Reactions of 1-(alk-1-ynyl)-1-chlorocyclopropanes with arenethiols and alkanethiols in dimethyl sulfoxide in the presense of KOH

K. N. Shavrin, V. D. Gvozdev, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: vgvozdev2006@yandex.ru

The reaction of 1-(alk-1-ynyl)-1-chlorocyclopropanes with arenethiols in DMSO in the presence of KOH at 90—100 °C affords the corresponding 1-(alk-1-ynyl)-2-arylsulfanylcyclopropanes in the yields up to 67%. At the same time, [1,2-bis(alkylsulfanylalk-1-enyl]cyclopropanes or mixtures of isomeric 1-(alk-1-ynyl)-2-alkyltsulfanylcyclopropanes and (alkylsulfanyl)alkenylidenecyclopropanes are formed in analogous reactions with alkanethiols depending on the substituent at the triple bond of the starting compound.

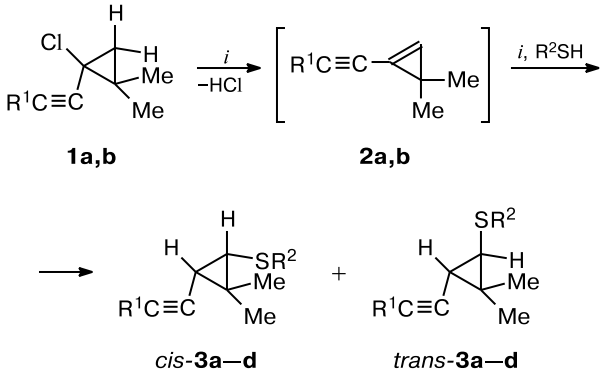
Key words: cyclopropanes, cyclopropenes, allenes, alkynes, thiols, arenethiols, sulfides, nucleophilic addition, nucleophilic substitution.

1-Alkynyl-1-halogenocyclopropanes, first of all, 1-alkynyl-1-chlorocyclopropanes are convenient and available building blocks easily obtainable by [1+2] cycloaddition of alkynyl(chloro)carbenes to alkenes[1,2] or by the reaction of trichlorovinyl(chloro)cyclopropanes with Bu^nLi followed by hydrolysis.[3] At present, rather numerous transformations of 1-alkynyl-1-chlorocyclopropanes are known, *viz.*, metallation at the chlorine atom followed by reactions with various electrophiles,[3,4] the Pauson—Khand cycloaddition.[3] They are also used in the synthesis of nitrogen-containing heterocycles,[5] conjugated alkynyl- and iminoalkylcyclopropenes.[6,7]

Recently,[8] we have found that reactions of 1-alkynyl-1-chlorocyclopropanes with alcohols and phenols in DMSO in the presence of KOH is a convenient approach to 1-alkynyl-2-alkoxy- and 1-alkynyl-2-phenoxycyclopropanes, which had widely been applied previously in the synthesis of various carbocyclic compounds.[9—11] In continuation of these works, it was of interest to study the addition of thiols to these substrates.

Easily accessible 1-alkynyl-1-chloro-2,2-dimethylcyclopropanes **1a,b** were chosen as the starting compounds. The presence of two geminal methyl groups in their molecules unambiguously determines the direction of dehydrochlorination and excludes the possibility of isomerization of cyclopropene intermediates if formed during the reaction. It was shown that the addition of cyclopropanes **1a,b** to a fivefold excess of benzenethiol or 4-methylbenzenethiol and 7.5-fold excess of powdered KOH in DMSO at 90—100 °C affords the corresponding 1-alkynyl-2-arylsulfanylcyclopropanes **3a—d** as a mixture of *cis*- and *trans*-isomers in 56-67% yield (Scheme 1, Table 1).

Scheme 1



1, 2: R^1 = Ph (**a**), Bu^t (**b**)
3: $R^1 = R^2$ = Ph (**a**); R^1 = Ph, R^2 = 4-MeC_6H_4 (**b**); $R^1 = Bu^t$, R^2 = Ph (**c**); $R^1 = Bu^t$, R^2 = 4-MeC_6H_4 (**d**)

Reagents and conditions: *i*. KOH, DMSO, 90—100 °C.

As follows from the structures of the products obtained, sulfides **3a—d** most probably formed from chlorocyclopropanes **1a,b** according to the elimination—addition mechanism *via* alkynylcyclopropenes **2a,b** resulting from dehydrochlorination of the starting chlorocyclopropanes under the action of the hydroxide anions. Then, similarly to analogous reactions with alcohols described by us previously,[8] the arenethiolate ions present in the reaction mixture add to the double bond of the cyclopropene fragment, exclusively at the unsubstituted carbon atom, affording cyclopropane sulfides **3a—d**.

The nature of the substituent at the triple bond greatly influences the rate of the reaction under study. Thus,

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Table 1. Preparation of sulfides **3a—d** from 1-(alk-1-ynyl)-1-chloro-2,2-dimethylcyclopropanes **1a,b**[a]

Starting compound	RSH	*t*/h	*T*/°C	Product	Yield (%)	*trans* : *cis* ratio [b]
1a	PhSH	3	90	**3a**	67[c]	1.4 : 1
1a	4-MeC_6H_4SH	3	90	**3b**	56[c]	1.5 : 1
1b	PhSH	8	100	**3c**	64[d]	1.7 : 1
1b	4-MeC_6H_4SH	8	100	**3d**	59[d]	1.6 : 1

[a] Fivefold excess of RSH, 7.5-fold excess of KOH, DMSO, 80—100 °C.
[b] Based on the NMR spectra of isolated products.
[c] Isolated by column chromatography.
[d] Isolated by vacuum microdistillation.

chlorocyclopropane **1a** containing the phenyl substituent at the triple bond reacts completely at 90 °C for 3 h, while heating at 100 °C for 8 h is required for complete conversion of chloride **1b** containing the *tert*-butyl substituent. Presumably, this is related to a more pronounced $-I$-effect of the phenylethynyl fragment, which favors easier elimination of HCl from chlorocyclopropane **1a**.

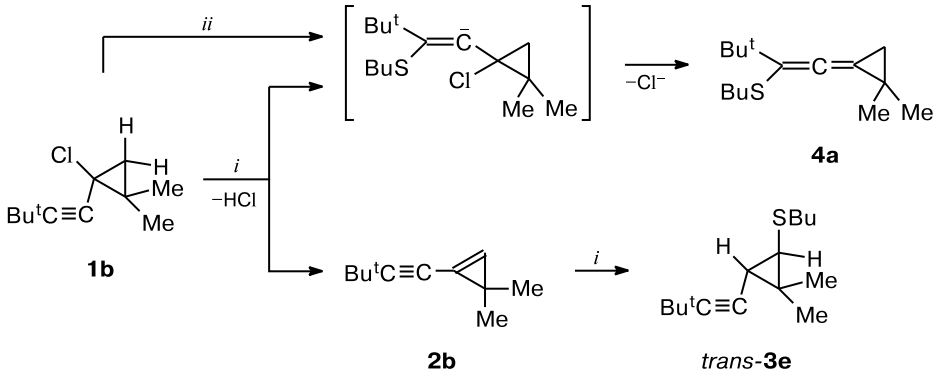
In contrast to the reactions with arenethiols, the reactions of alkanethiols with the same alkynyl(chloro)-cyclopropanes **1** are more complicated. Thus, in addition to *trans*-cyclopropane **3e** isomeric allene **4a** formed in the reaction of 2,2-dimethyl-1-(3,3-dimethylbut-1-ynyl)-1-chlorocyclopropane **1b** with butanethiol (fivefold excess) (the ratio **3e** : **4a** = 1 : 1.4) (Scheme 2). The total yield of these two products was 34%, they were characterized without separation.

Most probably, the formation of alkenylidenecyclopropane **4a** is the result of addition of the butanethiolate anion at the triple bond of compound **1b** followed by elimination of the chloride anion. The possibility of proceeding of related processes was described in literature.[12,13] The experimental confirmation of this assumption is the fact that compound **4a** was obtained in 30% yield without admixture of the acetylenic isomer **3e** upon heating of cyclopropane **1b** with a fivefold excess of sodium butanethiolate (obtained previously from butanethiol and sodium hydride) in DMSO at 100 °C for 16 h. On the contrary, *trans*-cyclopropane **3e** was obtained in 45% yield upon reaction of cyclopropene **2b** prepared as described previously,[8] with butanethiol in DMSO in the presence of KOH at 100 °C. Hence, product **4a** was obtained directly from chloride **1b**.

The reaction of chlorocyclopropane **1a** with butanethiol (fivefold excess) and KOH (fivefold excess) as suspension in DMSO at 90—100 °C afforded olefinic bissulfide **5a** in a yield of 60% (a mixture of *Z*- and *E*-isomers, ratio 9 : 1) (Scheme 3). Probably, in this case exclusive addition of the thiolate anion followed by elimination of the chloride anion occurs in the first step rather than elimination of HCl due to increased electrophilicity of the triple bond. In contrast to analogous product **4a**, alkenylidenecyclopropane **4b** formed primarily adds one more molecule of butanethiol at the central carbon atom of the allene system due to activating influence of the phenyl substituent.

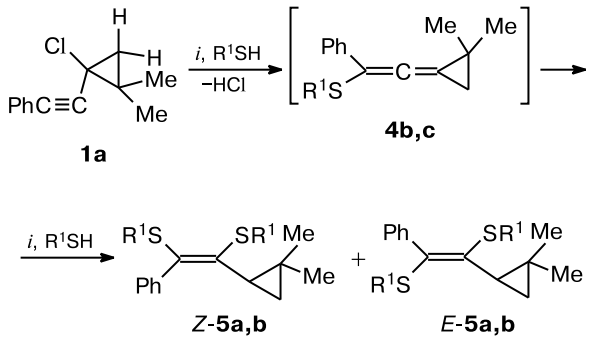
Analogous results were obtained in the reaction of cyclopropane **1a** with 2-aminoethanethiol (see Scheme 3). In this case, the reaction proceeds exclusively at the SH group to give vinylcyclopropanes **5b** (a mixture of *Z*- and *E*-isomers in a 3.2 : 1 ratio, the yield was 65%); no reac-

Scheme 2



Reagents and conditions: *i*. KOH, DMSO, BuSH, 80—100 °C; *ii*. BuSNa, DMSO, 100 °C.

Scheme 3



R^1 = Bu (**4b, 5a**), $NH_2CH_2CH_2$ (**4c, 5b**)

Reagent and conditions: *i*. KOH, DMSO, 80—100 °C.

tion products with involvement of the amino group was observed. Such a chemospecificity could be explained by formation, under the reaction conditions, of small amounts of the 2-aminoethanethiolate anion, which is the true reactive species.

The structure of the products obtained **3—5** was established based on data from NMR and mass spectra. The mass spectra of all compounds show rather abundant peaks of the molecular ions. In the ^{13}C NMR spectra of sulfides **3a—e**, two signals typical of carbon atoms of the acetylene fragment at δ 74—91 are observed. In the ^1H NMR spectra, the expected groups of signals for the substituents at the triple bond and in the cyclopropane ring, pairs of douplets for the cyclopropane protons are observed, too. The vicinal spin—spin coupling constants of these protons (4.6—4.7 Hz for the major isomer and 6.9—7.9 Hz for the minor isomer) unambiguously point to the prevalence of *trans*-isomer in all the cases.

In the ^{13}C NMR spectra of alkenylidenecyclopropane **4a**, typical signals for the allene fragment at δ 95.4, 116.4, and 179.5 were observed, corresponding to two terminal and one central carbon atoms. In the ^1H NMR spectra of akenylcyclopropanes **5a,b**, typical sets of doublets of doublets corresponding to the protons of 1,1,2-trisubstituted cyclopropane ring and a doubled set of signals of the alkulsulfanyl substituents were observed, which confirmed the presence of two isomers. The additional confirmation of the structure is the presence, in the ^{13}C NMR spectra, of two weak signals at δ 137—139 corresponding to tetrasubstituted double bond and the absence of signals for the acetylene fragment. The configuration of the double bond in cyclopropanes **5a,b** was determined based on NOESY-2D spectra, according to which the cyclopropane and phenyl substituents in the major isomer are *cis*.

Thus, the ability of 1-(alk-1-ynyl)-1-chlorocyclopropanes to react with arenethiols and alkanethiols in a basic system KOH/DMSO was revealed. Some regularities of the effect of the structure of the starting compound on the regio- and stereoselection of these processes were demonstrated. It was shown that arenethiols react regioselectively to afford hetherto unkown 1-alynyl-2-arylsulfanylcyclopropanes. At the same time, in the case of alkanethiols the formation of (1,2-bisalkylsulfanylalkenyl)cyclopropanes or mixtures of isomeric 1-(alk-1-ynyl)-2-alkylsulfanylcyclopropanes and alkylsulfanylalkenylidenecyclopropanes is observed, which results probably from the addition of the thiolate anion present in the reaction mixture to the triple bond.

Experimental

The GLC analysis of the starting compounds and the products obtained was performed on a Hewlett—Packard 5890 Series II instrument equipped with a capillary column (30 m × 0.153 mm) and a Hewlett—Packard 3396A automatic integrator. ^1H and ^{13}C NMR spectra of solutions in $CDCl_3$ (except for compound **5b**) were recorded on a Bruker AC-200p spectrometer using Me_4Si as the internal standard. Mass spectra were obtained on a Finningan MAT INCOS-50 chromato-mass spectrometer.

The starting 1-(alk-1-ynyl)-1-chlorocyclopropanes **1** were synthesized by cycloaddition of (alk-1-ynyl)chlorocarbenes to 2-methylpropene according to the procedures published earlier.[1,2]

Reaction of 1-(alk-1-ynyl)-1-chloro-2,2-dimethylcyclopropanes 1a,b with arenethiols in the presence of KOH (general procedure). Powdered KOH (840 mg, 15 mmol) was added to a solution of arenethiol (10 mmol) in DMSO (2—3 mL). Then a solution of (alk-1-ynyl)chlorocyclopropane (2 mmol) in DMSO (0.5 mL) was added and the reaction mixture was heated with vigorous stirring (conditions are given in Table 1). After completion of the reaction, water (5 mL) and ether (10 mL) were added, the organic layer was separated, the aqueous layer was extracted with ether three times. The combined organic layers were successively washed with 10% NaOH and water two times, and dried with $MgSO_4$. The solvent was evaporated, and the product was isolated from the residue by column chromatography or by vacuum microdistillation. The yields and isomers ratio of the products obtained are presented in Table 1.

3,3-Dimethyl-1-phenylsulfanyl-2-phenylethynylcyclopropane (3a) was prepared in 67% yield from chlorocyclopropane **1a** and benzenethiol. It was isolated by column chromatography on silica gel (eluent, hexane—Et_2O, 10 : 1).

trans-Isomer. ^1H NMR, δ: 1.48 (s, 3 H, Me); 1.62 (s, 3 H, Me); 1.74 (d, 1 H, CHC≡C, J = 4.7 Hz); 2.53 (d, 1 H, CHSPh, J = 4.7 Hz); 7.20—7.70 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 20.5, 22.6, 23.5 (2 Me + C≡CCH); 27.2 (CMe_2); 35.0 (CHSPh); 80.6, 88.4 (C≡C); 123.5 (C(1), C_6H_5C≡C); 126.2, 127.7, 128.0, 128.2, 128.8, 131.5 (2 Ph); 138.0 (C(1), Ph).

cis-Isomer. ^1H NMR, δ: 1.45 (s, 3 H, Me); 1.53 (s, 3 H, Me); 2.07 (d, 1 H, CHC≡C, J = 7.9 Hz); 2.52 (d, 1 H, CHSPh, J = 7.9 Hz); 7.20—7.70 (m, 10 H, 2 Ph). ^{13}C NMR, δ: 16.8, 21.0, 26.5 (2 Me + C≡CCH); 25.5 (CMe_2); 33.2 (CHSPh); 81.5, 85.7 (C≡C); 123.7 (C(1), C_6H_5C≡C); 124.9, 125.0, 126.9, 127.6, 128.7, 131.7 (2 Ph); 137.7 (C(1), Ph). MS, *m/z*: 278 $[M]^+$. Found (%): C, 81.82; H, 6.43; S, 11.71. $C_{19}H_{18}S$. Calculated (%): C, 81.97; H, 6.52; S, 11.52.

3,3-Dimethyl-1-(4-methylphenylsulfanyl)-2-phenylethynylcyclopropane (3b) was prepared in 56% yield from chlorocyclopropane **1a** and 4-methylbenzenehiol. It was isolated by column chromatography on silica gel (eluent, hexane—Et_2O, 10 : 1).

trans-Isomer. ^{1}H NMR, δ: 1.47 (s, 3 H, Me); 1.59 (s, 3 H, Me); 1.70 (d, 1 H, CHC≡C, J = 4.7 Hz); 2.51 (d, 1 H, CHS, J = 4.7 Hz); 7.15—7.6 (m, 9 H, Ph + Tol). ^{13}C NMR, δ: 20.6, 22.7, 23.6 (2 Me + C≡C<u>C</u>H); 21.1 (<u>C</u>H$_3$C$_6$H$_4$); 27.2 (<u>C</u>Me$_2$); 35.6 (<u>C</u>HS); 80.5, 88.5 (C≡C); 123.6 (C(1), <u>C</u>$_6$H$_5$C≡C); 126.7, 127.6, 128.2, 129.6, 131.5 (Ph + Tol); 134.1, 134.7 (C(1) + C(4), Tol).

cis-Isomer. ^{1}H NMR, δ: 1.41 (s, 3 H, Me); 1.51 (s, 3 H, Me); 2.01 (d, 1 H, CHC≡C, J = 7.9 Hz); 2.51 (d, 1 H, CHS, J = 7.9 Hz); 7.15—7.60 (m, 9 H, Ph + Tol). ^{13}C NMR, δ: 16.9, 20.9, 26.6 (2 Me + C≡C<u>C</u>H); 21.0 (<u>C</u>H$_3$C$_6$H$_4$); 25.5 (<u>C</u>Me$_2$); 34.0 (CHS); 81.6, 86.9 (C≡C); 123.7 (C(1), <u>C</u>$_6$H$_5$C≡C); 127.5, 127.6, 128.0, 129.5, 131.7 (Ph + Tol); 133.8, 134.9 (C(1) + C(4), Tol). MS, m/z: 292 [M]$^+$. Found (%): C, 81.98; H, 6.78; S, 11.01. $C_{20}H_{20}S$. Calculated (%): C, 82.14; H, 6.89; S, 10.97.

3,3-Dimethyl-2-(3,3-dimethylbut-1-ynyl)-1-phenylsulfanylcyclopropane (3c) was prepared in 64% yield from chlorocyclopropane **1b** and benzenethiol. It was isolated by vacuum microdistillation (150—160 °C (bath)/ 0.5 Torr).

trans-Isomer. ^{1}H NMR, δ: 1.26 (s, 9 H, Bu^t); 1.24 (s, 3 H, Me); 1.35 (d, 1 H, CHC≡C, J = 4.6 Hz); 1.36 (s, 3 H, Me); 2.17 (d, 1 H, CHS, J = 4.6 Hz); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 20.5, 20.8, 22.3, (2 Me, C≡C<u>C</u>H); 26.0 (<u>C</u>Me$_2$); 27.2 (<u>C</u>Me$_3$); 31.6 (C(<u>C</u>H$_3$)$_3$); 34.3 (<u>C</u>HS); 76.5, 90.0 (C≡C); 126.1, 127.0, 131.8 (Ph); 137.8 (C(1), Ph).

cis-Isomer. ^{1}H NMR, δ: 1.18 (s, 3 H, Me); 1.21 (s, 3 H, Me); 1.25 (s, 9 H, Bu^t); 1.71 (d, 1 H, CHC≡C, J = 7.9 Hz); 2.23 (d, 1 H, CHS, J = 7.9 Hz); 7.2—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 16.2, 20.2, 26.6 (2 Me, C≡C<u>C</u>H); 27.6 (<u>C</u>Me$_2$); 27.3 (<u>C</u>Me$_3$); 31.2 (C(<u>C</u>H$_3$)$_3$); 32.5 (<u>C</u>HS); 74.9, 90.0 (C≡C); 126.3, 127.4, 131.5 (Ph); 137.7 (C(1), Ph). MS, m/z: 258 [M]$^+$. Found (%): C, 78.85; H, 8.65; S, 12.33. $C_{17}H_{22}S$. Calculated (%): C, 79.01; H, 8.58; S, 12.41.

3,3-Dimethyl-2-(3,3-dimethylbut-1-ynyl)-1-(4-methylphenylsulfanyl)cyclopropane (3d) was prepared in 59% yield from chlorocyclopropane **1b** and 4-methylbenzenethiol. It was isolated by vacuum microdistillation (150—160 °C (bath)/0.5 Torr).

trans-Isomer. ^{1}H NMR, δ: 1.25 (s, 9 H, Bu^t); 1.28 (s, 3 H, Me); 1.31 (d, 1 H, CHC≡C, J = 4.6 Hz); 1.37 (s, 3 H, Me); 2.15 (d, 1 H, CHS, J = 4.6 Hz); 2.32 (s, 3 H, SC$_6$H$_4$C<u>H</u>$_3$); 7.05—7.30 (m, 4 H, C$_6$H$_4$). ^{13}C NMR, δ: 20.5, 20.8, 22.3, 23.0 (3 Me, C≡C<u>C</u>H); 25.9 (<u>C</u>Me$_2$); 27.2 (<u>C</u>Me$_3$); 31.3 (C(<u>C</u>H$_3$)$_3$); 34.8 (<u>C</u>HS); 76.8, 89.1 (C≡C); 126.4, 129.5 (C$_o$, C$_m$, Tol); 134.3, 134.6 (C(1) + C(4), Tol).

cis-Isomer. ^{1}H NMR, δ: 1.20 (s, 6 H, 2 Me); 1.25 (s, 9 H, Bu^t); 1.65 (d, 1 H, CHC≡C, J = 7.9 Hz); 2.22 (d, 1 H, CHS, J = 7.9 Hz); 2.32 (s, 3 H, SC$_6$H$_4$C<u>H</u>$_3$); 7.05—7.30 (m, 4 H, C$_6$H$_4$). ^{13}C NMR, δ: 16.6, 20.4, 26.5, 31.1 (3 Me, C≡C<u>C</u>H); 27.4 (<u>C</u>Me$_2$); 27.3 (<u>C</u>Me$_3$); 31.2 (C(<u>C</u>H$_3$)$_3$); 32.9 (<u>C</u>HS); 74.8, 90.1 (C≡C); 127.4, 129.3 (C$_o$, C$_m$, Tol); 134.2, 134.5 (C(1) + C(4), Tol). MS, m/z: 272 [M]$^+$. Found (%): C, 79.48; H, 8.65; S, 11.92. $C_{18}H_{24}S$. Calculated (%): C, 79.35; H, 8.88; S, 11.77.

Reaction of 1-chloro-1-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropane (1b) with butanethiol in the presence of KOH. Powdered KOH (560 mg, 10 mmol) was added to a solution of butanethiol (900 mg,10 mmol) in DMSO (5 mL). Then a solution of chlorocyclopropane **1b** (370mg, 2 mmol) in DMSO (0.5 mL) was added, and the reaction mixture was heated with vigorous stirring for 4 h at 100 °C. After completion of the reaction, water (5 mL) and ether (10 mL) were added, the organic layer was separated, the agueous layer was extracted with ether three times. The combined organic layers were washed with water twice and dried with $MgSO_4$. The solvent was evaporated, and the product was isolated from the residue by vacuum microdistillation (100—110 °C (bath)/1 Torr). The yield of the liquid compound was 160 mg (a mixture of *trans*-**3e** and **4a** in 1 : 1.5 ratio, NMR), which corresponds to 34% overall yield.

***trans*-1-Butylsulfanyl-3,3-dimethyl-2-(3,3-dimethylbut-1-ynyl)cyclopropane (*trans*-3e).** ^{1}H NMR, δ: 0.95 (t, 3 H, Me in Bu, J = 7.1 Hz); 1.12 (d, 1 H, CHC≡C, J = 4.7 Hz); 1.19 (s, 9 H, Bu^t); 1.21 (s, 1 H, Me); 1.22 (s, 1 H, Me); 1.20—1.70 (m, 4 H, C<u>H</u>$_2$C<u>H</u>$_2$Me); 1.80 (d, 1 H, C<u>H</u>SBu, J = 4.7 Hz); 2.55 (t, 2 H, CH$_2$S, J = 6.9). ^{13}C NMR, δ: 14.2 (Me in Bu); 20.7, 22.5, 23.1 (2 Me, C≡C<u>C</u>H); 25.8 (<u>C</u>Me$_2$); 27.5 (<u>C</u>Me$_3$); 31.4 (C(<u>C</u>H$_3$)$_3$); 32.0 (CH$_2$); 32.9 (CH$_2$); 35.8 (CHS); 77.3, 88.5 (C≡C). MS, m/z: 238 [M]$^+$.

2-(2-Butylsulfanyl-3,3-dimethylbut-1-enylidene)-1,1-dimethylcyclopropane (4a). ^{1}H NMR, δ: 0.90 (t, 3 H, Me in Bu, J = 7.1 Hz); 1.16 (s, 9 H, Bu^t); 1.27 (s, 1 H, Me); 1.28 (s, 1 H, Me); 1.38 (s, 2 H, CH$_2$); 1.20—1.70 (m, 4 H, C<u>H</u>$_2$C<u>H</u>$_2$Me); 2.52 (t, 2 H, CH$_2$S, J = 6.9 Hz); ^{13}C NMR, δ: 13.8 (Me in Bu); 21.4 (<u>C</u>Me$_2$); 22.1 (CH$_2$); 24.3, 24.4 (2 Me); 29.8 (C(<u>C</u>H$_3$)$_3$); 31.1 (CH$_2$ in *cyclo*-C$_3$H$_2$); 31.8 (CH$_2$); 32.7 (CH$_2$); 35.9 (<u>C</u>Me$_3$); 95.4 (C= in *cyclo*-C$_3$H$_2$); 116.4 (=<u>C</u>(Bu^t)SBu); 179.5 (=C=). MS, m/z: 238 [M]$^+$.

Reaction of 1-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropene 2b with butanethiol in the presence of KOH. Cyclopropene **2b** was synthesized by the action of lithium diethylamide on chlorocyclopropane **1b** according to the procedure published earlier.[8] The product obtained (87 mg, ~85% purity) was added to a mixture of DMSO (2 mL), BuSH (450 mg, 5 mmol), and KOH (112 mg, 2 mmol) preheated to 100 °C, and the reaction mixture was stirred for 15 min. After completion of the reaction, water (5 mL) and ether (10 mL) were added, the organic layer was separated, the aqueous layer was extracted with ether three times. The combined organic extracts were washed with water twice, and dried with $MgSO_4$. The solvent was evaporated, and toluene (50 mg) as the internal standard was added to the residue. The main product in the mixture obtained was sulfide *trans*-**3e** (^{1}H NMR data), the yield was 45% (with respect to the starting chloride **1b**) determined by comparison of integral intensities of the signal for CHS fragment and signals for aromatic protons of toluene.

Reaction of 1-chloro-1-(3,3-dimethylbut-1-ynyl)-2,2-dimethylcyclopropane (1b) with sodium butanethiolate. A 60% suspension of sodium hydride in mineral oil (400 mg, 10 mmol) was added to a solution of butanethiol (1.080 g, 12 mmol) in DMSO (10 mL). After evolution of hydrogen ceased, a solution of chlorocyclopropane **1b** (370 mg, 2 mmol) in DMSO (0.5 mL) was added and the reaction mixture was vigorously stirred for 16 h at 100 °C. After completion of the reaction, water (5 mL) and ether (10 mL) were added, the organic layer was separated, the aqueous layer was extracted with ether three times. The combined organic layers were washed with water twice, and dried with $MgSO_4$. The solvent was evaporated, and alkenylidenecyclopropane **4a** was isolated by vacuum microdistillation (100—110 °C (bath)/1 Torr). The yield of **4a** was 165 mg (35%),

purity was ~85%, it did not contain acetylene derivative **3e** isomeric to **4a**.

Reaction of 1-chloro-2,2-dimethyl-1-phenylethynylcyclopropane (1a) with alkanethiols in the presence of KOH. The reaction was carried out according to the general procedure at 80—90 °C for 4 h. The products were isolated by vacuum microdistillation (**5a**) or by passing a solution in a hexane—ether mixture through a thin layer of silica gel (**5b**).

2-[1,2-Di(butylsulfanyl)-2-phenylvinyl]-1,1-dimethylcyclopropane (5a) was obtained in 60% yield from chlorocyclopropane **1b** and butanethiol. It was isolated by the vacuum microdistillation (180—190 °C (bath)/0.5 Torr). ^{1}H NMR, δ: 0.32 (dd, 1 H, 1 H from CH_2 in *cyclo*-C_3H_3, J = 5.8 Hz, J = 4.6 Hz); 0.51 (dd, 1 H, 1 H from CH_2 in *cyclo*-C_3H_3, J = 8.4 Hz, J = 4.6 Hz); 0.76 (s, 3 H, Me); 0.77 (t, 3 H, Me in Bu, J = 7.2 Hz); 0.84 (s, 3 H, Me); 0.96 (t, 3 H, Me in Bu, J = 7.2 Hz); 1.15—1.75 (m, 9 H, 4 CH_2 + CHC=); 2.23 (t, 2 H, SCH_2—, J = 7.1 Hz); 2.83 (td, 2 H, SCH_2—, J = 7.2 Hz, J = 2.4 Hz); 7.15—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 13.6, 13.8 (2 Me in 2 Bu); 20.3, 26.3, 28.9 (2 Me, CHC=C); 20.9 (CMe_2); 21.7, 22.2, 22.8, 32.0, 31.9, 32.4, 32.5 (7 CH_2); 127.0, 127.7, 130.0 (Ph); 134.8, 137.7, 139.3 (C(1) в Ph, C=C). MS, *m/z*: 348 $[M]^+$. Found (%): C, 72.12; H, 9.16; S, 18.67. $C_{21}H_{32}S_2$. Calculated (%) C, 72.35; H, 9.25; S, 18.40.

2-[1,2-Bis(2-aminoethylsulfanyl)-2-phenylvinyl]-1,1-dimethylcyclopropane (5b) was obtained in 65% yield from chlorocyclopropane **1b** and 2-aminoethanethiol. It was isolated by passing a solution in hexane—ether mixture (10 : 1) through a thin layer of silica gel.

Z-Isomer. ^{1}H NMR (DMSO-d_6), δ: 0.25 (dd, 1 H, 1 H from CH_2 in *cyclo*-C_3H_3, J = 6.0 Hz, J = 4.6 Hz); 0.57 (dd, 1 H, 1 H from CH_2 in *cyclo*-C_3H_3, J = 8.4 Hz, J = 4.6 Hz); 0.68 (s, 3 H, Me); 0.72 (s, 3 H, Me); 1.48 (dd, 1 H, CH in *cyclo*-C_3H_3, J = 6.0 Hz, J = 8.4 Hz); 1.70 (br.s, 2 H, 2 NH_2); 2.27 (t, 2 H, SCH_2—, J = 6.6 Hz); 2.53 (m, 2 H, SCH_2—); 2.75—2.95 (m, 4 H, 2 CH_2NH_2); 7.15—7.4 (n, 5 H, Ph). ^{13}C NMR, δ: 19.9 (CHC=C); 20.5 (CMe_2); 22.3 (CH_2); 25.8, 28.2 (2 Me); 36.6 (2 CH_2NH_2); 41.0, 41.4 (2 SCH_2); 126.8, 127.5, 129.4 (Ph); 134.5, 138.0, 138.3 (C(1) в Ph, C=C). MS, *m/z*: 322 $[M]^+$.

E-Isomer. ^{1}H NMR (DMSO-d_6), δ: 0.81 (dd, 1 H, 1 H from CH_2 in *cyclo*-C_3H_3, J = 6.0 Hz, J = 4.1 Hz); 0.95 (dd, 1 H, 1 H from CH_2 in *cyclo*-C_3H_3, J = 8.2 Hz, J = 4.1 Hz); 1.06 (s, 3 H, Me); 1.27 (s, 3 H, Me); 1.53 (dd, 1 H, CH in *cyclo*-C_3H_3, J = 6.0 Hz, J = 8.2 Hz); 1.70 (br.s, 2 H, 2 NH_2); 2.27 (t, 2 H, SCH_2—, J = 6.5 Hz); 2.75—2.95 (m, 6 H, 2 CH_2NH_2, SCH_2—); 7.15—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 19.3 (CHC=C); 20.5 (CMe_2); 21.7 (CH_2); 26.6, 27.7 (2 Me); 29.2 (CMe_2); 36.2, 37.0 (2 CH_2NH_2); 40.8, 41.6 (2 SCH_2); 126.9, 127.6, 129.2 (Ph); 138.3, 138.7, 141.9 (C(1) в Ph, C=C). MS, *m/z*: 322 $[M]^+$. Found: C, 63.58; H, 7.95; S, 19.74. $C_{17}H_{26}N_2S_2$. Calculated (%): C, 63.31; H, 8.13; S, 19.88.

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References

1. K. N. Shavrin, I. V. Krylova, I. B. Shvedova, G. P. Okonnishnikova, I. E. Dolgy, O. M. Nefedov, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1875.
2. K. N. Shavrin, V. D. Gvozdev, O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1143 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1237].
3. T. Liese, A. de Meijere, *Chem. Ber.*, 1986, **119**, 2995.
4. D. Merkel, G. Koebrich, *Chem. Ber.*, 1973, **106**, 2040.
5. K. N. Shavrin, V. D. Gvozdev, O. M. Nefedov, *Mendeleev Commun.*, 2008, **18**, 300.
6. K. N. Shavrin, V. D. Gvozdev, D. V. Budanov, S. V. Yurov, O. M. Nefedov, *Mendeleev Commun.*, 2006, **16**, 73.
7. K. N. Shavrin, V. D. Gvozdev, O. M. Nefedov, *Mendeleev Commun.*, 2008, **18**, 16.
8. K. N. Shavrin, V. D. Gvozdev, O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 2078 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 2117].
9. S. Braese, S. Schoemenauer, G. McGaffin, A. Stolle, A. de Meijere, *Chem. Eur. J.*, 1996, **2**, 545.
10. G. McGaffin, A. de Meijere, *Synthesis*, 1994, 583.
11. H.-C. Militzer, S. Schoemenauer, C. Otte, C. Puls, J. Hein, *Synthesis*, 1993, 998.
12. A. Roedig, G. Zaby, *Liebigs Ann. Chem.*, 1979, 1614.
13. A. Roedig, G. Zaby, *Tetrahedron Lett.*, 1977, 1771.

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