **2**, which is why, in this case, allyl propyl selenide is practically not formed.

If allyl selenides are removed from the solution in hydrazine hydrate to give a separate organic phase, they do not undergo further hydrogenation. This is confirmed by the synthesis of unsymmetrical allyl chalcogenides R^1YR^2 (Y = S, Se, and Te; $R^1 = CH_2=CHCH_2$; R^2 = Me, Et, Pr^n, Ph, *etc.*) from dialkyl or diaryl dichalcogenides, which is based on generation of chalcogenide anions with subsequent alkylation with allyl halides, where no hydrogenation product is observed both in an inert atmosphere and in the presence of atmospheric oxygen.[3,4] Conversely, thiolate anions generated from allyl mercaptan or selenolate anions generated from diallyl diselenide in the $N_2H_4\cdot H_2O—KOH$ system according to the known procedure[3] in the presence of atmospheric oxygen are alkylated with alkyl halides to give the corresponding saturated dialkyl sulfides or dialkyl selenides in almost quantitative yields. In an inert atmosphere, only the expected alkyl allyl sulfides or alkyl allyl selenides are formed (Table 1).

$$RY \xrightarrow{KOH,\ N_2H_4\cdot H_2O} \underset{\mathbf{4a-d}}{RYK}$$

$$\mathbf{4a{-}d} + R'X \longrightarrow RYR' + KX$$

$$\mathbf{4a,c} + N_2H_2 \longrightarrow MeCH_2CH_2YK \xrightarrow[-KX]{R'X} MeCH_2CH_2YR'$$

RY = AllSH (**a**), EtSSEt (**b**), AllSeSeAll (**c**), Bu^{n}SeSeBu^n (**d**); R'X = EtBr, Bu^{n}Br, AllCl

Thus, the double bond of potassium allyl chalcogenides dissolved in hydrazine hydrate is hydrogenated

Table 1. Synthesis of unsymmetrical dialkyl chalcogenides and alkyl allyl chalcogenides from RY and R'X in the $N_2H_4\cdot H_2O—KOH$ system

RY	R'X	RY : R'X	Medium	RYR'	Yield (%)
AllSH	EtBr	1 : 1	N_2	AllSEt	95
AllSH	EtBr	1 : 1	O_2	Pr^{n}SEt	94
EtSSEt	AllCl	1 : 2	N_2	AllSEt	93
EtSSEt	AllCl	1 : 2	O_2	AllSEt	87
AllSeSeAll	Bu^{n}Br	1 : 2	N_2	AllSeBu	73
AllSeSeAll	Bu^{n}Br	1 : 2	O_2	Pr^{n}SeBu	72
Bu^{n}SeSeBu^n	AllCl	1 : 2	N_2	AllSeBu	68
Bu^{n}SeSeBu^n	AllCl	1 : 2	O_2	AllSeBu	65

in the synthesis of allyl chalcogenides in the Y—$N_2H_4 \cdot H_2O$—KOH system in the presence of atmospheric oxygen, which can explain why subsequent alkylation gives both alkyl allyl and unsymmetrical dialkyl chalcogenides.

Experimental

The reaction products were analyzed by GLC on an LKhM-8MD-2 chromatograph (stainless steel column (2000×3 mm), liquid phase XE-60, 5% on Chromaton-N-AW-HMDS, helium as carrier gas). The temperature was programmed linearly from 30 to 200 °C at a rate of 12 deg per min. ^{1}H NMR spectra were obtained on a Tesla BS 567 A instrument (100 MHz) in $CDCl_3$ (HMDS as the internal standard).

Synthesis of allyl chalcogenides (general procedure). Reactions were carried out in a flask equipped with an effective stirrer, a reflux condenser, a dropping funnel or a tube for introduction of selenium, and a bubbling tube for inlet of either CO_2-free air or nitrogen. Temperature conditions and ratio of reagents correspond to the literature data.[2,3,6]

Diallyl selenide was obtained by dissolution of selenium (11.1 g) in the $N_2H_4 \cdot H_2O$—KOH system in an atmosphere of nitrogen (or argon) with subsequent alkylation by allyl chloride (21.4 g). The organic layer was washed, dried, and distilled to give the target product (95%); b.p. 67—70 °C (50 Torr), which coincides with the literature data.[2]

Allyl propyl selenide in a mixture with diallyl selenide was obtained similarly, but in an air atmosphere. Yield according to GLC was ~65%. The characteristics of the product isolated by preparative GLC coincide with the literature data.[6]

Unsymmetrical allyl and propyl chalcogenides (see Table 1) were obtained according to the procedures described earlier.[3,8] Pure allyl derivatives were obtained in a flow of an inert gas. **Allyl ethyl sulfide**: b.p. 120 °C, n_D^{20} 1.4837. Found (%): C, 58.76; H, 9.73; S, 31.45. $C_5H_{10}S$. Calculated (%): C, 58.82; H, 9.80; S, 31.30. ^{1}H NMR, δ: 1.19 (t, 3 H, CH_3); 2.65 (q, 2 H, $C\underline{H}_2CH_3$); 3.49 (m, 2 H, $CH_2C=C$); 4.95 (m, 2 H, $=CH_2$); 5.80 (m, 1 H, $-CH=$). **Allyl butyl selenide**: b.p. 170 °C. Found (%): C, 47.23; H, 7.95; Se, 44.82. $C_7H_{14}Se$. Calculated (%): C, 47.19; H, 7.87; Se, 44.94. ^{1}H NMR, δ: 1.00 (t, 3 H, CH_3); 1.40—1.90 (m, 4 H, CCH_2C); 2.64 (t, 2 H, $SeC\underline{H}_2CH_2$); 3.15 (d, 2 H, $SeC\underline{H}_2CH=CH_2$); 4.96 (dd, 2 H, $=CH_2$); 5.82 (m, 1 H, $-CH=$).

Propyl selenides and propyl sulfides were isolated with minor admixtures of the corresponding alkyl allyl sulfides(selenides). Their yields were calculated from GLC data and from ^{1}H NMR spectra by comparing them with the spectra of authentic samples. The ^{1}H NMR spectra of allyl chalcogenides exhibit signals of the allyl groups (δ 3.15—5.85), the integral intensity of which was used for calculation of the content of allyl ethyl sulfide in a mixture with ethyl propyl sulfide[9] or allyl butyl selenide in a mixture with butyl propyl selenide.[8]

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