ISSN 1070-4280, Russian Journal of Organic Chemistry, 2015, Vol. 51, No. 2, pp. 161–166. © Pleiades Publishing, Ltd., 2015.
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Features of the Synthesis of Unsaturated Sulfides Proceeding from (2-Chloroprop-2-en-1-yl)isothiouronium Chloride

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Received October 2, 2014

Abstract—Procedure of synthesis of sulfides containing a chloropropenyl fragment sensitive to bases was modified. The change in the sequence of reagents addition ensuring a contact of isothiouronium salt with a minimal base quantity and the application of a mixture hydrazine hydrate–alkali allowed the preparation of target sulfides under mild conditions in up to 93% yields.

DOI: 10.1134/S1070428015020037

Organic sulfides have versatile technical applications as additives to lubricants, corrosion inhibitors, extraction agents, polymer stabilizers, vulcanizing reagents, odorants of technical gases [1]. The structural fragment of organic sulfides C–S–C is present in the composition of many drugs and pesticides [1, 2]. Sulfides are especially important as synthons in organic synthesis [2, 3]. The synthetic potential of sulfides is significantly increased by introducing in their structure multiple bonds and functional groups [4]. For instance, the presence in the molecule of 2-chloro-1-propen-3-yl fragment makes it possible to prepare highly reactive allenyl and propynyl sulfides [4]. However the easily occurring dehydrochlorination in this fragment at treating with bases curbs the preparation of the corresponding sulfides using 2,3-dichloro-1-propene [5].

Alkali metals thiolates, the most important reagents in the synthesis of unsymmetrical sulfides, readily form at treating isothiouronium salts with alkali [6]. In view of the high ability of thiolates to oxidation at the contact with air oxygen *one-pot* processes were developed for the preparation of unsymmetrical sulfides from isothiouronium salts [7, 8]. In [7] *S*-alkylisothiouronium salts were decomposed under the action of a strong base (NaH or C_2H_5ONa) in anhydrous solvent (THF or anhydrous C_2H_5OH). The target sulfides were obtained by adding to the thiolate solution at boiling the corresponding alkyl halide. In [8] a phase-transfer catalyst (tetrabutylammonium bromide) was utilized that was stirred with a mixture of isothiouronium salt, aqueous alkali, benzene, and organic halide at room temperature in a stream of nitrogen.

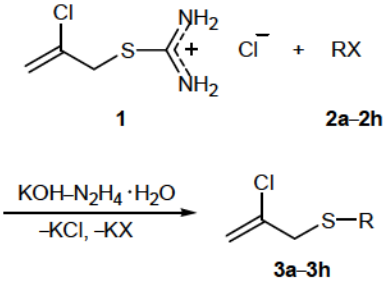
However both these procedures cannot be applied to the synthesis of unsymmetrical sulfides from (2-chloroprop-2-en-1-yl)isothiouronium chloride since its contact with alkali not only causes the cleavage of the isothiouronium group but also induces the already mentioned dehydrochlorination leading to the formation of highly reactive allene and acetylene structures. The latter are involved in further transformations to give a complex mixture of products. Both methods described in [7, 8] include the contact of isothiouronium salts with excess base.

Thus the use of the known approaches proved to be impossible for the synthesis of 2-chloroprop-1-en-3-yl sulfides.

In order to prepare unsymmetrical sulfides from (2-chloroprop-2-en-1-yl)isothiouronium chloride **1** we applied the succession of reagents addition which in the total course of the reaction ensured the contact of salt **1** with a minimal quantity of alkali. In the developed procedure to the mixture of isothiouronium salt **1** with the organic halide **2a**–**2h** a solution of KOH in hydrazine hydrate is gradually added. The reaction is carried out at 20–25°C, and the presence in the

reaction mixture of a strong reducer, hydrazine, inhibits the side oxidation with air oxygen of the intermediate thiolates (Scheme 1).

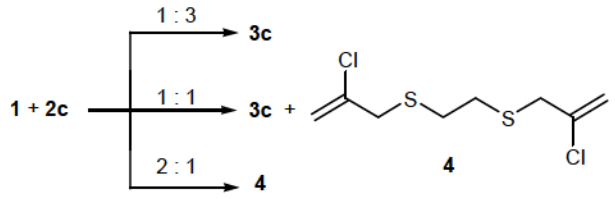
Scheme 1.



R: **2**, R = C_3H_7, X = Br (**a**); X = Cl, R = CH_2CH_2OH (**b**), CH_2CH_2Cl (**c**), $CH_2C(Cl)=CH_2$ (**d**), $CH_2CH=CHCl$ (**e**); R = $CH_2CH=CH_2$, X = Br (**f**); X = Cl, R = CH_2Ph (**g**), CH_2COOH (**h**); **3**, R = C_3H_7 (**a**), CH_2CH_2OH (**b**), CH_2CH_2Cl (**c**), $CH_2C(Cl)=CH_2$ (**d**), $CH_2CH=CHCl$ (**e**), $CH_2CH=CH_2$ (**f**), CH_2Ph (**g**), CH_2COOH (**h**).

Reagents **1** and **2** were used in equimolar quantities. In event of 1,2-dichloroethane **2c** at the equimolar reagents ratio two products were obtained: unsymmetrical sulfide **3c** and the product of the replacement of both chlorine atoms in dichloroethane by the 2-chloroprop-1-en-3-yl residue, compound **4**. The ratio of compounds **3c** and **4** varies from 4 : 1 to 5 : 1 and depends on the rate of the addition of KOH solution in hydrazine hydrate. At faster addition a larger amount of bissulfide **4** is obtained. At the reagents ratio **1**–**2** 2 : 1 symmetric bissulfide **4** formed in a 76% yield (Scheme 2).

Scheme 2.



We formerly obtained compound **4** by a reaction of 2,3-dichloro-1-propene with ethanedithiolate at 0°C (yield 68%) [9]. The preparation of bissulfide **4** by the reaction shown in Scheme 2 has obvious advantages in the temperature condition and the product yield.

Sulfide **3b** prepared along Scheme 1 was described in [10]. It was formerly synthesized in 83% yield by the reaction of 2,3-dichloro-1-propene with an equimolar mixture of mercaptoethanethiol and sodium hydroxide. The method developed in this study makes it possible to prepare sulfide **3c** in 87% yield and excludes the application of mercaptoethanol, a substance with an extremely unpleasant odor.

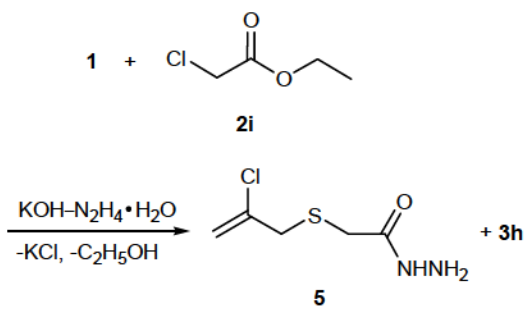
Reaction of isothiouronium salt **1** with 2,3-dichloropropene **2d** results in a symmetric sulfide **3d** that has been previously prepared by treating the 2,3-dichloropropene with potassium disulfide which in its turn has been obtained in 78% yield from elemental sulfur and KOH in hydrazine solution, therefore the process has been accompanied with the formation of 2-chloro-1-propenylhydrazine [11]. In our procedure the yield of sulfide **3d** is higher, and it is isolated from the reaction mixture in practically pure state. 1,3-Dichloropropene **2e**, same as sulfide **3e** obtained from it, is a mixture of *Z*- and *E*-isomers in the ratio 1 : 0.9 (according to ^{1}H NMR data).

Sulfide **3g** we obtained earlier by the reaction of 2,3-dichloro-1-propene **2d** with dibenzyl disulfide in the system hydrazine hydrate–KOH at –10 to –20°C in a 60% yield [12]. The higher yield of sulfide **3g** obtained at the use of benzyl chloride **2g** along the modified procedure (Scheme 1) and the more preparatively convenient temperature of the process (25°C) show the advantages of the developed method.

Chloroacetic acid **2h** selectively reacts with isothiouronium salt **1** affording sulfide **3h** containing a carboxy group whose presence provides a possibility of further functionalization of the obtained sulfide.

However bringing into the reaction ethyl chloroacetate **2i** even at lower temperature (15–20°C) led to the formation of a mixture of sulfide **5** (yield 60%) containing a hydrazide group and sulfide **3h** (yield 11%) (Scheme 3).

Scheme 3.

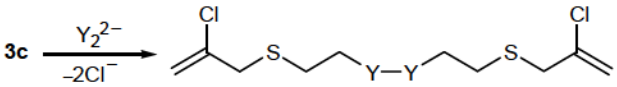


Evidently under the reaction conditions the ester moiety readily suffers the attack of nucleophilic reagents, hydrazine and HO^-. The obtained compounds

5 and **3h** were easily separated. Sulfide **5** was extracted with dichloromethane from the reaction mixture containing the base (hydrazine), further acidifying of the raffinate (to pH 1.0) allowed extracting sulfide **3h**.

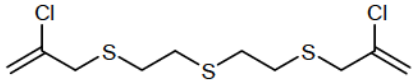
By an example of sulfide **3c** we showed the prospects of application of compounds obtained to the organic synthesis. In reactions of compound **3c** with dichalcogenide anions generated from elemental chalcogens in the system hydrazine hydrate – base [13], the corresponding disulfide **6a** and diselenide **6b** derivatives were obtained in 60 and 76% yields respectively (Scheme 4).

Scheme 4.



6a, **6b**

In the synthesis of disulfide **6a** the disulfide anions (S_2^{2-}) were obtained by the use of the system hydrazine hydrate–monoethanolamine, diselenide **6b** was prepared in the system hydrazine hydrate–KOH [13]. In the synthesis of disulfide **6a** a side product monosulfide **7** was identified by GC-MS method, in the synthesis of diselenide **6b** by ^{77}Se NMR traces of triselenide **8** were found.



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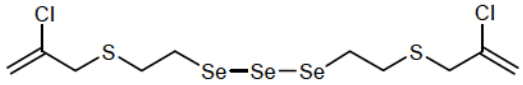

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Compounds **6a** and **6b** beside the chloropropenyl fragments contain bonds S–S and Se–Se easily suffering the reductive cleavage, therefore these compounds are promising reagents for organochalcogen synthesis.

The structure of obtained compounds was confirmed by IR, ^{1}H, ^{13}C, ^{77}Se NMR spectroscopy and chromato-mass spectrometry. IR spectra of all synthesized compounds containing 2-chloropropenyl fragment are characterized by a strong band at 1627–1628 cm^{-1} ($\nu_{C=C}$).

Hence we have developed a method for preparation of sulfides containing a chloropropenyl moiety of a high synthetic potential. The method utilizes accessible reagents, is carried out in mild conditions and does not require the use of inert atmosphere. The developed approach may be used in the syntheses of other unsymmetrical sulfides containing fragments labile in the presence of bases.

EXPERIMENTAL

The purity of initial organic halides was checked and the analysis of the products obtained was performed on a chromatograph LKhM 80-MD-2 (column 2000 × 3 mm, stationary phase silicone XE-60, 5% on Chromaton N-AW-HMDS, ramp from 30 to 230°C at a rate 12 deg/min, carrier gas helium). IR spectra were recorded on a spectrophotometer Bruker IFS-25 from thin layer. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were registered on a spectrometer Bruker DPX-400 (operating frequencies 400.13, 100.61, and 76.31 MHz respectively) in $CDCl_3$, internal reference TMS, for $^{77}Se(CH_3)_2$ Se.

Mass spectra were obtained on a GC-MS instrument Shimadzu GCMS-QP5050A (column SPB-5, 60000 × 0.25 mm), the stationary phase 0.25 μm thick, injector temperature 250°C, carrier gas helium, flow rate 0.7 mL/min, ramp from 60 to 260°C at a rate 15 deg/min. Detector temperature 250°C, quadrupole mass analyzer, electron impact, electrons energy 70 eV, temperature of the ion source 200°C, range of detected masses 34–650 Da.

(2-Chloroprop-2-en-1-yl)isothiouronium chloride **1** was prepared from 2,3-dichloroprop-1-ene **2d** and thiourea [14].

Unsymmetrical sulfides. General procedure. To a mixture of 3 g (16 mmol) of isothiouronium salt **1** and 16 mmol of organic halide **2a**–**2h** was added dropwise at stirring a solution of KOH in hydrazine hydrate (molar ratio **1**–KOH 1 : 2). The reaction mixture was stirred for 10.5 h at 20–25°C. The mixture was diluted with 30 mL of water and extracted with dichloromethane (3 × 30 mL) and once with ether. The combined extracts were dried with $MgSO_4$. On removing the solvent the target product was isolated from the residue.

2-Chloro-3-(propylsulfanyl)prop-1-ene (3a). Yield 61%, bp 52–54°C (4 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.98 t (3H, CH_3, ^3J 7.3 Hz), 1.60 sextet (2H, CCH_2C, ^3J 7.3 Hz), 2.48 t (2H, S$\underline{CH_2}$Et, ^3J 7.3 Hz), 3.34 s (2H, $=CCH_2S$), 5.28 d, 5.35 d (2H,

CH_2=, ^2J 1.3 Hz). ^{13}C NMR spectrum, δ, ppm: 13.45 (Me), 22.49 ($\underline{C}H_2Me$), 33.64 ($S\underline{C}H_2Et$), 39.86 (=$C\underline{C}H_2S$), 114.08 (=CH_2), 138.89 (=CCl). Mass spectrum, *m/z* (I_{rel}, %): 152 (5.5) $[M]^{+\bullet}$ (^{37}Cl), 150 (15.2) $[M]^{+\bullet}$ (^{35}Cl), 123 (0.7) $[M - Et]^+$ (^{37}Cl), 121 (2.2) $[M - Et]^+$ (^{35}Cl), 110 (1.4) $[M - C_3H_6]^{+\bullet}$ (^{37}Cl), 108 (4.1) $[M - C_3H_8]^{+\bullet}$ (^{35}Cl), 85 (15.4) $[C_4H_5S]^+$, 75 (9.4) $[C_3H_4Cl]^+$ (^{35}Cl), 74 (23.4) $[C_3H_4S]^+$, 73 (8.7) $[C_3H_3S]^+$. Found, %: C 47.95; H 7.63; Cl 23.38; S 20.96. $C_6H_{11}ClS$. Calculated, %: C 47.83; H 7.36; Cl 23.53; S 21.28.

2-Chloro-3-(2'-hydroxyethylsulfanyl)prop-1-ene (3b). Yield 87%, bp 92°C (3 mmHg) {92–95°C (3 mmHg) [10]}. IR spectrum, ν, cm^{-1}: 3369 (OH), 1628 (C=C) {3355 (OH), 1635 (C=C) [10]}. ^{1}H NMR spectrum, δ, ppm: 2.67 br.s (1H, OH), 2.72 t (2H, $S\underline{C}H_2CH_2OH$, ^3J 6.1 Hz), 3.39 s (2H, SCH_2C=), 3.73 t (2H, OCH_2, ^3J 6.1 Hz), 5.30 br.s (1H), 5.38 br.s (1H, CH_2=). ^{13}C NMR spectrum, δ, ppm: 34.32 ($S\underline{C}H_2CH_2OH$), 39.61 ($S\underline{C}H_2C$=), 60.56 (CH_2O), 114.75 (=CH_2), 138.44 (=CCl). Mass spectrum, *m/z* (I_{rel}, %): 154 (4.7) $[M]^{+\bullet}$ (^{37}Cl), 152 (13.1) $[M]^{+\bullet}$ (^{35}Cl), 123 (1.3) $[M - CH_2OH]^+$ (^{37}Cl), 121 (3.8) $[M - CH_2OH]^+$ (^{35}Cl), 109 (1.6) $[M — CH_2CH_2OH]^+$ (^{37}Cl), 108 (4.7) $[M - EtOH]^{+\bullet}$ (^{37}Cl), 107 (2.4) $[M - CH_2CH_2OH]^+$ (^{35}Cl), 106 (6.6) $[M -– EtOH]^{+\bullet}$ (^{35}Cl), 99 (1.8) $[C_5H_7S]^+$, 85 (12.7) $[C_4H_5S]^+$, 79 (0.8) $[C_3H_6Cl]^+$ (^{37}Cl), 77 (4.5) $[C_3H_6Cl]^+$ (^{35}Cl) and $[C_3H_4Cl]^+$ (^{37}Cl), 76 (2.8) $[C_3H_6S]^{+\bullet}$, 75 (6.6) $[C_3H_4Cl]^+$ (^{35}Cl), 73 (2.7) $[C_3H_3S]^+$, 71 (2.7), 61 (2.0), 59 (2.4), 49 (1.8), 47 (4.6). Found, %: C 39.69; H 5.86; Cl 23.37; S 21.02. C_5H_9ClOS. Calculated, %: C 39.34; H 5.91; Cl 23.23; S 21.00.

2-Chloro-3-(2'-chloroethylsulfanyl)prop-1-ene (3c) was obtained from isothiouronium salt **1** and organic halide **2c**, 1 : 3. Yield 90%, bp 94–98°C (5 mmHg). ^{1}H NMR spectrum, δ, ppm: 2.86 t (2H, $S\underline{C}H_2CH_2Cl$, ^3J 7.0 Hz), 3.41 s (2H, SCH_2C=), 3.63 t (2H, CH_2Cl, ^3J 7.0 Hz), 5.33 br.s (1H), 5.39 br.s (1H, CH_2=). ^{13}C NMR spectrum, δ, ppm: 33.40 ($S\underline{C}H_2CH_2$), 40.15 ($S\underline{C}H_2C$=), 42.81 (CH_2Cl), 115.09 (CH_2=), 138.23 (=CCl). Mass spectrum , *m/z* (I_{rel}, %): 174 (1.5), 172 (8.4), 170 (11.5) $[M]^{+\bullet}$ (^{37}Cl and ^{35}Cl), 137 (1.4) $[M - Cl]^+$ (^{37}Cl), 135 (4.5) $[M - Cl]^+$ (^{35}Cl), 123 (2.6) $[M - CH_2Cl]^+$ (^{37}Cl), 121 (7.0) $[M - CH_2Cl]^+$ (^{35}Cl), 109 (1.5) $[M - CH_2CH_2Cl]^+$ (^{37}Cl), 107 (2.0) $[M - CH_2CH_2Cl]^+$ (^{35}Cl), 96 (2.6) $[C_2H_3ClS]^{+\bullet}$ (^{37}Cl), 94 (6.9) $[C_2H_3ClS]^{+\bullet}$ (^{35}Cl), 85 (13.1) $[C_4H_5S]^+$, 77 (3.0) $[C_3H_4Cl]^+$ (^{37}Cl), 75 (6.8) $[C_3H_4Cl]^+$ (^{35}Cl), 73 (2.8) $[C_3H_3S]^+$, 71 (2.7), 63 (3.0), 49 (1.5), 47 (1.4). Found, %: C 35.06; H 4.56; Cl 41.44; S 18.96. $C_5H_8Cl_2S$. Calculated, %: C 35.10; H 4.71; Cl 41.45; S 18.74.

Bis(2-chloroprop-1-en-3-yl) sulfide (3d). Yield 88%, bp 78–79°C (4 mmHg) {78–79°C (4 mmHg) [11]}. Spectral characteristics and elemental analysis data are completely consistent with published findings [11, 12].

2-Chloro-3-(1-chloroprop-1-en-3-ylsulfanyl)-prop-1-ene (3e) was obtained as a mixture of *Z*- and *E*-isomers in a ratio 1 : 0.9. Yield 93%, bp 64–65°C (2 mmHg). IR spectrum, ν, cm^{-1}: 1636, 1628 (C=C). ^{1}H NMR spectrum, δ, ppm, *Z*-isomer: 3.32 d.d (2H, $S\underline{C}H_2CH$=, ^3J 7.4, ^4J 1.3 Hz), 3.34 br.s (2H, $S\underline{C}H_2CCl$=), 5.31 d (1H, *Z*-$\underline{C}H$=$CClCH_2$, ^2J 1.4 Hz), 5.42 d.t (1H, *E*-$\underline{C}H$=$CClCH_2$, ^2J 1.4 Hz), 5.84 d.t (1H, $SCH_2\underline{C}H$=CHCl, $^3J_{cis}$ 7.1, $^3J_{CH-CH2}$ 7.4 Hz), 6.16 d.t (1H, SCH_2CH=$\underline{C}H$Cl, $^3J_{cis}$ 7.1, $^3J_{trans}$ 13.2 Hz); *E*-isomer: 3.13 d.d (2H, $S\underline{C}H_2CH$=CH, ^3J 7.6, ^4J 1.2 Hz), 3.32 br.s (2H, CH_2CCl=), 5.30 d (1H, *Z*-$\underline{C}H$=C(Cl)-CH_2, ^2J 1.4 Hz), 5.34 d.t [1H, *E*-$\underline{C}H$=C(Cl)CH_2, $^2J \approx {}^4J \approx$ 1.4 Hz), 5.88 d.t (1H, $CH_2\underline{C}H$=CH, $^3J_{CH-CH2}$ 7.6, $^3J_{trans}$ 13.2 Hz), 6.07 d.t (1H, CH_2CH=$\underline{C}H$, $^3J_{trans}$ 13.2, $^4J_{CH-CH2}$ 1.2 Hz). ^{13}C NMR spectrum, δ, ppm, *Z*-isomer: 27.10 ($S\underline{C}H_2CH$=CH), 38.73 ($S\underline{C}H_2CCl$=), 114.31 (=CH_2), 120.30 ($SCH_2\underline{C}H$=CH), 127.57 ($Cl\underline{C}H$=CH), 138.02 (=$\underline{C}Cl$–CH_2); *E*-isomer: 30.74 ($S\underline{C}H_2CH$=CH), 38.12 ($S\underline{C}H_2CCl$=), 114.31 (CH_2=), 119.97 (SCH_2–$\underline{C}H$=CH), 128.84 ($Cl\underline{C}H$=CH), 138.02 (=$\underline{C}Cl$–CH_2). Mass spectrum, *m/z* (I_{rel}, %): 186 (0.4) $[M]^{+\bullet}$ (^{37}Cl, ^{35}Cl), 184 (2.4) $[M]^{+\bullet}$ (^{37}Cl, ^{35}Cl), 182 (3.5) $[M]^{+\bullet}$ (^{37}Cl, ^{35}Cl), 149 (4.6) $[M - Cl]^+$ (^{37}Cl), 147 (12.0) $[M - Cl]^+$ (^{35}Cl), 111 (7.2), 109 (2.8), 108 (5.7), 107 (6.6), 106 (14.0) $[C_3H_3ClS]^{+\bullet}$, 85 (2.0) $[C_4H_5S]^+$, 77 (8.3) $[C_3H_4Cl]^+$ (^{37}Cl), 75 (21.2) $[C_3H_4Cl]^+$ (^{35}Cl), 71 (6.1), 49 (3.3). Found, %: C 39.38; H 4.25; Cl 38.64; S 17.51. $C_6H_8Cl_2S$. Calculated, %: C 39.36; H 4.40; Cl 38.73; S 17.51.

2-Chloro-3-(prop-1-en-3-ylsulfanyl)prop-1-ene (3f). Yield 64%, bp 49–50°C (4 mmHg). ^{1}H NMR spectrum, δ, ppm: 3.13 d.t (2H, $S\underline{C}H_2CH$=, ^3J 7.1, ^4J 0.9 Hz), 3.30 d (2H, $S\underline{C}H_2CCl$=, ^4J 0.8 Hz), 5.09 d.d.t (1H, *E*-$\underline{C}H$=$CHCH_2$, J_{trans} 16.9, ^2J 1.5, ^4J 0.9 Hz), 5.13 d.d.t (1H, *Z*-$\underline{C}H$=$CHCH_2$, J_{cis} 9.9, ^2J 1.5, ^4J 0.9 Hz), 5.30 d (1H, *E*-CH=CCl, ^2J 1.3 Hz), 5.33 d.t (1H, *Z*-CH=CCl, ^2J 1.3, ^4J 0.8 Hz), 5.76 d.d.t (1H, $CH_2\underline{C}H$=CH, J_{trans} 16.9, J_{cis} 9.9, ^3J 7.1 Hz). Mass spectrum , *m/z* (I_{rel}, %): 148 (traces) $[M]^{+\bullet}$ (^{35}Cl), 113 (30.1) $[M - Cl]^+$, 106 (2.8) $[C_3H_3ClS]^+$, 85 (3.1), 79 (8.4), 77 (2.8), 75 (4.3) $[C_3H_4Cl]^+$, 73 (10.2) $[C_3H_5S]^+$, 72 (9.6) $[C_3H_4S]^{+\bullet}$, 71

(9.6) $[C_3H_3S]^+$, 67 (1.9), 47 (3.7). Found, %: C 48.44; H 6.25; Cl 23.35; S 21.63. C_6H_9ClS. Calculated, %: C 48.48; H 6.10; Cl 23.85; S 21.57.

2-Chloro-3-benzylsulfanylprop-1-ene (3g). Yield 90%, bp 92–95°C (1.5 mmHg) {89–92°C (1.5 mmHg) [12]}. Spectral characteristics and elemental analysis data are completely consistent with published findings [11, 12].

2-Chloro-3-carboxymethylsulfanylprop-1-ene (3h). Yield 81%, bp 122–123°C (2 mmHg). IR spectrum, ν, cm^{-1}: 3107 (OH), 1710, 1628 (C=O). ^1H NMR spectrum, δ, ppm: 3.26 s (2H, CH_2COOH), 3.54 br.s (2H, $SCH_2C=C$), 5.35 br.s and 5.39 br.s (4H, $CH_2=$), 11.60 br.s (OH). ^{13}C NMR spectrum, δ, ppm: 31.61 ($S\underline{C}H_2C=C$), 39.89 ($S\underline{C}H_2COOH$), 115.98 ($CH_2=$), 136.76 (=CCl–), 176.03 (COOH). Mass spectrum, *m/z* (I_{rel}, %): 168 (7.5) $[M]^{+\bullet}$ (^{37}Cl), 166 (20.0) $[M]^{+\bullet}$ (^{35}Cl), 123 (0.7) $[M - COOH]^+$ (^{37}Cl), 121 (2.2) $[M - COOH]^+$ (^{35}Cl), 109 (8.5) $[C_3H_4ClS]^+$ (^{37}Cl), 107 (23.5) $[C_3H_4ClS]^+$ (^{35}Cl), 85 (9.4) $[M - HCl\text{-}COOH]^+$, 77 (2.7) $[C_3H_4Cl]^+$ (^{37}Cl), 75 (5.6) $[C_3H_4Cl]^+$ (^{35}Cl), 71 (3.6), 60 (4.8), 57 (1.7), 49 (1.9), 47 (3.6), 46 (4.4). Found, %: C 36.12; H 4.37; Cl 21.06; S 19.55. $C_5H_7ClO_2S$. Calculated, %: C 36.04; H 4.23; Cl 21.28; S 19.24.

1,2-Bis(2-chloroprop-1-en-3-ylsulfanyl)ethane (4) was obtained from 4.0 g (21.4 mmol) of isothiouronium salt **1**, 1.06 g (10.7 mmol) of 1,2-dichloroethane, and 2.4 g (42.8 mmol) of KOH dissolved in 10 mL of hydrazine hydrate. The reaction mixture was stirred for 22 h at 25°C, then it was worked up as described above. The residue after removal of the extraction agent (1.97 g) was virtually pure compound **4** (yield 76%). The spectral characteristics were totally identical to those published in [9].

Reaction of isothiouronium salt 1 with ethyl chloroacetate (2i). A mixture of 4.0 g (21.4 mmol) of isothiouronium salt **1**, 2.62 g (21.4 mmol) of ethyl chloroacetate **2i** after adding a solution of 2.4 g (42.8 mmol) of KOH in 10 mL of hydrazine hydrate was stirred for 16 h at 25°C. After the usual workup we obtained 2.16 g (60%) of acetic acid (2-chloro-1-propen-3-ylsulfanyl)hydrazide **5**, bp 174–178°C (2 mmHg). IR spectrum, ν, cm^{-1}: 3312, 3277, 3208 (NH, NH_2), 1661 (C=O), 1628 (C=C). ^1H NMR spectrum, δ, ppm: 3.22 s (2H, SCH_2CO), 3.45 s (2H, $S\underline{C}H_2C=C$), 4.09 br.s (2H, NH_2), 5.33 br.s (1H, *Z*-CH=CCl), 5.40 br.s (1H, *E*-CH=CCl), 8.49 br.s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 32.55 ($S\underline{C}H_2C=C$), 40.25 ($S\underline{C}H_2CO$), 115.73 ($CH_2=$), 169.32 (CONH). Mass spectrum, *m/z* (I_{rel}, %): 181 (0.3) $[M - H]^+$ (^{37}Cl), 179 (0.5) $[M - H]^+$ (^{35}Cl), 168 (2.8) $[CH_2=CClCH_2SCH_2CON^+H_3]$ (^{37}Cl), 166 (7.4) $[CH_2=CClCH_2SCH_2CON^+H_3]$ (^{35}Cl), 151 (6.0) $[CH_2=CClCH_2SCH_2C\equiv O^+]$ (^{37}Cl), 149 (8.3) $[CH_2=CClCH_2SCH_2C\equiv O^+]$ (^{35}Cl), 137 (1.1), 121 (0.9), 116 (3.7), 114 (3.2), 109 (4.0) $[C_3H_4ClS]^+$ (^{37}Cl), 107 (10.3) $[C_3H_4ClS]^+$ (^{35}Cl), 104 (2.9), 103 (4.6), 85 (3.7) $[C_4H_5S]^+$, 79 (2.8), 77 (7.5) $[C_3H_4Cl]^+$ (^{37}Cl), 75 (14.8) $[C_3H_4Cl]^+$ (^{35}Cl), 71 (3.2), 64 (1.7), 49 (3.1). Found, %: C 33.13; H 5.17; Cl 20.24; N 15.11; S 17.47. $C_5H_9ClN_2OS$. Calculated, %: C 33.24; H 5.02; Cl 19.62; N 15.51; S 17.75. After extraction of compound **5** the reaction mixture was acidified with 30 mL of conc. HCl (pH 0–1) and extracted again with CH_2Cl_2 (2 × 30 mL). On removing the solvent from the extract we obtained 0.39 g (11%) of sulfide **3h** identical to the compound obtained by the reaction of chloroacetic acid with isothiouronium salt **1**.

Bis[2-(2-chloroprop-1-en-3-ylsulfanyl)ethyl] disulfide (6a). To a solution of 0.24 g (7.6 mmol) of sulfur in the mixture of 1.5 mL of hydrazine hydrate and 0.15 g of ethanolamine prepared at 60–65°C within 2 h was added dropwise at 40–45°C 1.3 g (7.6 mmol) of sulfide **3c**. The obtained mixture was stirred at 40–50°C for 13 h, diluted with 10 mL of water, and extracted with CH_2Cl_2 (2 × 30 mL). On removing the solvent the obtained residue (0.86 g) contained according to ^1H NMR data initial sulfide **3c** and target product **6a** (0.765 g, 60%). IR spectrum, ν, cm^{-1}: 1627 (C=C). ^1H NMR spectrum, δ, ppm: 2.86 m (4H, SCH_2CH_2S), 3.39 br.s (2H, $SCH_2CCl=$), 5.32 br.s and 5.40 br.s (4H, $CH_2=$). ^{13}C NMR spectrum, δ, ppm: 30.85 ($S\underline{C}H_2CH_2SS$), 38.17 (CH_2SS), 40.04 ($S\underline{C}H_2CCl=$), 114.93 ($CH_2=$), 138.35 (=CCl). Mass spectrum, *m/z* (I_{rel}, %): 334 $[M]^{+\bullet}$ (^{35}Cl) has very low intensity, 169 (0.6) $[C_5H_8ClS_2]^+$ (^{37}Cl), 167 (1.9) $[C_5H_8ClS_2]^+$ (^{35}Cl), 137 (15.4) $[C_5H_8ClS]^+$ (^{37}Cl), 135 (41.5) $[C_5H_8ClS]^+$ (^{35}Cl), 124 (3.0) $[C_2H_4S_3]^{+\bullet}$, 109 (3.4) $[C_3H_4ClS]^+$ (^{37}Cl), 107 (10.2) $[C_3H_4ClS]^+$ (^{35}Cl), 99 (5.6) $[C_5H_7S]^+$, 92 (3.4) $[C_2H_4S_2]^+$, 77 (2.1) $[C_3H_4Cl]^+$ (^{37}Cl), 75 $[C_3H_4Cl]^+$ (^{35}Cl), 59 (4.7), 47 (1.7). The GC-MS method showed in the residue the presence of trace amount of monosulfide **7**. Mass spectrum, *m/z* (I_{rel}, %): 302 $[M]^{+\bullet}$ (^{35}Cl) absent, 201 (1.4) $[C_5H_8ClS_3]^+$ (^{37}Cl), 199 (3.1) $[C_5H_8ClS_3]^+$ (^{35}Cl), 137 (12.5) $[C_5H_8ClS]^+$ (^{37}Cl), 135 (33.6) $[C_5H_8ClS]^+$ (^{35}Cl), 124 (4.2) $[C_2H_4S_3]^{+\bullet}$, 109 (3.8) $[C_3H_4ClS]^+$ (^{37}Cl), 107 (10.7) $[C_3H_4ClS]^+$ (^{35}Cl), 99 (5.5) $[C_5H_7S]^+$, 92 (2.1) $[C_2H_4S_2]^{+\bullet}$, 77 (3.1) $[C_3H_4Cl]^+$ (^{37}Cl), 75 (8.6) $[C_3H_4Cl]^+$ (^{35}Cl), 59 (5.2), 47 (2.1).

Bis[2-(2-chloroprop-1-en-3-ylsulfanyl)ethyl]-diselenide (6b). To a solution of K_2Se_2 obtained from 0.92 g (11.7 mmol) of selenium, 2 mL of water, 0.3 mL of hydrazine hydrate, and 0.66 g (11.7 mmol) of KOH at 85°C was added dropwise at 20°C within 3 h 2.0 g (11.7 mmol) of sulfide **3c**. The reaction mixture was stirred for 6.5 h at 45–50°C, cooled, and extracted with CH_2Cl_2 (3 × 10 mL). After the workup of the extract we obtained 1.91 g of the residue containing according to ^{1}H NMR data diselenide **6b** with an impurity (~10%) of initial sulfide **3c**. IR spectrum, ν, cm^{-1}: 1627 (C=C). ^{1}H NMR spectrum, δ, ppm: 2.89 m (4H, CH_2Se), 3.09 m (4H, $S\underline{C}H_2CH_2$), 3.40 s (4H, SCH_2CCl=), 5.31 s (1H) and 5.40 s (1H) (CH_2=). ^{13}C NMR spectrum, δ, ppm: 28.44 (CH_2Se, J_{C-Se} 75 Hz), 32.73 ($S\underline{C}H_2CH_2$), 39.87 ($S\underline{C}H_2CCl$=), 114.76 (CH_2=), 138.45 (=CCl). ^{77}Se NMR spectrum, δ, ppm: 394.3 t ($^2J_{Se-H}$ 16.1 Hz); two weak signals were additionally found corresponding to the resonance of selenium nuclei in a chain $CH_2SeSeSeCH_2$ of compound **8**: 562.8 s (central selenium atom), 487.8 t (CH_2Se, $^2J_{Se-H}$ 15.2 Hz). We failed to obtain GC-MS spectra of compounds **6b** and **8** apparently due to their instability under the chromatography conditions.

Main results were obtained using the equipment of the Baikal Analytic center of joint usage of the Siberian Branch of the Russian Academy of Sciences.

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