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New Method of Synthesis of β-Haloalkyl Alkynyl Sulfides: Reaction of Alkynesulfenamides with Olefins in the Presence of Phosphoryl Halides

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Abstract—Reactions of alkynelsufenamides with olefins (such as cyclohexene, norbornene, 1-hexene, 1-octene, allylbenzene, and styrene) in the presence of phosphoryl halides ($POCl_3$, $POBr_3$) afforded 70–95% of β-halo-substituted alkyl alkynyl sulfides. The reactions with cyclohexene and norbornene are characterized by *trans* stereoselectivity. Alkynylsulfenylation of terminal alkyl- and benzylacetylenes occurs in a regioselective fashion with predominant formation of the corresponding anti-Markownikoff adducts, while the addition to styrene yields halogen-containing sulfides according to the Markownikoff rule.

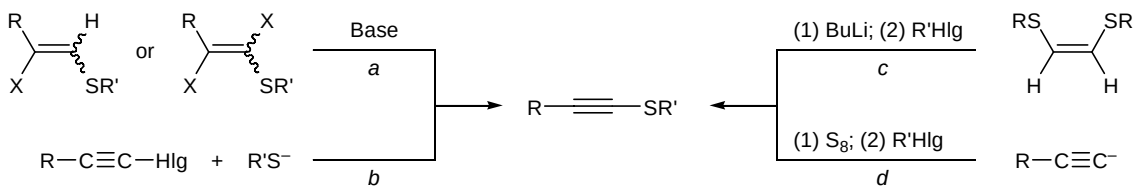
At present, the most thoroughly studied and widely used method for halosulfenylation of unsaturated compounds is classical addition of sulfenyl halides (see, e.g., reviews [1, 2]). However, a considerable disadvantage of this procedure is very low stability of sulfenyl chlorides and especially sulfenyl bromides. Arenesulfenyl chlorides usually add to alkenes to give the corresponding products in preparative yields, reactions with alkanesulfenyl halides result mainly in decomposition of the reagent, while compounds like ethene- and alkynesulfenyl chlorides were not reported previously. Therefore, the application of direct chloro- and bromosulfenylation of alkenes and alkynes for preparative purposes is limited almost exclusively to arenesulfenylation reactions.

We previously developed new procedures for electrophilic aryl- [3], alkyl- [4], and vinylsulfenylation [5] of unsaturated compounds with sulfenamides in the presence of phosphoryl halides ($POCl_3$, $POBr_3$). As far as sulfenamides are considerably more stable that the corresponding sulfenyl chlorides, the initial reactants do not undergo decomposition during the process, and the desired halogen-containing aryl, alkyl, and vinyl sulfides can be obtained in high yields under mild conditions.

In the present work we made an attempt to extend the developed approach to the synthesis of β-halo-substituted alkyl alkynyl sulfides. These compounds attract interest from the viewpoint of their further chemical modification at various functional groups present therein. For example, the sulfur(II) atom readily undergo oxidation, the triple C≡C bond may be involved in electrophilic, nucleophilic, and radical addition reactions, and the halogen atom in the β-position with respect to the alkynylsulfanyl group can be replaced by various nucleophiles.

The known synthetic approaches to alkynyl sulfides include the following ones: elimination of HX or XX

Scheme 1.



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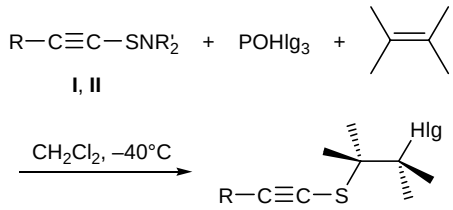
species from halo-substituted sulfides (Scheme 1, path *a*; see, e.g., [6–10]); nucleophilic substitution at *sp*-hybridized carbon atom by the action of sulfur-containing nucleophiles (path *b*) [11]; splitting of 1,2-bis-(organylsulfanyl)ethylenes with butyllithium (path *c*) [12, 13]; and reactions of metal acetylides with elemental sulfur or sulfur-containing compounds (*d*) [14, 15]. Some specific syntheses of optically active alkynyl sulfides [16] and those possessing unusual electronic properties [17] or used as ligands for the preparation of metal complexes [18] have also been reported. We can conclude that all known methods for building up an S–C≡C fragment are based on elimination processes or substitution reactions leading to formation of a bond between sulfur atom and *sp*-hybridized carbon atom. Therefore, the procedure proposed by us for electrophilic introduction of a R–C≡C–S fragment may be regarded as a new approach to alkynyl sulfides.

We examined reactions of alkynesulfenamides **I** and **II** with olefins in the presence of phosphoryl halides. The reactions were carried out under mild conditions (CH_2Cl_2, –40°C), and in most cases the products were the corresponding β-haloalkyl alkynyl sulfides which were formed in high yields (Scheme 2).

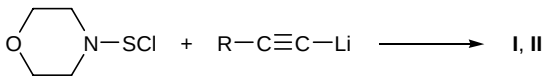
Scheme 2.



I, R = Ph; **II**, R = Bu; Hlg = Cl, Br.

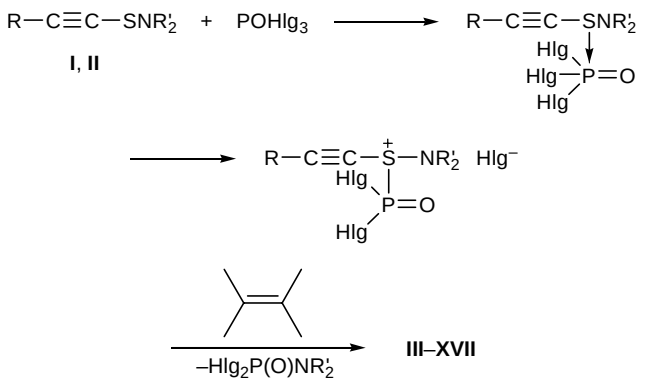
Initial *N*-(2-phenylethynylsulfanyl)morpholine (**I**) and *N*-(1-hexynylsulfanyl)morpholine (**II**) were prepared by addition of *N*-(chlorosulfanyl)morpholine to the corresponding lithium acetylide by analogy with the procedure described in [19] (Scheme 3).

Scheme 3.



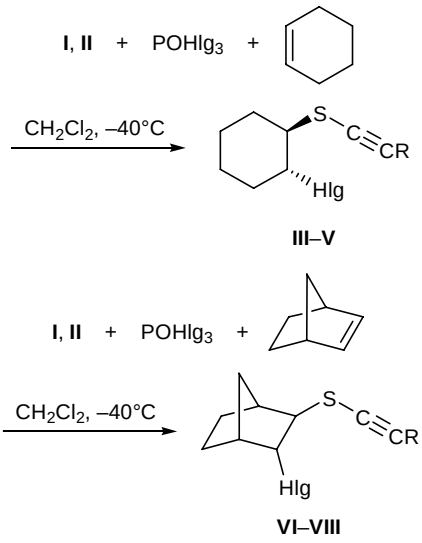
Sulfenamides are weak electrophiles which are incapable of adding at multiple bonds without additional activation. Presumably, the reaction mechanism is analogous to that proposed previously for arenesulfenamides [20]; it includes coordination of Lewis acid (phosphoryl halide) at the sulfur atom, generation of electrophilic species (sulfonium salt) by replacement of one halogen atom at the phosphorus, electrophilic addition of this species at the double C=C bond, and nucleophilic attack by halide ion (abstracted from the phosphoryl halide) to give *trans*-1,2-halosulfenylation product (Scheme 4).

Scheme 4.



The structure of the products was confirmed by the ^{1}H NMR and mass spectra. Using the reactions with norbornene and cyclohexene as examples (Scheme 5), we showed that the process is characterized by *trans* stereoselectivity. The *trans* configuration of compounds **VI**–**VIII** directly follows from the coupling constant between the HCS and HCHlg protons (^3J = 3.7–4.2 Hz), which corresponds to *trans* interaction [21]. The configuration of cyclohexane derivatives **III**–**V** was proved by broadening of signals from both

Scheme 5.

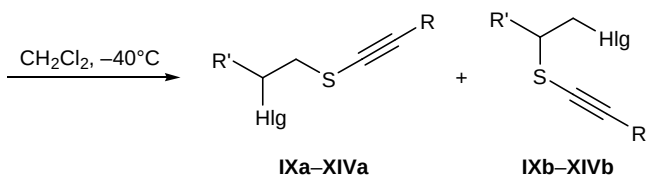


III, **VI**, R = Ph, Hlg = Cl; **IV**, **VII**, R = Bu, Hlg = Cl; **V**, **VIII**, R = Bu, Hlg = Br.

protons in positions *1* and *2* in going from more polar solvent ($CDCl_3$) to less polar (C_6D_6) (*W*-criterion [22]).

Different regioselectivities were observed in the addition to alkyl- and arylethenes. The major products obtained from alkylethenes (1-hexene, 1-octene, and allylbenzene) were the corresponding anti-Markownikoff adducts **IXb**–**XIVb** (Scheme 6). Presumably, the reaction direction is determined by steric factors operating in the second stage of the Ad_E reaction, i.e., addition of halide ion. According to the ^1H NMR spectra of the products recorded in $CDCl_3$ in 1, 7, and 30 days after isolation, the ratio **a**:**b** decreases. This means that Markownikoff adducts **IXa**–**XIVa** undergo partial isomerization into anti-Markownikoff adducts **IXb**–**XIVb**. Obviously, as in the arylsulfenylation reactions [23–25], compounds **IXb**–**XIVb** are thermodynamically controlled products (the **a**:**b** ratios given in Scheme 6 refer to the products immediately after isolation).

Scheme 6.

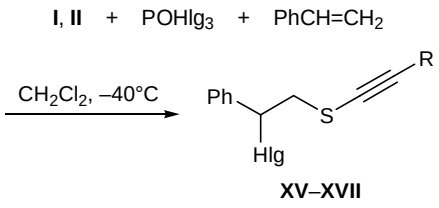


IX, **XIII**, R = Ph, R' = Bu, Hlg = Cl; **X**, R = Ph, R' = C_6H_{13}, Hlg = Cl; **XI**, R = Bu, R' = C_6H_{13}, Hlg = Cl; **XII**, R = Bu, R' = C_6H_{13}, Hlg = Br; **XIV**, R = Bu, R' = Bu, Hlg = Cl. **IXa**:**IXb** = 1:6, **Xa**:**Xb** = 1:5, **XIa**:**XIb** = 1:2, **XIIa**:**XIIb** = 2:5, **XIIIa**:**XIIIb** = 1:3, **XIVa**:**XIVb** = 1:2.

By contrast, the reactions of **I** and **II** with styrene afforded almost exclusively the corresponding Markownikoff adducts **XV**–**XVII** (Scheme 7), i.e., in this case the regioselectivity of the process is determined by stabilization of intermediate cation.

Using the reaction of sulfenamide **II** with norbornene as an example, we compared the activating power of phosphoryl halides with those of thiophosphoryl chloride and phosphorus(III) bromide (Scheme 8). In the presence of $PSCl_3$ and PBr_3, the products were chloro- and bromo-substituted sulfides **VII** and **VIII**, respectively, but their yields were lower than in the reactions activated by $POCl_3$ and $POBr_3$.

Scheme 7.



XV, R = Ph, Hlg = Cl; **XVI**, R = Bu, Hlg = Cl; **XVII**, R = Bu, Hlg = Br.

Scheme 8.

The structure of compounds **III**, **IV**, **VII**–**XIV**, and **XVI** was confirmed by mass spectrometry. All these compounds showed in the mass spectra the molecular ion peak with a relative intensity of 11 to 100%. The molecular ion was the most abundant for phenylethynyl sulfides. Primary fragmentation of the molecular ion of halogenated sulfides **III**, **IV**, **VII**–**XIV**, and **XVI** includes mainly elimination of the R–C≡C–SH molecule or R–C≡C–S fragment (R = Ph, Bu) with formation of ions with *m*/*z* 113 (**IV**), 114 (**VII**–**XI**, R = Bu), 133 (**XII**, **XIII**), or 134 (**III**, R = Ph). In the mass spectra of some compounds (**VII**, **VIII**, **XIII**), $[M - R–C≡C–S]^+$ ion peaks were observed; but in most cases, this ion undergoes further fragmentation to give smaller hydrocarbon ions (C_3H_5, C_5H_9, C_5H_{11}, C_6H_5, C_7H_7). Bromine-containing sulfide **VIII** also showed a fairly intense $[M - R–C≡C–S – H]^+$ ion peak with *m*/*z* 173. The isotope peak ratios were consistent with the assumed structures.

Thus alkynylsulfenylation of alkenes by the action of alkynesulfenamides in the presence of phosphoryl halides provides a convenient method for the preparation of β-halo-substituted alkyl alkynyl sulfides. Phosphoryl halide-activated sulfenylation of unsaturated compounds may be regarded as general synthetic approach to substituted aryl, alkyl, vinyl, and alkynyl sulfides.

EXPERIMENTAL

The NMR spectra were recorded on a Varian VXR-400 spectrometer from solutions in $CDCl_3$. The progress of reactions and the purity of products were monitored by chromatography. The mass spectra were obtained on a JMS-D300 mass spectrometer coupled with a JMA-2000 computer and an HP 5890 gas chromatograph; the scan rate was varied from 1 to 2 s in the mass range from 10 to 300 a.m.u or from 40 to 450 a.m.u.; total ion current chromatograms were

recorded; ion source temperature 150°C, energy of ionizing electrons 70 eV, accelerating voltage 3 kV.

N-(Chlorosulfanyl)morpholine was prepared from *N*,*N*′-disulfanyldimorpholine and sulfuryl chloride by the procedure described in [26]; lithium acetylides were prepared from phenylacetylene or 1-hexyne and *n*-butyllithium as described in [27]. Alkynesulfenamides were synthesized by adding at –10°C a freshly prepared suspension of the corresponding lithium acetylide to a solution of *N*-(chlorosulfanyl)morpholine in dry hexane (cf. [19]).

***N*-(2-Phenylethynylsulfanyl)morpholine (I).** ^{1}H NMR spectrum, δ, ppm: 7.43 m (2H), 7.30 m (3H), 3.73 m (4H, CH_2O), 3.00 m (4H, CH_2N). ^{13}C NMR spectrum, δ_C, ppm: 131.39, 128.60, 128.33 (C_{arom}); 112.72, 107.97 (C≡); 67.27 (C–O); 55.53 (C–N).

***N*-(1-Hexynylsulfanyl)morpholine (II).** ^{1}H NMR spectrum, δ, ppm: 3.72 m (4H, CH_2O), 2.91 m (4H, CH_2N), 2.45 t (2H, CH_2C≡, J = 6.8 Hz), 1.60–1.26 m (4H), 0.86 m (3H, CH_3, J = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 110.07, 99.53 (C≡), 69.53 (C–O), 54.13 (C–N), 30.80, 21.94, 20.08, 13.54.

Addition of alkynesulfenamides to olefins in the presence of phosphoryl halides (*general procedure*). A solution of 1 mmol of alkynesulfenamide **I** or **II** in 10 ml of dry methylene chloride was cooled to –40°C, 1.5 mmol of the corresponding alkene was added, and a solution of 1 mmol phosphoryl halide in 5 ml of methylene chloride was slowly added under stirring at –40°C. The mixture was allowed to warm up to room temperature and was stirred until initial sulfenamide **I** or **II** disappeared completely (5–10 h, TLC). The solvent was removed under reduced pressure, and the product was purified by chromatography on silica gel using petroleum ether–chloroform (7:1) as eluent.

***trans*-1-Chloro-2-(2-phenylethynylsulfanyl)cyclohexane (III).** Yield 84%, R_f 0.92. ^{1}H NMR spectrum, δ, ppm: 7.20–7.25 (H_{arom}), 4.08 d.d.d (HCHlg, J_1 = 9.2, J_2 = 9.2, J_3 = 4.2 Hz), 3.04 d.d.d (HCS, J_1 = 9.2, J_2 = 9.2, J_3 = 4.1 Hz), 2.30–1.50 [$(CH_2)_4$]. Mass spectrum, *m*/*z*, (I_{rel}, %): 250 (39) M^+, 134 (100) $[PhC{\equiv}CSH]^+$, 89 (61) $[C_4H_9S]^+$, 81 (100) $[C_6H_9]^+$, 53 (24) $[C_4H_5]^+$, 39 (25) $[C_3H_3]^+$.

***trans*-1-Chloro-2-(1-hexynylsulfanyl)cyclohexane (IV).** Yield 70%, R_f 0.90. ^{1}H NMR spectrum, δ, ppm: 4.05 d.d.d (HCHlg, J_1 = 13.1, J_2 = 13.1, J_3 = 8.9 Hz), 2.95 d.d.d (HCS, J_1 = 13.0, J_2 = 8.9, J_3 = 4.2 Hz), 2.30 t (2H, CH_2C≡, J = 6.7 Hz), 1.82–1.23 m (12H); 0.90 t (3H, CH_3, J = 6.6 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 230 (100) M^+, 113 (96) $[BuC{\equiv}CS]^+$, 80 (98) $[C_4H_4]^+$, 71 (98) $[C_5H_{11}]^+$, 55 (89) $[C_4H_7]^+$, 41 (100) $[C_3H_5]^+$.

***trans*-1-Bromo-2-(1-hexynylsulfanyl)cyclohexane (V).** Yield 85%, R_f 0.85. ^{1}H NMR spectrum, δ, ppm: 4.33 d.d (HCHlg, J_1 = 9.2, J_2 = 5.7 Hz), 3.58 d.d (HCS, J_1 = 10.2, J_2 = 5.7 Hz), 2.23 t (2H, CH_2C≡, J = 7.4 Hz), 1.95–1.20 m (12H), 0.90 t (3H, CH_3, J = 7.2 Hz).

***endo*-2-Chloro-*exo*-3-(2-phenylethynylsulfanyl)-bicyclo[2.2.1]heptane (VI).** Yield 80%, R_f 0.82. ^{1}H NMR spectrum, δ, ppm: 7.43–7.24 m (H_{arom}), 4.18 d.d.d (HCHlg, $J_{1,2}$ = 4.0, $J_{2,3}$ = 4.0, $J_{2,exo\text{-}6}$ = 1.8 Hz), 3.02 d.d (HCS, $J_{2,3}$ = 3.7, $J_{3,anti\text{-}7}$ = 2.7 Hz), 2.40 d ($J_{4,5}$ = 4.2 Hz), 2.1 t ($J_{1,2}$ = 4.0, $J_{1,6}$ = 4.0 Hz), 2.00 d.d.d.d (*endo*-6-H, J_1 = 13.1, J_2 = 8.8, J_3 = 4.0, J_4 = 2.5 Hz), 1.90 d.d.d (*syn*-7-H, J_1 = 11.0, J_2 = 2.5, J_3 = 2.5 Hz), 1.72 d.d.d (*exo*-6-H, J_1 = 13.1, J_2 = 6.4, J_3 = 4.6), 1.53–1.33 m (3H).

***endo*-2-Chloro-*exo*-3-(1-hexynylsulfanyl)bicyclo-[2.2.1]heptane (VII).** Yield 84%, R_f 0.86. ^{1}H NMR spectrum, δ, ppm: 4.07 d.d.d (HCHlg, $J_{2,1}$ = 4.0, $J_{2,3}$ = 4.0, $J_{2,exo\text{-}6}$ = 1.9 Hz), 3.02 d.d (HCS, $J_{2,3}$ = 4.0, $J_{3,anti\text{-}7}$ = 2.7 Hz), 2.47 br.s and 2.32 br.s, 2.30 t (CH_2C≡, J = 7.0 Hz), 1.95 m (2H, *endo*-5-H, *endo*-6-H), 1.85 d.d.d (*syn*-7-H, J_1 = 10.5, J_2 = 2.5, J_3 = 2.5 Hz), 1.69 m (2H, *exo*-5-H, *exo*-6-H), 1.55–1.35 m (5H), 0.90 t (3H, CH_3, J = 7.0 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 242 (50) M^+, 129 (89) $[M - BuC{\equiv}CS]^+$, 114 (61) $[BuC{\equiv}CSH]^+$, 93 (90) $[C_7H_9]^+$, 81 (99) $[C_6H_9]^+$, 67 (100) $[C_5H_7]^+$, 41 (99) $[C_3H_5]^+$.

***endo*-2-Bromo-*exo*-3-(1-hexynylsulfanyl)bicyclo-[2.2.1]heptane (VIII).** Yield 95%, R_f 0.85. ^{1}H NMR spectrum, δ, ppm: 3.99 d.d.d (HCHlg, $J_{2,1}$ = 4.2, $J_{2,3}$ = 4.2, $J_{2,exo\text{-}6}$ = 1.8 Hz), 3.19 d.d (HCS, $J_{2,3}$ = 4.2, $J_{3,anti\text{-}7}$ = 3.0 Hz), 2.49 br.s, 2.28 br.s, 2.30 t (CH_2C≡, J = 7.0 Hz), 2.04 m (2H, *endo*-5-H, *endo*-6-H), 1.76 d.d.d (*syn*-7-H, J_1 = 10.6, J_2 = 2.0, J_3 = 2.0 Hz), 1.68 m (2H, *exo*-5-H, *exo*-6-H), 1.58–1.47 m (5H), 0.90 t (3H, CH_3, J = 7.1 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 288 (12) M^+, 173 (20) $[M - BuC{\equiv}CS - 2H]^+$, 114 (19) $[BuC{\equiv}CSH]^+$, 93 (100) $[C_7H_9]^+$, 77 (28) $[C_6H_5]^+$, 67 (37) $[C_5H_7]^+$, 41 (19) $[C_3H_5]^+$.

2-Chloro-1-(2-phenylethynylsulfanyl)hexane (IXa) and 1-Chloro-2-(2-phenylethynylsulfanyl)-hexane (IXb) (mixture of isomers)**.** Yield 83%, R_f 0.93. ^{1}H NMR spectrum, δ, ppm: **IXa**: 7.43–7.23 m (5H, Ph), 4.19 m (HCHlg), 3.19 d.d (HCS, J_1 = 13.5, J_2 = 6.1 Hz), 3.02 d.d (HCS, J_1 = 13.5, J_2 = 7.6 Hz), 2.19–1.06 m (C_4H_9); **IXb**: 7.43–7.23 m (5H, Ph), 3.94 d.d (HCHlg, J_1 = 11.1, J_2 = 4.8 Hz), 3.69 d.d (HCHlg, J_1 = 11.1, J_2 = 8.4 Hz), 3.06 m (HCS).

2-Chloro-1-(2-phenylethynylsulfanyl)octane (Xa) and 1-chloro-2-(2-phenylethynylsulfanyl)octane (Xb) (mixture of isomers)**.** Yield 93%, R_f 0.92. ^{1}H NMR spectrum, δ, ppm: **Xa**: 7.42–7.26 m (5H, Ph), 4.20 m (HCHlg), 3.19 d.d (HCS, J_1 = 13.4, J_2 = 6.3 Hz), 3.03 d.d (HCS, J_1 = 13.4, J_2 = 7.4 Hz), 2.19–1.06 m (C_4H_9); **Xb**: 7.42–7.26 m (5H, Ph), 3.95 d.d (HCHlg, J_1 = 11.0, J_2 = 4.5 Hz), 3.70 d.d (HCHlg, J_1 = 11.0, J_2 = 8.4 Hz), 3.09 m (HCS), 2.19–1.06 m (C_4H_9).

2-Chloro-1-(1-hexynylsulfanyl)octane (XIa) and 1-chloro-2-(1-hexynylsulfanyl)octane (XIb) (mixture of isomers)**.** Yield 77%, R_f 0.93. ^{1}H NMR spectrum, δ, ppm: **XIa**: 3.96 m (HCHlg), 3.29 d.d (HCS, J_1 = 13.4, J_2 = 5.9 Hz), 3.03 d.d (HCS, J_1 = 13.4, J_2 = 6.0 Hz), 2.32 t (J = 6.7 Hz), 2.0–1.1 m (CH_2), 0.93 t (CH_3, J = 6.9 Hz); **XIb**: 3.95 d.d (HCHlg, J_1 = 11.1, J_2 = 4.7 Hz), 3.61 d.d (HCHlg, J_1 = 11.1, J_2 = 8.7 Hz), 3.38 m (HCS), 2.30 t (J = 6.7 Hz), 2.0–1.1 m (CH_2), 0.90 t (CH_3, J = 6.9 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 260 (11) M^+, 114 (29) $[BuC{\equiv}CSH]^+$, 81 (100) $[C_6H_5]^+$, 71 (33) $[C_5H_{11}]^+$, 55 (34) $[C_4H_7]^+$, 41 (44) $[C_3H_5]^+$.

2-Bromo-1-(1-hexynylsulfanyl)octane (XIIa) and 1-bromo-2-(1-hexynylsulfanyl)octane (XIIb) (mixture of isomers). Yield 80%, R_f 0.92. ^{1}H NMR spectrum, δ, ppm: **XIIa**: 4.05 m (HCHlg), 3.34 d.d (HCS, J_1 = 14.0, J_2 = 5.2 Hz), 3.16 d.d (HCS, J_1 = 14.0, J_2 = 8.1 Hz), 2.24 t (J = 6.7 Hz), 2.05–1.2 m (CH_2), 0.90 t (CH_3, J = 6.9 Hz); **XIIb**: 3.75 d.d (HCS, J_1 = 9.6, J_2 = 3.0 Hz), 3.65 d.d (HCS, J_1 = 9.6, J_2 = 6.4 Hz), 3.16 m (HCS), 2.21 t (J = 6.7 Hz), 2.05–1.2 m (CH_2), 0.90 t (CH_3, J = 6.9 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 266 (32) M^+, 133 (95) $[PhC{\equiv}CS]^+$, 117 (79) $[C_6H_5C_3H_4]^+$, 91 (100) $[C_7H_7]^+$, 81 (29) $[C_6H_9]^+$, 71 (28) $[C_5H_{11}]^+$, 41 (15) $[C_3H_5]^+$.

2-Chloro-3-phenyl-1-(2-phenylethynylsulfanyl)-propane (XIIIa) and 1-chloro-3-phenyl-2-(2-phenylethynylsulfanyl)propane (XIIIb) (mixture of isomers)**.** Yield 88%, R_f 0.91. ^{1}H NMR spectrum, δ, ppm: **XIIIa**: 7.50–7.00 m (Ph), 3.92 m (HCHlg), 3.60 d.d (HCS, J_1 = 11.2, J_2 = 4.7 Hz), 3.48 d.d (HCS, J_1 = 11.2, J_2 = 8.1 Hz), 3.19 d.d (J_1 = 13.4, J_2 = 5.8 Hz), 3.04 d.d (J_1 = 13.4, J_2 = 7.3 Hz); **XIIIb**: 7.50–7.00 m (Ph), 3.85 d.d (HCHlg, J_1 = 11.2, J_2 = 4.3 Hz), 3.74 d.d (HCHlg, J_1 = 11.2, J_2 = 3.7 Hz), 3.33 m (HCS), 3.33 d.d (J_1 = 14.1, J_2 = 7.6 Hz), 3.07 d.d (J_1 = 14.1, J_2 = 7.9 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 280 (80) M^+, 251 (10) $[M - Cl]^+$, 223 (34) $[M - Cl - C_2H_4]^+$, 133 (92) $[PhC{\equiv}CS]^+$, 117 (100) $[C_6H_5C_3H_4]^+$, 103 (25) $[C_6H_5C_2H_2]^+$, 91 (100) $[C_7H_7]^+$, 77 (16) $[C_6H_5]^+$, 63 (42) $[C_5H_3]^+$, 39 (29) $[C_3H_3]^+$.

2-Chloro-1-(1-hexynylsulfanyl)-3-phenylpropane (XIVa) and 1-chloro-2-(1-hexynylsulfanyl)-3-phenylpropane (XIVb) (mixture of isomers)**.** Yield 60%, R_f 0.94. ^{1}H NMR spectrum, δ, ppm: **XIVa**: 7.50–7.00 m (Ph), 4.20 m (HCHlg), 3.60 d.d (HCS, J_1 = 11.4, J_2 = 4.6 Hz), 3.47 d.d (HCS, J_1 = 11.4, J_2 = 6.3 Hz), 2.35 t (J = 7.0 Hz), 3.17 d.d (J_1 = 13.2, J_2 = 5.0 Hz), 3.04 d.d (J_1 = 13.2, J_2 = 7.3 Hz), 2.0–1.0 m (C_3H_7); **XIVb**: 7.50–7.00 m (Ph), 3.85 d.d (HCHlg, J_1 = 11.4, J_2 = 4.4 Hz), 3.68 d.d (HCHlg, J_1 = 11.4, J_2 = 3.2 Hz), 3.35 m (HCS), 2.32 t (J = 7.0 Hz), 3.35 d.d (J_1 = 13.7, J_2 = 7.6 Hz), 3.12 d.d (J_1 = 13.7, J_2 = 5.8 Hz), 2.0–1.0 m (C_3H_7). Mass spectrum, *m*/*z* (I_{rel}, %): 266 (32) M^+, 117 (79) $[C_6H_5C_3H_4]^+$, 91 (100) $[C_7H_7]^+$, 81 (29) $[C_6H_9]^+$, 71 (28) $[C_5H_{11}]^+$, 41 (15) $[C_3H_5]^+$.

1-Chloro-1-phenyl-2-(2-phenylethynylsulfanyl)-ethane (XV). Yield 78%, R_f 0.96. ^{1}H NMR spectrum, δ, ppm: 7.50–7.20 m (Ph), 4.80 d.d (HCHlg, J_1 = 8.6, J_2 = 8.0 Hz), 4.75 d.d (HCHlg, J_1 = 8.6, J_2 = 6.5 Hz), 5.17 d.d (HCS, J_1 = 8.0, J_2 = 6.5 Hz). According to the ^{1}H NMR data, the reaction mixture contained about 5% of the corresponding anti-Markownikoff adduct.

1-Chloro-2-(1-hexynylsulfanyl)-1-phenylethane (XVI). Yield 91%, R_f 0.93. ^{1}H NMR spectrum, δ, ppm: 7.40–7.19 m (Ph), 4.79 d.d (HCHlg, J_1 = 8.4, J_2 = 6.9 Hz), 4.50 d.d (HCHlg, J_1 = 8.4, J_2 = 6.5 Hz), 5.10 d.d (HCS, J_1 = 6.9, J_2 = 6.5 Hz), 2.25 t (J = 6.9 Hz), 1.50–1.30 (CH_2), 0.95 t (J = 6.9 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 252 (11) M^+ 139 (100) $[M - BuC{\equiv}CS]^+$, 103 (46) $[C_6H_5C_2H_2]^+$, 71 (19) $[C_5H_{11}]^+$, 51 (10) $[C_4H_3]^+$, 41 (10) $[C_3H_5]^+$. According to the ^{1}H NMR data, the reaction mixture contained about 5% of the corresponding anti-Markownikoff adduct.

1-Bromo-2-(1-hexynylsulfanyl)-1-phenylethane (XVII). Yield 94%, R_f 0.92. ^{1}H NMR spectrum, δ, ppm: 7.35–7.20 m (Ph), 5.09 d.d (HCS, J_1 = 9.8, J_2 = 6.2 Hz), 4.99 d.d (HCHlg, J_1 = 9.5, J_2 = 6.2 Hz), 4.54 m (HCHlg), 2.35 t (J = 7.0 Hz), 1.60–1.20 (CH_2), 0.90 t (J = 7.0 Hz).

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REFERENCES

1. Kuhle, E., *Synthesis*, 1971, p. 563.
2. Kuhle, E., *Synthesis*, 1971, p. 617.

3. Zyk, N.V., Beloglazkina, E.K., Gazzaeva, R.A., Tyurin, V.S., and Titanyuk, I.D., *Phosphorus Sulfur*, 1999, vol. 155, p. 33.
4. Titanyuk, I.D., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1998.
5. Zyk, N.V., Beloglazkina, E.K., Belova, M.A., and Dubinina, N.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, p. 1348.
6. Arens, J.F., Volger, H.C., and Doornobos, T., *Recl. Trav. Chim. Pays–Bas*, 1956, vol. 75, p. 1459.
7. Angeletti, E., Montanari, F., and Negriri, A., *Gazz. Chim. Ital.*, 1957, vol. 87, p. 1115.
8. Le Guillanton, G. and Martynov, A.V., *Bull. Soc. Chim. Fr.*, 1997, vol. 134, p. 823.
9. Brandsma, L. and Arens, J.F., *Recl. Trav. Chim. Pays–Bas*, 1961, vol. 80, p. 241.
10. Brandsma, L. and Arens, J.F., *Recl. Trav. Chim. Pays–Bas*, 1962, vol. 81, p. 510.
11. Le Guillanton, G., Martynov, A.V., Quang, T.D., Elothmani, D., and Simonet, J., *Electrochim. Acta*, 1999, vol. 44, p. 4787.
12. Parham, W.E. and Stright, P.L., *J. Am. Chem. Soc.*, 1959, vol. 78, p. 4783.
13. Boonstra, H.J. and Arens, J.F., *Recl. Trav. Chim. Pays–Bas*, 1960, vol. 79, p. 866.
14. Nooi, J.R. and Arens, J.F., *Recl. Trav. Chim. Pays–Bas*, 1961, vol. 80, p. 244.
15. Brandsma, L., WiJers, H.E., and Jonker, C., *Recl. Trav. Chim. Pays–Bas*, 1963, vol. 82, p. 208.
16. Maesaki, N., Yagi, S., Ohsawa, S., Ohishi, H., and Tanaka, T., *Tetrahedron: Asymmetry*, 2002, vol. 13, p. 1961.
17. Lee, A.W.M., Yueng, A.B.W., Yuen, M.S., Zhang, H., Zho, X.M., and Wong, W., *J. Chem. Soc., Chem. Commun.*, 2000, p. 75.
18. Zhang, H., Lee, A.W.M., Wong, W., and Yuen, M.S., *J. Chem. Soc., Dalton Trans.*, 2000, p. 3675.
19. Baudin, J., Julia, S.A., and Lorne, R., *Bull. Soc. Chim. Fr.*, 1987, p. 181.
20. Zyk, N.V., Beloglazkina, E.K., and Titanyuk, I.D., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, p. 3180.
21. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972. Translated under the title *Sputnik khimika*, Moscow: Mir, 1976, p. 293.
22. Zefirov, N.S., Samoshin, V.V., and Subbotin, O.A., *Tetrahedron*, 1978, vol. 34, p. 2953.
23. Rasteikene, L.P., Greichute, D.I., Lin'kova, M.T., and Knunyants, I.A., *Usp. Khim.*, 1977, vol. 46, p. 1041.
24. Mueller, W.H. and Butler, P.E., *J. Am. Chem. Soc.*, 1968, vol. 90, p. 2075.
25. Dean, C.L., Garratt, D.G., Tichvell, T.T., and Schmid, G.H., *J. Am. Chem. Soc.*, 1947, vol. 69, p. 4958.