Reaction of unsaturated compounds with ethyl benzenesulfenate and trimethylsilyl isothiocyanate

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A new method for the synthesis of thiocyanato- and isothiocyanatoalkyl phenyl sulfides by the reaction of unsaturated compounds with ethyl benzenesulfenate and trimethylsilyl isothiocyanate has been suggested. Regio- and stereoselectivity of the reaction was studied, having taken alkenes, dienes, and alkynes as examples.

Key words: ethyl benzenesulfenate, trimethylsilyl isothiocyanate, alkenes, alkynes, sulfenylation, thiocyanates, electrophilic addition.

Addition of sulfenic acid derivatives (RS—X) to unsaturated compounds is one of the principal methods for the functionalization of multiple bonds, which furnishes β-substituted sulfides. Earlier,[1] we have suggested a new method for the halosulfenylation of olefins and dienes with the ethyl benzenesulfenate—trimethylsilyl halides system. In continuation of our studies in this field, we investigated a possibility of sulfenylation of unsaturated compounds with the ethyl benzenesulfenate—trimethylsilyl isothiocyanate system in order to prepare thiocyanate or isothiocyanate-containing sulfides. There are only two examples of the formation of thiocyanatoalkyl aryl sulfides,[2,3] in which sulfenethiocyanates were used. At fist glance, this is the simplest approach. However, it should be noted that the yields in these reactions are moderate, in some cases no reaction occurs, since the rate of a competing process, *viz.*, disproportionation of the reagent with the formation of the corresponding disulfide, turned out to be higher than the rate of addition at the double bond. At the same time, the importance of accomplishing such transformations is obvious, since an introduction of thiocyanate or isothiocyanate group into a molecule opens a possibility for the preparation of a wide variety of biologically active compounds and heterocycles.[4—6]

Trimethylsilyl isothiocyanate was obtained *in situ* from sodium isothiocyanate and trimethylsilyl chloride in chloroform (or dichloromethane) with stirring for 1 h.* The formation of trimethylsilyl isothiocyanate in the reaction mixture was confirmed spectroscopically: the ^{1}H NMR spectrum exhibited a singlet for the methyl groups with $\delta = 0.34$. The ^{13}C and ^{29}Si NMR spectra exhibited a spin-spin interaction of the carbon ^{13}C and silicon ^{29}Si nuclei with the nitrogen ^{14}N nucleus. For instance, the ^{13}C NMR spectrum, together with a singlet for the trimethylsilyl group at $\delta = 1.78$, contains a triplet of lines of equal intensities for the isothiocyanate group $\delta = 141.26$ and the spin-spin coupling constant ^1J (^{13}C—^{14}N) = 25.6 Hz. In the ^{29}Si NMR spectrum, the signal for the silicon is found as a triplet of lines of equal intensities with $\delta = 5.53$ (see Refs 7 and 8) and ^1J (^{29}Si—^{14}N) = 7.9 Hz, that is an evidence that the nitrogen and silicon nuclei in the molecule are bound directly to each other. The ^{14}N NMR spectrum of the reagent obtained *in situ* is characterized by a singlet at $\delta = -263.7$ characteristic of isothiocyanates[9] and unusually narrow line half-widths, which is only 5.3 Hz, that is an evidence of a high symmetry in the charge distribution at the nitrogen nucleus and a small contribution of the quadrupole relaxation into the overall time of the spin-lattice relaxation. The high symmetry of the charge distribution at the nitrogen nucleus in trimethylsilyl isothiocyanate is apparently due to the delocalization of the lone pair of electrons on the nitrogen atom to the vacant d-orbitals of the silicon atom.[8] A broad absorption band at 2100 cm^{-1} characteristic of isothiocyanates[10] was observed in the IR spectrum of the reagent.

To synthesize β-substituted sulfides (Scheme 1), a solution of olefin and ethyl benzenesulfenate in chloroform (or dichloromethane) was slowly added to trimethylsilyl isothiocyanate obtained *in situ* and the mixture was stirred at room temperature until the reaction was completed (30—40 min).

The structures of the thiocyanato- and isothiocyanatoalkyl phenyl sulfides obtained were established by IR and ^{1}H and ^{13}C NMR spectroscopy. Compositions of the

* If the stirring time is shorter, β-chlorophenylthioalkanes are formed as the side reaction products upon subsequent addition of an olefin.

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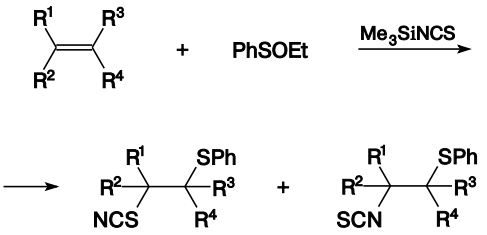
Scheme 1



new compounds were confirmed by the elemental analysis and mass spectrometric data. The formation of thiocyanates is confirmed by the presence in the ^{13}C NMR spectra of the signal characteristic of the thiocyanate carbon (—SCN) in the region δ 111.50—116.0, as well as by the presence in the IR spectrum of a narrow absorption band of medium intensity in the region 2170 cm^{-1} (see Ref. 10). Despite the available literature data[11,12] on the fact that chemical shift for the carbon atom of an isothiocyanate group (—NCS) is in the region δ 128.0—137.0, we in most cases failed in the registration of the signal for the quaternary isothiocyanate carbon atom, apparently, because of the broadening due to the spin-spin interaction with the nitrogen atom. Nevertheless, the formation of isothiocyanates is unambiguously confirmed by the IR and ^{14}N NMR spectroscopic data. For instance, the IR spectra of isothiocyanates exhibit a broad intensive band at 2050—2200 cm^{-1} (see Ref. 10). In the ^{14}N NMR spectra, the signals for the nitrogen atom of the isothiocyanate group is found in the region δ −(260—290), whereas the signals for the nitrogen atom of the thiocyanate group, in the narrow region δ ~100 (see Ref. 9).

Using alkenes of different structures as examples, regio- and stereoselectivity of the addition reaction of ethyl benzenesulfenate to them in the presence of Me_3SiNCS were studied. Thus, the reaction with cyclohexene (**1**) and norbornene (**2**) (Scheme 2) proceeds chemo- and stereospecifically with the formation of *trans*-β-thiocyanatoalkyl phenyl sulfides **3** and **4** in the yields close to quantitative (Table 1).

Scheme 2

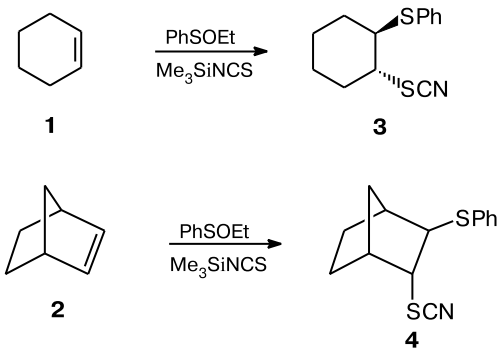


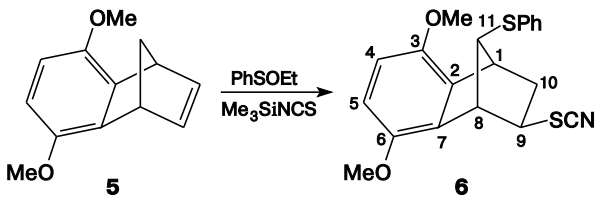
Table 1. Yields of the reaction products of ethyl benzenesulfenate with unsaturated compounds in the presence of Me_3SiNCS

Substrate	Product (ratio of isomers (%))	Yield (%)
1	**3**	99
2	**4**	99
5	**6**	99
7	**8a** + **8b** (67 : 33)	37
	9a + **9b** (75 : 25)	19
	10a + **10b** (75 : 25)	36
11	**12**	99
13	**14a** + **14b** (25 : 75)	99
15	**16**	99
18	**20**	85
19	**21**	99
22	**24a** + **24b** (90 : 10)	99
23	**25a** + **25b** (83 : 17)	99
26	**27a** + **27b** (87 : 13)	99

The *trans*-arrangement of substituents was inferred from the spin-spin coupling constants of the protons on substituents: for compound **3**, the signals are two triplets of doublets with the spin-spin coupling constants 10.1 Hz and 4.0 Hz, that corresponds to the diequatorial arrangement of the substituents.[13] In the ^1H NMR spectrum of compound **4**, the signals for the protons HCSCN and HCSPh have the shape of doublet of doublets of doublets at δ 3.53 and 2.80 with the following set of spin-spin coupling constants: $J_{2,3}$ = 5.0, $J_{2,1}$ = 4.3, $J_{2,6exo}$ = 2.2 and $J_{3,7anti}$ = 2.4, $J_{3,2}$ = 5.0, respectively. The vicinal constant value $^3J_{3,2}$ = 5.0 Hz corresponds to the *trans*-arrangement of the substituents. The *exo*-arrangement of the HCSCN proton is indicated by the presence of the spin-spin coupling constant $J_{2,1}$ = 4.3 Hz. The HCSPh proton has no spin-spin coupling constant with the bridgehead proton (H(4)), but is characterized by the interaction with the bridge proton H(7) ($J_{3,7anti}$ = 2.4, the W constant).[13]

The absence of the Wagner—Meerwein rearrangement products in the case of norbornene indicates, that effective electrophilicity of the reagent is low enough.[14] Nevertheless, the reaction of ethyl benzenesulfenate with 3,6-dimethoxybenzonorbornadiene (**5**) in the presence of trimethylsilyl isothiocyanate exclusively affords the rearranged thiocyanate **6** (Scheme 3).

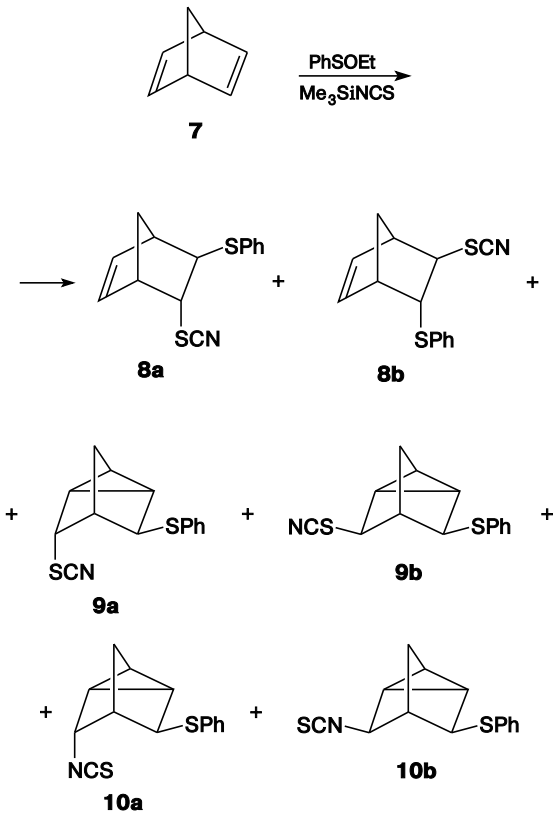
Scheme 3



The rearranged character of product **6** is indicated by the presence in the ^{1}H NMR spectrum of this compound of two vicinal spin-spin coupling constants of the HCSCN proton with the protons of neighboring $H_2C(10)$ methylene group ($J_{9,10endo}$ = 8.6, $J_{9,10exo}$ = 4.5 Hz). The *endo*-arrangement of the HCSCN proton was confirmed by the absence of a large constant of the spin-spin interaction of the HCSCN proton with the bridgehead proton H(8).

The reaction with norbornadiene (**7**) led to a complex mixture of substituted alkyl phenyl sulfides **8—10** (Scheme 4) with predominance of products of the *exo*-attack of the electrophile, that is more favorable from the point of view of steric factors. Using chromatographic separation, we successfully isolated three pairs of isomers: 6-phenylthio-5-thiocyanatobicyclo[2.2.1]hept-2-enes **8a,b** and nortricyclane products **9a,b** and **10a,b**, which resulted from the homoallylic participation by the second double bond in the reaction, with isothiocyanates **10a,b** being predominant among the nortricyclane products (*cf.* Table 1).

Scheme 4



The structures of the reaction products **8—10** were established by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of compounds **8a** and **8b** exhibit signals for the olefin protons. The spin-spin coupling constant value of the protons on the substituents ($J_{5,6}$ 3.8 Hz) indicate the *trans*-arrangement of the phenylthio and thiocyanate groups.

To establish structure of the nortricyclane products, the data on the effect of substituents on the ^{1}H nuclei chemical shifts and the data on the nuclear Overhauser effect (NOE) were used. Analysis of the literature data[15] allowed us to exclude from our consideration 5-*endo*-phenylthio-3-*exo*-thiocyanatotricyclo[2.2.1.0^{2,6}]heptane and 3-*exo*-isothiocyanato-5-*endo*-phenylthiotricyclo-[2.2.1.0^{2,6}]heptane, since the calculated* chemical shifts for the protons H(3) of these compounds were δ 4.14 and 4.48, respectively, that was considerably higher than the chemical shifts for the protons observed experimentally (Table 2).

Isothiocyanate-containing isomers **10a**,**b** were isolated as a mixture. The ^{14}N NMR spectrum of the mixture of isomers contains a signal with the chemical shift δ −277.1 characteristic of isothiocyanates.[9] In the ^{1}H NMR spectrum, two sets of signals are observed, with the ratio of their intensities being 3 : 1. Signals for the protons on the substituent are found as singlets, whose chemical shifts are δ 3.81 and 3.83 for the predominant and δ 3.22 and 3.64 for the minor isomers, respectively. As it has been shown earlier,[15] a considerable downfield shift of the signal for the H(5) is due to the change in the orientation of substituent on the C(3) atom (*exo*→*endo*). This allowed us to suggest that compound **10a** has the structure of 3-*endo*-isothiocyanato-5-*exo*-phenylthiotricyclo[2.2.1.0^{2,6}]heptane, whereas compound **10b** is 3-*exo*-isothiocyanato-5-*exo*-phenylthiotricyclo[2.2.1.0^{2,6}]heptane. Our suggestion was confirmed when the NOE experiment was performed. When the signal for the H(3)CNCS proton (δ 3.64) of the minor isomer **10b** was irradiated, the Overhauser effect was observed on the proton H(5)CSPh (η = 3.6%) (Table 3). For the predominant isomer **10a**, the NOE was observed upon irradiation of the bridge proton H(7′) (δ 1.44): the intensity of the signal at δ 3.83 (H(3)) increased by 2.6%. To sum up, the structure of *exo*-*exo*-adduct can be assigned to the minor isomer **10b**, whereas to the predominant isomer **10a**, the structure of *exo*-*endo*-adduct.

The structures of isomers **9a,b** were established similarly. In the case of product **9a**, the Overhauser effect on the *ortho*-proton of the phenylthio group (η = 2.0%) upon irradiation of the proton at δ 3.81 allowed us to assign the latter to the proton H—C—SPh. At the same time, the absence of the NOE on the bridge protons allows us to draw a conclusion on the *exo*-arrangement of the arylthio group. The *endo*-arrangement of the thiocyanate group

* The calculation was performed using the following formula $\delta_3 = \delta_0 + \Delta_s + \Delta_{de}$, where δ_3 is the chemical shift for the proton HCSCN or HCNCS in 3,5-disubstituted nortricyclane, δ_0 is the chemical shift for the proton C(3) in 3-nortricyclane system (δ_0(HCSCN) = 3.28, δ_0(HCNCS) = 3.62), Δ_s is the change in the chemical shift for the proton H(3) due to the substituent at position 5 (*endo* or *exo*) (for HCSCN and HCNCS Δ_s = 0.0 ppm), and Δ_{de} is a deshielding effect of the *endo*-substituent at position 5 (Δ_{de}(HCSPh) = 0.86 + 0.02 ppm).[15]

Table 2. ^{1}H NMR spectra of compounds **8—10** (in $CDCl_3$)

Compound	δ ($J_{H,H}$/Hz)[a]							
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(7′)
8a	2.95 (m)	6.28 (dd, $J_{2,3}$ = 5.7, $J_{2,1}$ = 2.8)	6.35[b] (m)	2.83 (ddd, $J_{4,5}$ = 3.9, $J_{4,3}$ = 2.4, J = 0.5)	3.64 (dd, $J_{5,4}$ = 3.9, $J_{5,6}$ = 3.7)	3.30 (m)	1.95 (dm, $J_{7,7'}$ = 9.5)	1.80 (dm, $J_{7,7'}$ = 9.5)
8b	3.05 (dd, $J_{1,6}$ = 3.8, $J_{1,2}$ = 2.1)	6.32—6.39[b] (m, 2 H)		3.19 (m, 2 H)		3.28 (t, $J_{6,1} \approx J_{6,5}$ = 3.8)	1.85[c] (dm)	1.80[c] (dm)
9a	1.56—1.64[d]		3.60 (t, $J_{3,2} \approx J_{3,4}$ = 1.4)	2.32 (br.s)	3.81 (br.s)	1.60[d,e]	2.22 (dd, $J_{7,7'}$ = 11.6, J = 1.5)	1.54 (d, $J_{7',7}$ = 11.6)
9a[f]	0.89 (tq, $J_{1,2} \approx J_{1,6}$ = 5.1, $J_{1,7} \approx J_{1,7'} \approx J_{1,4}$ = 1.1)	0.80[g]	2.72 (t, $J_{3,2} \approx J_{3,4}$ = 1.5)	1.87 (m)	3.71 (br.s)	1.11 (tt, $J_{6,1} \approx J_{6,2}$ = 5.1, $J_{6,5} \approx J_{6,4}$ = 1.1)	1.94 (dt, $J_{7,7'}$ = 11.2, $J_{7,1} = J_{7,4}$ = 1.1)	0.80[g] (d, $J_{7',7}$ = 11.2)
9b	1.56—1.64[d]		3.47 (br.s)	2.30 (br.s)	3.28 (br.s)	1.62[d,e]	2.17 (d, $J_{7,7'}$ = 11.9)	1.86 (d, $J_{7',7}$ = 11.9)
9b[f]	0.95 (tq, $J_{1,2} \approx J_{1,6}$ = 5.1, $J_{1,7} \approx J_{1,7'} \approx J_{1,4}$ = 1.1)	0.90[h]	2.72[i]	1.78 (m)	2.57 (br.s)	1.02 (tt, $J_{6,1} \approx J_{6,2}$ = 5.1, $J_{6,5} \approx J_{6,4}$ = 1.1)	1.91[j]	1.48 (d, $J_{7',7}$ = 12.0)
10a	1.52 (tddd, $J_{1,2} \approx J_{1,6}$ = 5.2, $J_{1,7}$ = 1.4, $J_{1,7'}$ = 1.2, $J_{1,4}$ = 1.0)	1.63 (tt, $J_{2,1} \approx J_{2,6}$ = 5.2, $J_{2,3} \approx J_{2,4}$ = 1.6)	3.83 (t, $J_{3,2} \approx J_{3,4}$ = 1.6)	2.22 (m)	3.81 (br.s)	1.60 (tt, $J_{6,1} \approx J_{6,2}$ = 5.2, $J_{6,5} \approx J_{6,4}$ = 1.0)	2.06 (ddd, $J_{7,7'}$ = 11.4, $J_{7,4}$ = 1.8, $J_{7,1}$ = 1.4)	1.44 (ddd, $J_{7',7}$ = 11.4, $J_{7',4}$ = 1.6, $J_{7',1}$ = 1.2)
10b	1.50—1.66[k]		3.64 (t, $J_{3,2} \approx J_{3,4}$ = 1.6)	2.27 (br.s)	3.22 (br.s)	1.50—1.66[k]	2.14 (dt, $J_{7,7'}$ = 11.4, $J_{7,1} = J_{7,4}$ = 1.1)	1.88 (dt, $J_{7',7}$ = 11.4, $J_{7',1} = J_{7',4}$ = 1.4)

[a] The signals for the protons of the PhS group are found in the region δ 7.20—7.40.
[b] The signals for the olefin protons of compounds **8a** and **8b** overlap.
[c] The signal for the proton overlaps with the signal for the proton H(7′) of compound **8a**.
[d] The signals for the protons H(1), H(2), H(6) of compounds **9a** and **9b** overlap and are found in the region δ 1.56—1.64.
[e] Position of the signal was inferred from the NOE experimental data.
[f] C_6D_6 was the solvent
[g] The signals for the protons H(2) and H(7′) overlap.
[h] The signal overlaps with the signal for the proton H(1) of compound **9a**.
[i] The signal overlaps with the signal for the proton H(3) of compound **9a**.
[j] The signal overlaps with the signals for compound **9a**.
[k] The signal overlaps with the signals for compound **10a**.

was confirmed by the presence of the NOE on the bridge proton H(7′) (η = 2.6%) upon irradiation of the signal at δ 3.60 (H(3)CSCN). Thus, the *exo-endo*-configuration of adduct **9a** was confirmed. In the case of minor isomer **9b** upon irradiation of the signal at δ 3.28 (H(5)CSPh), the Overhauser effect (η = 6.6%) was observed on the proton at the second substituent, that unambiguously confirms the *exo-exo*-arrangement of the phenylthio and thiocyanate groups.

In the case of 1,5-cyclooctadiene (**11**), the 1,2-addition product, thiocyanate **12**, is formed in quantitative yield, with the second double bond remained intact (Scheme 5). Moreover, when the reaction is carried out with a two-fold excess of the reagent, the addition involves exclusively one bond. In the ^{1}H NMR spectrum of compound **12**, the signals for the protons on substituents are two triplets of doublets with the spin-spin coupling constants $^3J \approx 8.1$ Hz and $^3J \approx 3.5$ Hz,

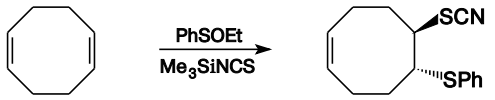
Table 3. The NOE (η) data for compounds **9a,b** and **10a,b** (in $CDCl_3$)

Compound	Irradiated protons	η (%)						
		H(3)	H(4)	H(5)	H(6)	H(7)	H(7′)	C_6H_5
9a	H(5)CSPh	—	1.0	—	2.0	—	—	2.0
	H(3)CSCN	—	1.0	—	—	—	2.6	—
9b	H(5)CSPh	6.6	3.6	—	4.1	—	—	—*
10a	H(7)	—	—	—	—	—	13.0	—
	H(7′)	2.6	—	—	—	11.7	—	—
10b	H(3)CNCS	—	—	3.6	—	—	—	—

* No NOE was detected for the minor isomer in the mixture.

that is an evidence of the *trans*-arrangement of the substituents.[16]

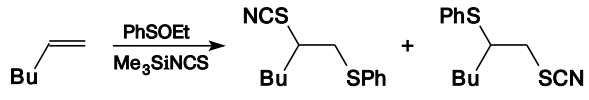
Scheme 5



11 **12**

Regioselectivity of the addition was studied using the reaction of ethyl benzenesulfenate with terminal olefin, hex-1-ene (**13**), as an example (Scheme 6). Based on the ^{1}H NMR spectrum of the reaction mixture, it was found that the reaction proceeds with the formation of a mixture of β-thiocyanatoalkyl phenyl sulfides **14a** and **14b** in the ratio 1 : 3.

Scheme 6

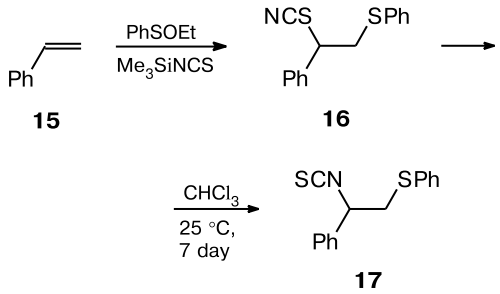


13 **14a** **14b**

It should be noted that it is difficult to assign signals to this or that isomer based only on the ^{1}H NMR spectrum, since chemical shifts for the protons on substituents are close. However, the ^{13}C NMR spectrum exhibits two sets of signals of different intensities. To establish structures of the isomers obtained, the ^{13}C NMR spectrum was recorded without proton decoupling. The signal for the SCN carbon atom of the predominant isomer with the chemical shift δ 110.7 is a doublet of doublets with ^3J = 4.4 and ^3J = 7.3 Hz, whereas the signal for the SCN carbon atom of the minor isomer is found at δ 109.3 as a doublet with ^3J = 6.6 Hz. This indicates that the SCN group in the predominant isomer **14b** is bound to the CH_2 group, whereas the SCN group in the minor isomer **14a**, to the CH group. Therefore, the major product is the anti-Markovnikov addition product, *i.e.*, the reaction is kinetically controlled.[17]

The reaction of styrene with ethyl benzenesulfenate in the presence of trimethylsilyl isothiocyanate yields the Markovnikov addition product, thiocyanate **16** (Scheme 7). To establish its structure, the ^{13}C NMR spectrum was recorded without proton decoupling: the signal for the SCN carbon atom is a doublet with ^3J = 4.0 Hz, therefore, the SCN group is bound to the CH, rather than the CH_2 group.

Scheme 7

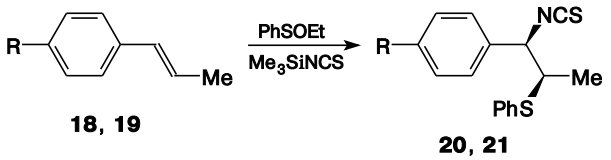


15 **16** **17**

The formation of Markovnikov addition product is characteristic of the sulfenylation reaction of styrene.[1] It should be noted that if thiocyanate **16** is kept in chloroform for 1 week at room temperature, its partial isomerization to the thermodynamically more stable isothiocyanate **17** takes place (the ratio **16** : **17** = 59 : 41) (see Scheme 7).

The formation of isothiocyanates **20** and **21** is the only direction of the reaction in the case of *E*-1-phenylpropene (**18**) and *E*-1-(4-methoxyphenyl)propene (**19**) (Scheme 8). In the ^{1}H NMR spectrum, the spin-spin coupling constants for the protons HCS and HCN in compounds **20** and **21** are 3.5 Hz and 3.8 Hz, that indicates formation of the 1*R**,2*R**-isomers in both cases. This agrees with the data obtained earlier for the selenothiocyanation of *E*-1-phenylpropene.[12,18–20]

Scheme 8



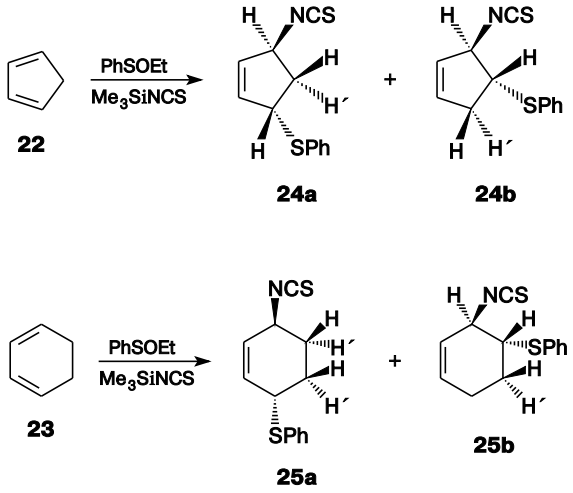
18, 19 **20, 21**

R = H (**18**, **20**), MeO (**19**, **21**)

To sum up, as it was noted earlier[12,21] an increase in stability of the intermediately formed carbocation leads to the increase in the amount of the isothiocyanate-substituted adducts in the reaction. It is obvious that the forma-

tion of the allylic carbocation in the course of the reaction should also favor an increase in the yield of isothiocyanates. In fact, we have found that cyclopentadiene (**22**) and cyclohexa-1,3-diene (**23**) react with ethyl benzenesulfenate and trimethylsilyl isothiocyanate with the formation of isothiocyanates **24** and **25** (Scheme 9), with the products of 1,4-addition being predominant (**24a** and **25a**).

Scheme 9



The structures of the products were established by ^{1}H NMR spectroscopy. Configurational assignments for the compounds were made based on the analysis of the spin-spin coupling constant values similarly to the halo-substituted cyclopentadienes and cyclohexadienes.[1,22—24]

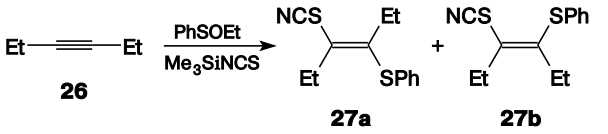
To establish the structure of compound **24a**, the ^{1}H—^{1}H homonuclear double resonance was used, which allowed us to make full analysis of the ^{1}H NMR spectrum and determine all the spin-spin coupling constant values (see Experimental). It was shown that both protons on the substituents (H—CSPh and H—CNCS) have the spin-spin coupling constants with the protons at the double bond equal to 2.1—2.3 Hz, which confirms the structure of the 1,4-adduct. In addition, according to the literature data[22—24] in substituted cyclopentenes $^3J_{trans}$ = 3.0—4.0 Hz, whereas $^3J_{cis}$ = 6.0—8.0 Hz. Therefore, the H(4′) proton has the *cis*-arrangement with respect to the H—CNCS proton and *trans*-arrangement with respect to the H—CSPh proton. Configurational relation of the H(4) proton to the protons on the substituents is reverse. Thus, compound **24a** is the *trans*-isomer of 3-isothiocyanato-5-phenylthiocyclopent-1-ene.

In the ^{1}H NMR spectrum of compound **24b**, the signals for the protons H—CNCS and H(5′) overlap with the corresponding signals for the predominant isomer. However, it was established that the signal for the proton H—CSPh, first, has no mutual spin-spin coupling constant with the olefin protons, second, has a mutual spin-spin coupling constant with the proton H(5) ($^3J_{cis}$ = 8.2 Hz), and, third, has two constants $^3J_{trans}$ with the protons H—CNCS and H(5′) ($J_{4,3}$ = 4.5 Hz and $J_{4,5}$ = 3.8 Hz). Therefore, compound **24b** is the *trans*-3-isothiocyanato-4-phenylthiocyclopent-1-ene.

Based on the ^{1}H—^{1}H homonuclear double resonance in the study of compounds **25a** and **25b**, it was established that in the first case both protons on the substituents have a mutual spin-spin coupling constant with the protons at the double bond, which confirms the structure of the 1,4-adduct, whereas in the second case only the HCNCS proton has a mutual spin-spin coupling constant with one of the olefin protons, *i.e.* compound **25b** is the 1,2-adduct. In the ^{1}H NMR spectrum of compound **25a**, all four spin-spin coupling constants for the protons on the substituents with the protons of neighboring CH_2 groups ($J_{3,4}$, $J_{3,4'}$, $J_{6,5}$, and $J_{6,5'}$) are equal to 5.0 Hz, therefore, the protons HCN and HCS have the pseudoequatorial arrangement,[25,26] *i.e.* isothiocyanate **25a** is the *trans*-isomer. In compound **25b**, the proton HCSPh is found as a doublet of doublets of doublets and has two large spin-spin coupling constants with the protons HCNCS and H(5′) ($^3J_{4,3}$ = 6.9 Hz and $^3J_{4,5'}$ = 9.6 Hz), as well as one small spin-spin coupling constant with the proton H(5) ($^3J_{4,5}$ = = 2.9 Hz), which indicates the diequatorial arrangement of the substituents.[25] Therefore, compound **25b** is the *trans*-3-isothiocyanato-4-phenylthiocyclohex-1-ene.

The reaction of terminal alkynes (pentyne and heptyne) with ethyl benzenesulfenate and trimethylsilyl isothiocyanate, in addition to the products of electrophilic addition to the triple bond, would give significant amounts of diphenyl disulfide and rearranged products, which is characteristic of the halosulfenylation of alkynes.[27,28] The reaction with nonterminal hex-3-yne led to the vinyl sulfides **27a,b** in quantitative yields (Scheme 10). A considerable increase in the rate of sulfenylation of internal alkynes as compared to terminal alkynes has been noted earlier.[29]

Scheme 10



The structures of isomers **27a,b** were established based on the fact that the signals for the protons of the CH_2 group in the ^{1}H NMR spectrum, as well as the signals for the carbon atoms of the CH_2 groups in the ^{13}C NMR spectrum of the *Z*-isomer, are found more upfield as compared to analogous signals for the *E*-isomer.[29]

In conclusion, a new method has been suggested for the synthesis of thiocyanato- and isothiocyanatoalkyl phenyl sulfides based on the activation of ethyl benzene-

sulfenate with trimethylsilyl isothiocyanate. The method is simple in accomplishing and characterized by high yields the target products. It was shown that linear and cyclic alkenes, dienes, and alkynes can be involved into the reaction. Isothiocyanates are the thermodynamically controlled products and they were isolated in those cases, when stable carbocations have been formed in the course of the reaction (benzylic and allylic type, or stabilization of carbocation due to the homoallylic involvement of a double bond (as in the case of norbornadiene)), as well as a result of isomerization of thiocyanates.

Experimental

^{1}H, ^{13}C, ^{29}Si, and ^{14}N NMR spectra were recorded on a Bruker Avance 400 spectrometer (400, 100.6, 79.5, and 28.9 MHz, respectively). Chemical shifts are given relatively to Me_4Si as an internal standard for the ^{1}H, ^{13}C, and ^{29}Si nuclei and relatively to nitromethane as an external standard for the ^{14}N nucleus. The NOE was measured in the regime of differential spectroscopy (the NOEDIF program). IR spectra were recorded on a UR-20 spectrometer (neat). Mass spectra were recorded on a Finnigan MIAT TSQ 7000 GLC-MS spectrometer (70 eV). Monitoring of the reaction progress and individuality of compounds synthesized was made by TLC on a fixed layer of silica gel (Silufol UV254).

Solvents were purified according to the standard procedures.[13] Ethyl benzenesulfenate was synthesized according to the known procedure.[30]

Reaction of unsaturated compounds with ethyl benzenesulfenate and trimethylsilyl isothiocyanate (general procedure). A solution of trimethylsilyl chloride in anhydrous $CHCl_3$ (or CH_2Cl_2) (2 mL) was added to sodium isothiocyanate (the molar ratio sodium isothiocyanate : trimethylsilyl chloride ≈ 3 : 1) with vigorous stirring at room temperature and the stirring was continued for 1 h, followed by a slow dropwise addition of a solution of a mixture of ethyl benzenesulfenate and olefin in the same solvent (the ratio olefin : sulfenate : trimethylsilyl isothiocyanate = 1 : 1 : 2). The stirring was continued until the reaction reached completion (TLC monitoring). Then, the reaction mixture was hydrolyzed with water, the organic phase was separated, the aqueous phase was thrice extracted with dichloromethane or chloroform, the organic extracts were combined and dried with Na_2SO_4. The solvent was evaporated *in vacuo*. Preparative column chromatographic separation of the reaction products was performed on silica gel Lancaster (0.04—0.063).

The yields of the reaction products are given in Table 1, chromatographic, elemental analysis, and IR spectroscopic data, in Table 4, mass spectrometric characteristics of compounds obtained, in Table 5. The ^{1}H NMR spectroscopic data of compounds **8—10** are given in Table 2.

***trans*-2-Phenylthio-1-thiocyanatocyclohexane (3).** ^{1}H NMR ($CDCl_3$), δ: 1.35 (m, 2 H, CH-framework); 1.53 (m, 1 H, CH-framework); 1.78 (m, 3 H, CH-framework); 2.22, 2.48 (both m, 1 H each, CH-framework); 3.05 (td, HCSPh or HCSCN, J = 10.1 Hz, J = 4.0 Hz); 3.24 (td, 1 H, HCSCN or HCSPh, J = 10.1 Hz, J = 4.0 Hz); 7.34—7.39 (m, 3 H, Ar); 7.50 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 25.0, 25.1 (C(4), C(5)); 33.3, 33.5 (C(3), C(6)); 51.5, 52.2 (CSPh, CSCN); 111.6 (SCN); 128.4, 129.2, 132.9, 134.1 (C_{Ar}).

***exo*-3-Phenylthio-*endo*-2-thiocyanatobicyclo[2.2.1]heptane (4).** ^{1}H NMR ($CDCl_3$), δ: 1.30 (m, 1 H, *endo*-H(5)); 1.55 (ddt, 1 H, *anti*-H(7), $^{2}J_{7,7}$ = 10.6 Hz, $J_{7,3}$ = 2.4 Hz, $J_{7,1} = J_{7,4}$ = 1.7 Hz); 1.58 (ddtd, 1 H, *exo*-H(6), $^{2}J_{6,6}$ = 12.9 Hz, $J_{6,5exo}$ = 12.4 Hz, $J_{6,5endo}$ $J_{6,1}$ = 4.3 Hz, $J_{6,2}$ = 2.2 Hz); 1.73 (tt, 1 H, *exo*-H(5), $^{2}J_{5,5}$ $J_{5,6exo}$ = 12.4 Hz, $J_{5,4}$ $J_{5,6endo}$ = 4.3 Hz); 1.86 (dddd, 1 H, *endo*-H(6), $^{2}J_{6,6}$ = 12.9 Hz, $J_{6,5endo}$ = 6.4 Hz, $J_{6,5exo}$ = 4.3 Hz, $J_{6,7syn}$ = 2.4 Hz); 1.89 (dm, 1 H, *syn*-H(7), $^{2}J_{7,7}$ = 10.6 Hz); 2.39 (d, 1 H, H(4), $J_{4,5exo}$ = 4.3 Hz); 2.62 (m, 1 H, H(1)); 2.80 (dd, 1 H, HCSPh, $J_{3,2}$ = 5.0 Hz, $J_{3,7anti}$ = 2.4 Hz); 3.53 (ddd, 1 H, HCSCN, $J_{2,3}$ = 5.0 Hz, $J_{2,1}$ = 4.3 Hz, $J_{2,6exo}$ = 2.2 Hz); 7.25 (tm, 1 H, Ar, J = 7.3 Hz); 7.33 (t, 2 H, Ar, J = 7.3 Hz); 7.44 (t, 2 H, Ar, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, δ: 22.5, 28.6 (C(5), C(6)); 36.5 (C(7)); 42.7, 43.9 (C(1), C(4)); 56.2, 56.4 (CSPh, CSCN); 111.5 (SCN); 127.6 (C_{Ar}(4)); 129.2, 131.8 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5), C_{Ar}(6)); 134.4 (C_{Ar}(1)).

3,6-Dimethoxy-*syn*-11-phenylthio-*exo*-9-thiocyanatotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (6). ^{1}H NMR ($CDCl_3$), δ: 2.16 (ddd, 1 H, *endo*-H(10), $^{2}J_{10,10}$ = 13.3 Hz, $J_{10,9}$ = 8.6 Hz, J = 0.6 Hz); 2.47 (dt, 1 H, *exo*-H(10), $^{2}J_{10,10}$ = 13.3 Hz, $J_{10,9}$ = 4.5 Hz, $J_{10,1}$ = 4.0 Hz); 3.29 (ddd, 1 H, HCSCN, $J_{9,10endo}$ = 8.6 Hz, $J_{9,10exo}$ = 4.5 Hz, J = 1.1 Hz); 3.60 (m, 1 H, HCSPh or H(8)); 3.68 (m, 1 H, H(1)); 3.76 (s, 3 H, OMe); 3.82 (s, 3 H, OMe); 3.92 (t, 1 H, H(8) or HCSPh, J = 1.4 Hz); 6.60 (d, 1 H, H(4) or H(5), ^{3}J = 8.9 Hz); 6.64 (d, 1 H, H(5) or H(4), ^{3}J = 8.9 Hz); 7.23 (t, 1 H, Ar, ^{3}J = 7.2 Hz); 7.31 (t, 2 H, Ar, ^{3}J = 7.2 Hz); 7.47 (d, 2 H, Ar, ^{3}J = 7.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 34.2 (C(10)); 45.0, 47.8 (C(1), C(8)); 50.8 (CSCN); 55.4, 55.6 (OCH_3); 63.2 (CSPh); 109.9, 110.3 (C(4), C(5)); 112.4 (SCN); 127.1 (C_{Ar}(4)); 129.1, 131.0 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5), C_{Ar}(6)); 133.1 (C(2), C(7)); 134.2 (C_{Ar}); 147.5 (C(3), C(6)).

A mixture of 6-*exo*-phenylthio-5-*endo*-thiocyanatobicyclo[2.2.1]hept-2-ene (8a) and 6-*endo*-phenylthio-5-*exo*-thiocyanatobicyclo[2.2.1]hept-2-ene (8b). ^{13}C NMR of compound **8a** ($CDCl_3$), δ: 46.6, 48.1, 49.1 (C(1), C(4), C(7)); 54.0, 54.3 (CSPh, CSCN); 111.6 (SCN); 127.7 (C_{Ar}(4)); 129.3, 132.0 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5) C_{Ar}(6)); 134.4 (C_{Ar}(1)); 135.0, 138.4 (C(2), C(3)). ^{13}C NMR of compound **8b** ($CDCl_3$), δ: 46.3, 48.1, 50.0 (C(1), C(4), C(7)); 53.7, 55.4 (CSPh, CSCN); 111.7 (SCN); 127.8 (C_{Ar}(4)); 129.3, 132.2 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5), C_{Ar}(6)); 134.7 (C_{Ar}(1)); 135.8, 137.0 (C(2), C(3)).

A mixture of 5-*exo*-phenylthio-3-*endo*-thiocyanatotricyclo[2.2.1.0^{2,6}]heptane (9a) and 5-*exo*-phenylthio-3-*exo*-thiocyanatotricyclo[2.2.1.0^{2,6}]heptane (9b). ^{13}C NMR of compound **9a** ($CDCl_3$), δ: 14.3, 16.5, 17.6 (C(1), C(2), C(6)); 30.4 (C(7)); 40.4 (C (4)); 50.2, 54.1 (CSPh, CSCN); 111.5 (SCN); 126.6 (C_{Ar}(4)); 129.1, 130.1 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5) C_{Ar}(6)); 135.5 (C_{Ar}(1)). ^{13}C NMR of compound **9b** ($CDCl_3$), δ: 12.0, 17.8, 18.7 (C(1), C(2), C(6)); 27.3 (C(7)); 40.7 (C(4)); 52.5, 52.7 (CSPh, CSCN); 127.2 (C_{Ar}(4)); 129.1, 131.2 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5), C_{Ar}(6)); 135.5 (C_{Ar}(1)).

A mixture of 3-*endo*-isothiocyanato-5-*exo*-phenylthiotricyclo[2.2.1.0^{2,6}]heptane (10a) and 3-*exo*-isothiocyanato-5-*exo*-phenylthiotricyclo[2.2.1.0^{2,6}]heptane (10b). ^{13}C NMR of compound **10a** ($CDCl_3$), δ: 13.2, 16.0, 18.7 C(1), C(2), C(6)); 28.5 (C(7)); 40.7 (C(4)); 50.3, 61.4 (CSPh, CNCS); 126.5 (C_{Ar}(4)); 129.1, 130.2 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5), C_{Ar}(6)); 135.5 (C_{Ar}(1)). ^{13}C NMR of compound **10b** ($CDCl_3$), δ: 11.5, 17.6, 18.9 C(1), C(2), C(6)); 27.7 (C(7)); 41.1(C(4)); 50.9, 59.8 (CSPh, CNCS);

Table 4. Chromatographic data, elemental analysis data, and characteristic absorption bands in the IR spectra of compounds **3**, **4**, **6**, **8—10**, **14**, **16**, **17**, **24**, **25**, **27**

Compound	Found / Calculated (%)			Molecular formula	R_f (EtOAc : LP[a])	IR (ν/cm^{-1})
	C	H	N			
3	62.57 / 62.65	5.92 / 6.02	5.58 / 5.62	$C_{13}H_{15}NS_2$	0.71 (1 : 3)	2165 (SCN)
4	64.21 / 64.37	5.65 / 5.74	5.30 / 5.36	$C_{14}H_{15}NS_2$	0.67 (1 : 3)	2170 (SCN)
6[b]	65.17 / 65.04	5.22 / 5.15	3.49 / 3.79	$C_{20}H_{19}NS_2O_2$	0.63 (1 : 3)	2165 (SCN)
8a + **8b**[c]	64.94 / 64.86	5.22 / 5.02	5.17 / 5.40	$C_{14}H_{13}NS_2$	0.72 (1 : 5)	2170 (SCN)
9a + **9b**[c]	64.94 / 64.86	5.22 / 5.02	5.17 / 5.40	$C_{14}H_{13}NS_2$	0.63 (1 : 5)	2165 (SCN)
10a + **10b**[c]	64.94 / 64.86	5.22 / 5.02	5.17 / 5.40	$C_{14}H_{13}NS_2$	0.80 (1 : 5)	2110 (NCS)
12[d]	65.04 / 65.45	6.20 / 6.18	5.27 / 5.09	$C_{15}H_{17}NS_2$	0.63 (1 : 3)	2165 (SCN)
14a + **14b**[e]	62.35 / 62.15	6.73 / 6.77	5.42 / 5.58	$C_{13}H_{17}NS_2$	0.76 (1 : 3)	2170 (SCN)
16[f]	66.21 / 66.42	4.81 / 4.80	5.01 / 5.17	$C_{15}H_{13}NS_2$	0.40 (1 : 3)	2170 (SCN)
17[f]	66.21 / 66.42	4.81 / 4.80	5.01 / 5.17	$C_{15}H_{13}NS_2$	0.40 (1 : 5)	2080 (NCS)
24a + **24b**	62.00 / 61.80	4.88 / 4.72	6.20 / 6.01	$C_{12}H_{11}NS_2$	0.73 (1 : 3)	2100 (NCS)
25a + **25b**	63.79 / 63.16	5.31 / 5.26	5.71 / 5.67	$C_{13}H_{13}NS_2$	0.78 (1 : 3)	2100 (NCS)
27a + **27b**[g]	62.54 / 62.65	6.08 / 6.02	5.52 / 5.62	$C_{13}H_{15}NS_2$	0.63 (1 : 3)	2170 (SCN)

[a] LP stands for light petroleum.
[b] Found (%): S, 17.11. $C_{20}H_{19}NS_2O_2$. Calculated (%): S, 17.34.
[c] For the mixture of isomers **8—10**.
[d] Found (%): S, 23.39. $C_{15}H_{17}NS_2$. Calculated (%): S, 23.27.
[e] Found (%): S, 25.38. $C_{13}H_{17}NS_2$. Calculated (%): S, 25.49.
[f] For the mixture of isomers **14a** and **14b**.
[g] Found (%): S, 25.50. $C_{13}H_{15}NS_2$. Calculated (%): S, 25.70.

127.0 (C_{Ar}(4)); 129.1, 130.2 (C_{Ar}(2), C_{Ar}(3), C_{Ar}(5), C_{Ar}(6)); 135.5 (C_{Ar}(1)). ^{14}N NMR of compounds **10a** and **10b** ($CDCl_3$), δ: −277.1.

***trans*-6-Phenylthio-5-thiocyanatocyclooctene (12).** ^{1}H NMR ($CDCl_3$), δ: 1.94 (m, 1 H, CH-framework); 2.06—2.66 (m, 7 H, CH-framework); 3.58 (td, 1 H, HCSPh or HCSCN, J = 8.4 Hz, J = 3.5 Hz); 3.91 (td, 1 H, HCSCN or HCSPh, J = 8.1 Hz, J = 3.7 Hz); 5.72 (m, 2 H, H(1), H(2)); 7.25—7.35 (m, 5 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 24.3, 24.5, 33.3, 34.4 (C(3), C(4), C(7), C(8)); 51.7, 54.8 (CSPh, CSCN); 113.4 (SCN); 128.0 (C_{Ar}(4)); 129.2 (C(1) or C(2)); 129.3 (C_{Ar}(2), C_{Ar}(6)); 130.2 (C(2) or C(1)); 132.4 (C_{Ar}(3), C_{Ar}(5)); 134.0 (C_{Ar}(1)).

A mixture of 1-phenylthio-2-thiocyanatohexane (14a) and 2-phenylthio-1-thiocyanatohexane (14b). ^{1}H NMR of compound **14a** ($CDCl_3$), δ: 0.94 (t, 3 H, CH_3, J = 7.2 Hz); 1.75, 2.08 (both m, 1 H each, H_2(3)); 3.21 (m, 1 H, HCSCN); 3.23 (dd, 1 H, CHSPh, $^2J_{1,1}$ = 13.2 Hz, $J_{1,2}$ = 8.0 Hz); 3.40 (dd, 1 H, CHSPh, $^2J_{1,1}$ = 13.2 Hz, $J_{1,2}$ = 4.6 Hz); 7.2—7.6 (m, 5 H, Ar). Signals for the protons H_2(4), H_2(5), and aromatic protons overlap with signals for compound **14b**. ^{1}H NMR of compound **14b** ($CDCl_3$), δ: 0.97 (t, 3 H, CH_3, J = 7.2 Hz); 1.30—1.67 (m, 5 H, H(3), H_2(4), H_2(5),); 1.88 (m, 1 H, H(3)); 3.06 (dd, 1 H, HCSCN, $^2J_{1,1}$ = 12.7 Hz, $J_{1,2}$ = 7.6 Hz); 3.29 (dd, 1 H, HCSCN, $^2J_{1,1}$ = 12.7 Hz, $J_{1,2}$ = 4.9 Hz); 3.34 (m, 1 H, HCSPh); 7.2—7.6 (m, 5 H, Ar). ^{13}C NMR of compound **14a** ($CDCl_3$+CCl_4), δ: 13.8 (C(6)); 22.1 (C(5)); 28.8 (C(4)); 33.1 (C(3)); 40.2 (C(1)); 50.3 (C(2)); 109.3 (SCN); 127.3 (C_{Ar}(4)); 129.4 (C_{Ar}(2), C_{Ar}(6)); 130.7 (C_{Ar}(3), C_{Ar}(5)); 134.3 (C_{Ar}(1)). ^{13}C NMR of compound **14b** ($CDCl_3$+CCl_4), δ: 13.9 (C(6)); 22.4 (C(5)); 28.9 (C(4)); 32.0 (C(3)); 39.3 (C(1)); 48.6 (C(2)); 110.7 (SCN); 128.2 (C_{Ar}(4)); 129.4 (C_{Ar}(2), C_{Ar}(6)); 133.1 (C_{Ar}(3), C_{Ar}(5)); 132.7 (C_{Ar}(1)).

1-Phenyl-2-phenylthio-1-thiocyanatoethane (16). ^{1}H NMR ($CDCl_3$), δ: 3.62 (dd, HCSPh, $^2J_{2,2}$ = 14.0 Hz, $J_{2,1}$ = 9.0 Hz); 3.70 (dd, HCSPh, $^2J_{2,2}$ = 14.0 Hz, $J_{2,1}$ = 6.6 Hz); 4.48 (dd, HCSCN, $J_{1,2}$ = 9.0 Hz, $J_{1,2}$ = 6.6 Hz); 7.25—7.50 (m, 10 H, Ar).

Table 5. Mass spectrometric characteristics of compounds **8—10**, **14**, **16**, **17**, **20**, **21**, **24**, **25**

Compound	Principal peaks in the MS, m/z (I_{rel} (%))
8a + **8b**	261 $[M + 2]^+$ (1.2); 260 $[M + 1]^+$ (2.2); 259 $[M]^+$ (12.5); 202 (21); 201 (100); 194 (22); 193 (100); 135 (85); 134 (33); 123 (27); 116 (54); 109 (44); 92 (22); 91 (100); 77 (28); 66 (41); 65 (65); 51 (27); 45 (22); 39 (37)
9a + **9b**	261 $[M + 2]^+$ (10); 260 $[M + 1]^+$ (18); 259 $[M]^+$ (97); 201 (94); 136 (20); 135 (28); 123 (34); 117 (23); 110 (21); 109 (35); 92 (37); 91 (100); 77 (27); 72 (53); 66 (22); 65 (71); 51 (27) 261 $[M + 2]^+$ (8); 260 $[M + 1]^+$ (14); 259 $[M]^+$ (78); 202 (21); 201 (100); 168 (11); 135 (21); 123 (52); 117 (38); 116 (24); 110 (31); 109 (34); 92 (41); 91 (100); 77 (26); 66 (22); 65 (72); 51 (25); 45 (27); 39 (37)
10a + **10b**	261 $[M + 2]^+$ (13); 260 $[M + 1]^+$ (21); 259 $[M]^+$ (100); 258 (16); 193 (18); 181 (18); 150 (25); 136 (29); 117 (45); 116 (25); 110 (20); 91 (85); 72 (58); 65 (25)
14a + **14b**	253 $[M + 2]^+$ (8); 252 $[M + 1]^+$ (13); 251 $[M]^+$ (77); 193 (28); 179 (52); 135 (12); 123 (100); 110 (54); 109 (31); 83 (30); 69 (16); 55 (25) 253 $[M + 2]^+$ (5); 252 $[M + 1]^+$ (8); 251 $[M]^+$ (54); 193 (23); 179 (18); 123 (100); 110 (23); 109 (21); 83 (35); 55 (19)
16	273 (2) $[M + 2]^+$; 272 (4) $[M + 1]^+$; 271 $[M]^{+\cdot}$(20); 148 (51); 135 (13); 123 (100); 121 (12); 109 (15); 104 (18); 103 (17); 78 (12); 77 (21)
17	273 (2) $[M + 2]^+$; 272 (2) $[M + 1]^+$; 271 $[M]^{+\cdot}$(18); 148 (51); 123 (100); 109 (17); 104 (20); 103 (20); 77 (25)
20	287 $[M + 2]^+$ (0.7); 286 $[M + 1]^+$ (1.2); 285 $[M]^+$ (6.5); 199 (24); 137 (100); 117 (14); 115 (10); 109 (13)
21	317 $[M + 2]^+$ (0.1); 316 $[M + 1]^+$ (0.2); 315 $[M]^+$ (1.2); 257 (4.5); 256 (21.5); 255 (5); 230 (16); 229 (100); 207 (11); 206 (67); 178 (17); 172 (12); 148 (62); 147 (28,5); 137 (30); 121 (17); 109 (19); 91 (17); 77 (22); 65 (15)
24a + **24b**	235 $[M + 2]^+$ (0.4); 234 $[M + 1]^+$ (0.9); 233 $[M]^+$ (6.2); 174 (100); 173 (69); 147 (27); 140 (32); 109 (23); 97 (25)
25a	249 $[M + 2]^+$ (4); 248 $[M + 1]^+$ (6); 247 $[M]^+$ (39); 188 (38); 161 (31); 155 (10); 137 (28); 110 (100); 109 (46); 84 (22); 79 (90); 78 (68); 77 (62)
25b	249 $[M + 2]^+$ (3); 248 $[M + 1]^+$ (4,5); 247 $[M]^+$ (31); 188 (24); 137 (36); 136 (51); 135 (31); 111 (25); 110 (100); 109 (40); 79 (94); 78 (48); 77 (59)

^{13}C NMR ($CDCl_3$), δ: 39.9 (C(1)); 52.4 (C(2)); 111.3 (SCN); 127.6 (C(4) SPh group); 127.9 (C(3), C(5) Ph group); 129.2, 129.4 (C(2), C(6) SPh group and Ph group); 129.5 (C(4) Ph group); 131.2 (C(3), C(5) SPh group); 133.6 (C(1) SPh group); 136.4 (C(1) Ph group).

(1*R,2*R**)-1-Isothiocyanato-1-phenyl-2-phenylthiopropane (20).** R_f 0.30 (light petroleum—ethyl acetate (5 : 1)). ^{1}H NMR ($CDCl_3$), δ: 1.28 (d, 3 H, CH_3, $J_{3,2}$ = 6.9 Hz); 3.57 (qd, 1 H, HCSPh, $J_{2,3}$ = 6.9 Hz, $J_{2,1}$ = 3.5 Hz); 4.98 (d, 1 H, HCNCS, $J_{1,2}$ = 3.5 Hz); 7.20—7.50 (m, 10 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.3 (C(3); 51.1 (CSPh); 64.6 (CNCS); 126.2, 127.2, 127.5, 128.7, 129.1, 129.4, 132.5, 133.3 (Ar). IR, ν/cm^{-1}: 2100 (NCS).

(1*R,2*R**)-1-Isothiocyanato-1-(4-methoxyphenyl)-2-phenylthiopropane (21).** R_f 0.83 (light petroleum—ethyl acetate (3 : 1)). ^{1}H NMR ($CDCl_3$), δ: 1.28 (d, 3 H, CH_3, $J_{3,2}$ = 6.9 Hz); 3.49 (qd, 1 H, HCSPh, $J_{2,3}$ = 6.9 Hz, $J_{2,1}$ = 3.8 Hz); 3.82 (s, 3 H, OCH_3); 4.87 (d, 1 H, HCNCS, $J_{1,2}$ = 3.8 Hz); 6.85 (d, 2 H, Ar, J = 6.7 Hz); 7.11 (d, 2 H, Ar, J = 6.7 Hz); 7.30—7.40 (m, 3 H, Ar); 7.52 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.5 (CH_3); 51.2 (CSPh); 55.2 (OCH_3); 64.2 (CNCS); 114.0 (C(3), C(5) Ar group); 127.5 (C(2), C(6) Ar group); 128.0 (C(4) SPh group); 129.2 (C(2), C(6) SPh group); 133.3 (C(3), C(5) SPh group); 133.8 (C(1) Ar group); 134.4 (C(1) SPh group); 159.5 (C(4) Ar group). IR, ν/cm^{-1}: 2090 (NCS).

A mixture of *trans*-3-isothiocyanato-5-phenylthiocyclopentene (24a) and *trans*-3-isothiocyanato-4-phenylthiocyclopentene (24b). ^{1}H NMR of compound **23a** ($CDCl_3$), δ: 2.44 (ddd, 1 H, H(4′), $^2J_{4',4}$ =14.1 Hz, $J_{4',3}$ = 7.3 Hz, $J_{4',5}$ = 4.5 Hz); 2.48 (ddd, 1 H, H(4), $^2J_{4,4'}$ = 14.1 Hz, $J_{4,5}$ = 6.9 Hz, $J_{4,3}$ = 5.7 Hz); 4.38 (ddddd, 1 H, HCSPh, $J_{5,4}$ = 6.9 Hz, $J_{5,4'}$ = 4.5 Hz, $J_{5,1}$ = 2.3 Hz, $J_{5,3}$ = 2.1 Hz, $J_{5,2}$ = 1.7 Hz); 4.65 (ddq, 1 H, HCNSC, $J_{3,4'}$ = 7.3 Hz, $J_{3,4}$ = 5.7 Hz, $J_{3,1}$ $J_{3,2}$ $J_{3,5}$ = 2.1 Hz); 5.84 (ddd, 1 H, H(2), $J_{2,1}$ = 5.5 Hz, $J_{2,3}$ = 2.1 Hz, $J_{2,5}$ = 1.7 Hz); 6.08 (ddd, 1 H, H(1), $J_{1,2}$ = 5.5 Hz, $J_{1,5}$ = 2.3 Hz, $J_{1,3}$ = 2.1 Hz); 7.20—7.45 (m, 5 H, Ar). ^{1}H NMR of compound **24b** ($CDCl_3$), δ: 3.07 (ddq, 1 H, H(5), $^2J_{5,5'}$ = 17.8 Hz, $J_{5,4}$ = 8.2 Hz, $J_{5,1}$ $J_{5,2}$ $J_{5,3}$ 2.2 Hz); 3.91 (ddd, 1 H, HCSPh, $J_{4,5}$ = 8.2 Hz, $J_{4,3}$ = 4.5 Hz, $J_{4,5'}$ = 3.8 Hz); 5.75 (dq, 1 H, H(2), $J_{2,1}$ = 5.7 Hz, $J_{2,3}$ = $J_{2,5}$ = $J_{2,5'}$ = 2.2 Hz); 6.04 (dtd, 1 H, H(1), $J_{1,2}$ = 5.7 Hz, $J_{1,5}$ = $J_{1,5'}$ = 2.2 Hz, $J_{1,3}$ = 1.6 Hz). The signal for the protons H(5′) (δ 2.45) and HCNSC (δ 4.65), as well as the signals for the aromatic protons overlap with signals for compound **24a**. ^{13}C NMR of compound **24a** ($CDCl_3$), δ: 39.9 (C(4)); 51.1 (CSPh); 60.8 (CNCS); 127.7 (C_{Ar}(4)); 129.1 (C_{Ar}(2), C_{Ar}(6)); 131.1 (C(1) or C(2)); 132.6 (C_{Ar}(3), C_{Ar}(5)); 133.7 (C_{Ar}(1)); 136.5 (C(2) or C(1)). ^{14}N NMR of compounds **23a** and **23b** ($CDCl_3$), δ: –274.4.

A mixture of *trans*-3-isothiocyanato-6-phenylthiocyclohexene (25a) and *trans*-3-isothiocyanato-4-phenylthiocyclohexene (25b). ^{1}H NMR of compound **25a** ($CDCl_3$), δ: 1.78 (dddd, 1 H, H(5), $^2J_{5,5'}$ = 13.0 Hz, $J_{5,4'}$ = 7.3 Hz, $J_{5,6}$ = 5.0 Hz, $J_{5,4}$ = 2.5 Hz); 1.89 (dddd, 1 H, H(4′), $^2J_{4,4'}$ = 13.1 Hz, $J_{4',5}$ = 7.3 Hz, $J_{4',3}$ = 5.0 Hz, $J_{4',5'}$ = 2.5 Hz); 2.17 (dddd, 1 H, H(5′), $^2J_{5',5}$ = 13.0 Hz, $J_{5',4}$ = 10.6 Hz, $J_{5',6}$ = 5.0 Hz, $J_{5',4'}$ = 2.5 Hz); 2.26 (dddd, 1 H, H(4), $^2J_{4,4'}$ = 13.1 Hz, $J_{4,5'}$ = 10.6 Hz, $J_{4,3}$ = 5.0 Hz, $J_{4,5}$ = 2.5 Hz); 3.87 (tdt, 1 H, HCSPh, $J_{6,5}$ $J_{6,5'}$ = = 5.0 Hz, $J_{6,1}$ = 4.0 Hz, $J_{6,2}$ = $J_{6,3}$ = 1.5 Hz); 4.24 (tdt, 1 H, HCNCS, $J_{3,4}$ $J_{3,4'}$ = 5.0 Hz, $J_{3,2}$ = 3.9 Hz, $J_{3,1}$ = $J_{3,6}$ = 1.5 Hz); 5.84 (ddd, 1 H, H(2), $J_{1,2}$ = 9.8 Hz, $J_{1,3}$ = 3.9 Hz, $J_{2,6}$ = 1.5 Hz); 6.03 (ddd, 1 H, H(1), $J_{1,2}$ = 9.8 Hz, $J_{1,6}$ = 4.0 Hz, $J_{1,3}$ = 1.5 Hz); 7.3—7.5 (m, 5 H, Ar). ^{1}H NMR of compound **25b** ($CDCl_3$), δ: 3.36 (ddd, 1 H, HCSPh, $J_{4,5'}$ = 9.6 Hz, $J_{4,3}$ = 6.9 Hz, $J_{4,5}$ = 2.9 Hz); 4.18 (ddq, 1 H, HCNCS, $J_{3,4}$ = 6.9 Hz, $J_{3,2}$ = 3.2 Hz, $J_{3,1}$ $J_{3,6}$

$J_{3,6'}$ = 1.8 Hz); 5.67 (ddt, 1 H, H(2), $J_{2,1}$ = 9.9 Hz, $J_{2,3}$ = 3.2 Hz, $J_{2,6}$ $J_{2,6'}$ = 2.0 Hz); 5.92 (dtd, 1 H, H(1), $J_{1,2}$ = 9.9 Hz, $J_{1,6}$ = = $J_{1,6'}$ = 3.8 Hz, $J_{1,3}$ = 1.8 Hz). The signals for the protons $H_2C(5)$, $H_2C(6)$, and aromatic protons overlap with signals for the protons of compound **25b**. ^{13}C NMR of compound **25a** ($CDCl_3$), δ: 25.0, 27.1 (C(4), C(5)); 42.9, 51.5 (CSPh, CNCS); 126.7 (C_{Ar}(4)); 127.5 (C(1) or C(2)); 129.1 (C_{Ar}(2), C_{Ar}(6)); 131.4 (C(2) or C(1)); 132.1 (C_{Ar}(3), C_{Ar}(5)); 134.3 (C_{Ar}(1)). ^{13}C NMR of compound **25b** ($CDCl_3$), δ: 23.8, 27.0 (C(5), C(6)); 49.2 (CSPh); 56.9 (CNCS); 123.8 (C(1) or C(2)); 128.1 (C_{Ar}(4)); 129.2 (C_{Ar}(2), C_{Ar}(6)); 130.9 (C(2) or C(1)); 133.6 (C_{Ar}(3), C_{Ar}(5)).

A mixture of *E*-4-phenylthio-3-thiocyanatohex-3-ene (27a) and *Z*-4-phenylthio-3-thiocyanatohex-3-ene (27b). ^{1}H NMR of compound **27a** ($CDCl_3$), δ: 1.02 (t, 3 H, CH_3, J = 7.4 Hz); 1.24 (t, 3 H, CH_3, J = 7.4 Hz); 2.35 (q, 2 H, CH_2, J = 7.4 Hz); 2.90 (q, 2 H, CH_2, J = 7.4 Hz); 7.25—7.40 (m, 5 H, Ar). ^{1}H NMR of compound **27b** ($CDCl_3$), δ: 1.03 (t, 3 H, CH_3, J = 7.4 Hz); 1.15 (t, 3 H, CH_3, J = 7.4 Hz); 2.30 (q, 2 H, CH_2, J = 7.4 Hz); 2.66 (q, 2 H, CH_2, J = 7.4 Hz). The signals for the aromatic protons overlap with signals for the protons of compound **27a**. ^{13}C NMR of compound **27a** ($CDCl_3$), δ: 12.9, 13.0 (C(1), C(6)); 27.9, 29.1 (C(2), C(5)); 110.1 (SCN); 127.0 (C(3)); 127.7 (C_{Ar}(4)); 129.3 (C_{Ar}(2), C_{Ar}(6)); 131.6 (C_{Ar}(3), C_{Ar}(5)); 133.0 (C_{Ar}(1)); 143.0 (C(4)). ^{13}C NMR of compound **27b** ($CDCl_3$), δ: 12.1, 13.1 (C(1), C(6)); 26.5, 27.7 (C(2), C(5)); 127.1; 129.1; 130.1; 144.8.

Isomerization of 1-phenyl-2-phenylthio-1-thiocyanatoethane (16). Compound **16** (0.2 g, 0.7 mmol) was dissolved in $CHCl_3$ (5 mL) and kept at room temperature for 7 days. The solvent was evaporated on a rotary evaporator to obtain a mixture of the starting **16** (59%) and 1-isothiocyanato-1-phenyl-2-phenylthioethane (**17**) (41%). ^{1}H NMR of compound **17** ($CDCl_3$), δ: 3.34 (dd, CHSPh, $^2J_{2,2}$ = 13.9 Hz, $J_{2,1}$ = 7.9 Hz); 3.38 (dd, CHSPh, $^2J_{2,2}$ = 13.9 Hz, $J_{2.1}$ = 5.8 Hz); 4.84 (dd, CHNCS, $J_{1,2}$ = 7.9 Hz, $J_{1,2}$ = 5.8 Hz); 7.25—7.63 (m, 10 H, Ar). ^{13}C NMR of compound **17** ($CDCl_3$), δ: 43.4 (C(1)); 61.1 (C(2)); 126.1 (C(3), C(5) Ph group); 127.4 (C(4) SPh group); 128.8 (C(4) Ph group); 129.0 (C(2), C(6) SPh group); 129.4 (C(2), C(6) Ph group); 131.1 (C(3), C(5) SPh group); 133.2 (NCS); 134.2 (C(1) SPh group); 137.6 (C(1) Ph group). Compound **17** was not isolated in the individual state and was characterized in the mixture with compound **16**.

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