(Alk-1-ynyl)organylthiocarbenes: generation and reactions with olefins*

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1-Substituted 1-chloro-3-organylthiopropa-1,2-dienes **1a—f** belonging to previously unknown type of allenic compounds were synthesized by chlorination of 1-organylthioalk-1-ynes **3a—f** with *N*-chlorosuccinimide. The reactions of compounds **1a—f** with Bu^{t}OK in hexane at −20 °C are accompanied by γ-elimination of HCl to give new alk-1-ynyl(organylthio)carbenes **2a—f**, which add to olefins to form the corresponding 1-(alk-1-ynyl)-1-organylthiocyclopropanes **5** in yields of up to 60%. The electrophilic properties of carbenes **2** were confirmed experimentally.

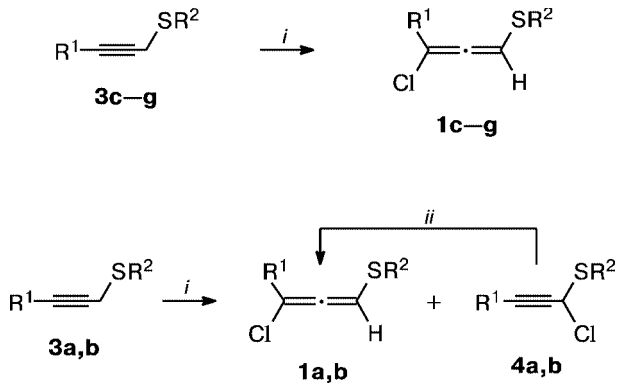
Key words: 1-substituted 1-chloro-3-organylthiopropa-1,2-dienes, alkyn-1-yl(organylthio)carbenes, 1-(alkyn-1-yl)-1-organylthiocyclopropanes, [1+2] cycloaddition, electrophilic carbenes.

A wide range of (alk-1-ynyl)carbenes containing various substituents at the carbene center,[2—11] including (alk-1-ynyl)halocarbenes,[4—7,9] (alk-1-ynyl)hetarylcarbenes,[10] and 4-methylpent-3-en-1-ynyl(methoxycarbonyl)carbene,[11] have been generated using various methods. In the present study, we examined the reactions of 1-substituted 1-chloro-3-organylthiopropa-1,2-dienes **1** with Bu^{t}OK yielding previously unknown alk-1-ynyl(organylthio)carbenes **2**. In the presence of olefins, the latter compounds give the corresponding 1-(alk-1-ynyl)-1-organylthiocyclopropanes.

Starting chlorosulfides **1a—f** were prepared by chlorination of 1-organylthioalk-2-ynes **3a—f** with *N*-chlorosuccinimide (NCS). The reaction was carried out by stirring equimolar amounts of the reagents in CCl_4 at 20 °C for 1—10 h. It should be noted that the reactions of sulfides **3c—f** gave chloroallenes **1c—f**, whereas compounds **3a,b** gave (according to the NMR spectroscopic data) mixtures of isomeric allenes **1a,b** and acetylenes **4a,b** (Scheme 1) in ratios of 1 : 1 and 1 : 3, respectively.

The NMR monitoring of these mixtures in $CDCl_3$ demonstrated that acetylenes **4a,b** undergo isomerization to the corresponding allenes **1a,b** at room temperature. The rate of this process depends substantially on the structures of compounds **4a,b**. For example, the rearrangement of **4a** into **1a** was completed in several hours, whereas acetylene **4b** was completely transformed into allene **4b** already during 15 min. These data indicate that the reactions of sulfides **3a—f** with NCS involve chlorination at the α position with respect to the sulfur atom to form acetylenes **4**, which undergo acetylene—allene isomer-

Scheme 1



Compound	R^1	R^2
1a, 3a, 4a	Bu^t	Ph
1b, 3b, 4b	Ph	Me
1c, 3c	Bu^t	Me
1d, 3d	Bu^t	*p*-Tol
1e, 3e	Bu^t	Bu^n
1f, 3f	Ad	Me
1g, 3g	H	Bu^n

Reagent and conditions: *i*. NCS, CCl_4, 20 °C; *ii*. $CDCl_3$, 20 °C.

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ization to give compound **1**. This reaction scheme is consistent with the published data on diorganyl sulfides.[12]

The structures of allenes **1a—f** were established by ^{1}H and ^{13}C NMR spectroscopy (Table 1). In particular, the ^{13}C NMR spectra show signals at δ 94—123 and 192—197 characteristic of the terminal and central carbon atoms of the allenic fragment, respectively. The ^{1}H NMR spectra have a singlet at δ 6.2—6.7 corresponding to the proton at the double bond. However, the spectroscopic data did not allow us to unambiguously determine whether the chlorine atom and the organylthio group in allenes **1a—f** are located at the same or different carbon atoms. To solve this problem, we carried out the reaction of NCS with butyl propargyl sulfide (**3g**) containing the hydrogen atom at the triple bond. This reaction afforded 3-butylthio-1-chloropropadiene (**1g**) as the major product. The ^{1}H NMR spectrum of this product has an AB system with the spin-spin coupling constant of 5.5 Hz at δ 6.3 corresponding to two nonequivalent allenic protons. The ^{13}C NMR spectrum of compound **1g** shows two signals for the sp^2-hybridized carbon atoms at δ 94.3 and 101.3 assigned (according to the results of DEPT experiments) to two CH groups. These results reliably prove the structure of allene **1g** and provide evidence for the formation of allenes **1** as a result of migration of the chlorine atom in the initially formed acetylenes **4**.

Table 1. The ^{1}H NMR ($CDCl_3$, 200.13 MHz) and ^{13}C NMR ($CDCl_3$, 50 MHz) spectra of allenes **1a—g**

Compound	^{1}H NMR (δ, *J*/Hz)			^{13}C NMR (δ)		
	R^2	R^1	—CH=	R^1	R^2	C=C=C
1a	7.30—7.55 (m, 5 H, Ph)	0.98 (s, 9 H, 3 Me)	6.29 (s, 1 H)	28.1 (3 Me); 37.2 (<u>C</u>Me$_3$)	129.4; 133.3; 134.6 (Ph); 131.6 (C(1), Ph)	98.5 (CH=); 122.1 (CCl=); 194.4 (=C=)
1b	2.23 (s, 3 H, Me)	7.20—7.50 (m, 5 H, Ph)	6.67 (s, 1 H)	126.4, 128.3, 128.5 (Ph); 133.8 (C(1))	13.8 (Me)	102.5 (CH=); 112.4 (CCl=); 195.8 (=C=)
1c	2.15 (s, 3 H, Me)	1.17 (s, 9 H, 3 Me)	6.23 (s, 1 H)	28.6 (3 Me); 37.5 (<u>C</u>Me$_3$)	14.2 (Me)	99.6 (CH=); 122.9 (CCl=); 192.5 (=C=)
1d	2.38 (s, 3 H, Me); 7.19 (br.d, 2 H, 2 CH, *J* = 7.5); 7.38 (br.d, 2 H, 2 CH, *J* = 7.5)	0.98 (s, 9 H, 3 Me)	6.28 (s, 1 H)	28.0 (3 Me); 37.1 (<u>C</u>Me$_3$)	21.0 (Me); 127.7 (C(4)); 129.3, 133.5 (C(2), C(3), C(5), C(6)); 138.5 (C(1))	99.1 (CH=); 121.8 (CCl=); 193.9 (=C=)
1e	0.95 (t, 3 H, Me, *J* = 7.7); 1.35—1.65 (m, 4 H, 2 CH_2); 2.62 (br.t, 2 H, CH_2S, *J* = 7.2)	1.19 (s, 9 H, 3 Me)	6.19 (s, 1 H)	28.5 (3 Me); 37.4 (<u>C</u>Me$_3$)	13.6 (Me); 22.1, 31.2, 31.3 (3 CH_2)	98.5 (CH=); 121.9 (CCl=); 192.7 (=C=)
1f	2.11 (s, 3 H, Me)	1.10—1.25 (m, 12 H, 6 CH_2); 1.95—2.05 (m, 3 H, 3 CH)	6.21 (s, 1 H)	28.2 (3 CH); 36.4 (3 CH_2); 40.6 (3 CH_2)	14.1 (Me)	99.7 (CH=); 122.7 (CCl=); 192.6 (=C=)
1g	0.92 (t, 3 H, Me, *J* = 7.7); 1.30—1.65 (m, 4 H, 2 CH_2); 2.62 (br.t, 2 H, CH_2S, *J* = 7.2)	6.30, 6.33 (both d, 1 H each, CH, *J* = 5.5)		—	13.6 (Me); 22.0, 30.4, 31.4 (3 CH_2)	94.3 (CH=); 101.3 (CH=); 197.3 (=C=)

It should be noted that the formation of allenes **1** was observed in the reactions with compounds, in which the substituent at the triple bond (R^1) contains no hydrogen atoms at the α position. Otherwise, the reactions afforded complex mixtures of products, in which the expected allene **1** was absent (example is the reaction of hex-2-ynyl methyl sulfide with NCS).

Allenes **1** are unstable and rapidly resinify during storage without a solvent at room temperature (in the case of compounds **1b** and **1g**, resinification occurs within several hours, other compounds resinify in a matter of days). As a result, we failed to purify these compounds by vacuum distillation and, hence, used them immediately after filtering off succinimide that formed in the course of their synthesis and removing the solvent under vacuum.

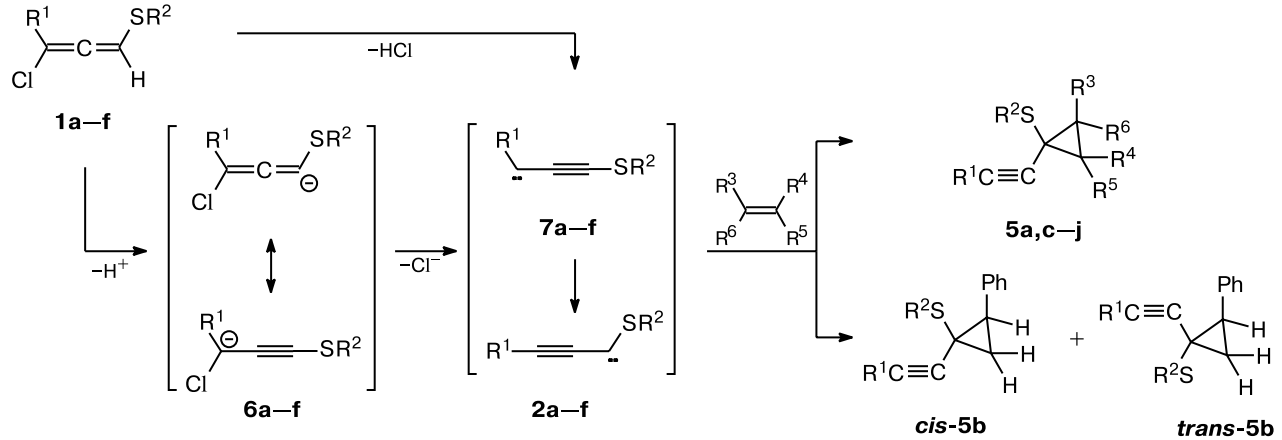
Treatment of chloro sulfides **1a—f** with Bu^tOK in hexane at −20 °C in the presence of alkenes afforded the corresponding 1-(alk-1-ynyl)-1-organylthiocyclopropanes **5a—j** in yields of up to 60%, which indicates that previously unknown alk-1-ynyl(organylthio)carbenes **2a—f** are generated under these conditions (Scheme 2, Table 2).

Quantum-chemical calculations[13] have demonstrated that the energetically most favorable pathway of formation of carbenes **2** upon the proton abstraction from allenes **1** involves the simultaneous cleavage of the C—Cl bond and migration of the carbene center to the carbon atom bound to the organylthio group. It cannot also be ruled out that these reactions proceed according to an alternative scheme involving deprotonation of allenes **1a—f** under the action of Bu^tOK to form anions **6a—f** followed by elimination of Cl^- giving rise to carbenes **7a—f** (analogously to the generation of (alk-1-ynyl)halocarbenes from 3-substituted 1,1-dichloropropadienes[7]). However, carbenes **7** undergo rapid propargylic isomerization to thermodynamically more stable carbenes **2a—f**. Actually, the reactions in the presence of an excess of olefins did not gave carbene adducts **7**, whereas the yields of carbene adducts **2** (cyclopropanes **5**) were 12—54%.

The reactivity of carbenes **2** with respect to olefins depends substantially on both the structure of the latter and the nature of the organylthio group. For example, the generation of carbenes **2c** and **2f** containing the methylthio group at the carbene center in the presence of 2,3-dimethylbut-2-ene afforded the corresponding cyclopropane adducts in 28—39% yields. The reactions with less nucleophilic 2-methylpropene instead of the above-mentioned alkene did not give cyclopropanation products. The replacement of the alkylthio group at the carbene center with the arylthio group not only leads to an increase in the yields of cyclopropane products but also extends the spectrum of alkenes, which can be successfully involved in cycloaddition (see Scheme 2, Table 2).

Only one of the possible isomers of cyclopropane **5g** was detected by GLC and NMR spectroscopy among the products prepared by the reaction with the use of 2-methylbut-2-ene for trapping the corresponding carbene **2d**. However, the spectroscopic data for compound **5g** did not allow us to establish the relative arrangement of the substituents. This unusual stereoselectivity is, apparently, attributable to steric factors as-

Scheme 2



1, 2, 6, 7: R^1 = Bu^t (**a, c—e**), Ph (**b**), Ad (**f**); R^2 = Ph (**a**), Me (**b, c, f**), *p*-Tol (**d**), Bu^n (**e**); **5:** R^1 = Bu^t (**a—h**), Ad (**i**), Ph (**j**)

5	R^2	R^3	R^4	R^5	R^6	5	R^2	R^3	R^4	R^5	R^6
a	Me	Me	Me	Me	Me	**f**	*p*-Tol	Me	Me	H	H
b	Me	Ph	H	H	H	**g**	*p*-Tol	Me	Me	H	Me
c	Ph	Me	Me	Me	Me	**h**	Bu^n	Me	Me	Me	Me
d	Ph	Me	Me	H	H	**i**	Me	Me	Me	Me	Me
e	*p*-Tol	Me	Me	Me	Me	**j**	Me	Me	Me	Me	Me

Table 2. Reactions of 1-substituted 1-chloro-3-organylthiopropadienes **1a—f** with Bu^{t}OK in the presence of alkenes

Carbene source	Carbene	Alkene				Product	Yield[a]	B.p./°C[b] (*p*/Torr)	Found / Calculated (%)		Molecular formula
		R^3	R^4	R^5	R^6				C	H	
1a	**2a**	Me	Me	Me	Me	**5c**	38	130—140 (1)[c]	79.31 79.66	9.02 9.15	$C_{19}H_{26}S$
1a	**2a**	H	Me	Me	H	**5d**	49	105—107 (1)	79.25 79.01	8.76 8.58	$C_{17}H_{22}S$
1b	**2b**	Me	Me	Me	Me	**5j**	12	120—130 (1)[c]	78.91 78.63	8.41 8.25	$C_{16}H_{20}S$
1c	**2c**	Me	Me	Me	Me	**5a**	28	80—100 (2)[c]	74.68 74.93	10.96 10.78	$C_{14}H_{24}S$
1c	**2c**	Ph	H	H	H	*trans*- : *cis*-**5b** = 5 : 1	18	150—160 (1)[c]	78.42 78.63	8.33 8.25	$C_{16}H_{20}S$
1c	**2c**	H	Me	Me	H	—[c]	—	—			
1d	**2d**	Me	Me	Me	Me	**5e**	50	160—170 (1)[c]	79.83 79.94	9.13 9.39	$C_{20}H_{28}S$
1d	**2d**	H	Me	Me	H	**5f**	54	120—135 (1)[c]	79.58 79.35	8.97 8.88	$C_{18}H_{24}S$
1d	**2d**	Me	Me	Me	H	**5g**	57	130—140 (1)[c]	79.32 79.66	9.29 9.15	$C_{19}H_{26}S$
1e	**2e**	Me	Me	Me	Me	**5h**	31	110—120 (1)[c]	76.68 76.62	11.14 11.35	$C_{14}H_{24}S$
1f	**2f**	Me	Me	Me	Me	**5i**	39	180—195 (1)[c]	79.19 79.41	9.81 10.00	$C_{20}H_{30}S$
1f	**2f**	H	Me	Me	H	—[c]	—	—			

[a] The yield of the product is given taking into account the purity of the starting chloroallene.
[b] The temperature of the bath used for vacuum microdistillation.
[c] A cyclopropanation product was not detected.

sociated with the presence of a bulky arylthio group. In the resulting isomer, the proton and the *para*-tolylthio group are, most likely, located on the same side of the plane of the cyclopropane ring.

The structures of cyclopropanes **5a—j** were established by elemental analysis, GLC-mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy (Tables 3 and 4). The ^{13}C NMR spectra of these cyclopropanes show signals at δ 75—91 characteristic of the triple bond. The ^{1}H NMR spectra have signals for the protons characteristic of the corresponding substituents at the cyclopropane fragment, the triple bond, and the sulfur atom.

The *trans* and *cis* isomers of cyclopropane **5b** were identified based on the chemical shifts for the protons of the cyclopropane fragment at the C atom bearing the phenyl group, on the assumption that the signals for the protons of the substituents in the *cis* position with respect to the methylthio group are shifted downfield due to the deshielding effect of the latter group. For the major isomer, the signal for this proton is present at lower field (δ 2.72) compared to the corresponding signal for the minor isomer (δ 2.51) due to the deshielding effect of the methylthio group. Other signals in the NMR spectra were assigned to the *cis* and *trans* isomers of **5b** based on comparison of the integral intensities of these signals.

The reaction with the use of 2-methylbuta-1,3-diene for trapping (3,3-dimethylbut-1-ynyl)phenylthiocarbene (**2a**), followed by treatment of the reaction mixture with water and removal of the solvent, afforded a residue consisting of cyclopropane **8a** and cycloheptatriene **9** in a ratio of 1 : 0.8 (Scheme 3), as evident from NMR spectroscopic data. We succeeded in isolating a mixture of these two products by vacuum microdistillation. The total yield was 47%.

The formation of compound **9** with a cycloheptatriene structure and only one of the possible geometric isomers of cyclopropane **8** can be explained as follows. Initially, carbene **2a** adds at the more substituted double bond of 2-methylbuta-1,3-diene to form two isomeric cyclopropanes **8a** and **8b**, and then cyclopropane **8b** with a *cis* arrangement of the vinyl and alkynyl groups undergoes isomerization accompanied by the opening of the three-membered ring to give triene **9**. Analogous transformations of cyclopropanes containing two unsaturated vicinal substituents in the *cis*-configuration have been described in the literature. For example, *cis*-1,2-divinylcyclo-

Table 3. The ^{1}H NMR spectra ($CDCl_3$, 200.13 MHz) of (alk-1-ynyl)organylthiocyclopropanes **5a—j**

Compound	^{1}H NMR (δ, *J*/Hz)					
	R^1	R^2	R^3	R^4	R^5	R^6
5a	1.21 (s, 9 H, Bu^t)	2.12 (s, 3 H, Me)		1.17 (s, 6 H, 2 Me); 1.19 (s, 6 H, Me)		
trans-**5b**	1.31 (s, 9 H, Bu^t)	2.39 (s, 3 H, Me)	7.25—7.35 (m, 5 H, Ph)	1.48 (dd, 1 H, CH_2, J_1 = 5.3, J_2 = 7.5)	1.63 (dd, 1 H, CH_2, J_1 = 5.3, J_2 = 8.6)	2.72 (dd, 1 H, CH_2, J_1 = 7.5, J_2 = 8.6)
cis-**5b**	1.26 (s, 9 H, Bu^t)	2.41 (s, 3 H, Me)	7.25—7.35 (m, 5 H, Ph)	1.20—1.39 (m, 2 H, CH_2)		2.51 (dd, 1 H, CH_2, J_1 = 6.3, J_2 = 9.1)
5c	1.13 (s, 9 H, Bu^t)	7.15 (br.t, 1 H, *p*-H, *J* = 7.1); 7.29 (br.t, 2 H, *m*-H, *J* = 7.1); 7.40 (br.d, 2 H, *o*-H, *J* = 7.1)	1.28, 1.33 (both s, 6 H each, 2 Me)			
5d	1.18 (s, 9 H, Bu^t)	7.20 (br.t, 1 H, *p*-H, *J* = 7.1); 7.33 (br.t, 2 H, *m*-H, *J* = 7.1); 7.45 (br.d, 2 H, *o*-H, *J* = 7.1)	1.16 (d, 1 H, *J* = 4.9)	1.39, 1.45 (both s, 3 H each, Me)		1.03 (d, 1 H, *J* = 4.9)
5e	1.19 (s, 9 H, Bu^t)	2.37 (s, 3 H, Me); 7.12 (br.d, 2 H, *o*-H, *J* = 8.3); 7.31 (br.d, 2 H, *m*-H, *J* = 8.3)		1.30, 1.33 (both s, 6 H each, Me)		
5f	1.22 (s, 9 H, Bu^t)	2.39 (s, 3 H, Me); 7.17 (br.d, 2 H, *o*-H, *J* = 8.3); 7.41 (br.d, 2 H, *m*-H, *J* = 8.3)	1.13 (d, 1 H, *J* = 4.8)	1.42, 1.47 (both s, 3 H each, Me)		1.02 (d, 1 H, *J* = 4.8)
5g	1.22 (s, 9 H, Bu^t)	2.37 (s, 3 H, Me); 7.14 (br.d, 2 H, *o*-H, *J* = 8.3); 7.34 (br.d, 2 H, *m*-H, *J* = 8.3)	R^3 + R^6: 1.05—1.30 (m, 4 H, CH, CH<u>Me</u>)	1.25, 1.37 (both s, 3 H each, Me)		—
5h	1.20 (s, 9 H, Bu^t)	0.89 (t, 3 H, Me, *J* = 7.1); 1.30—1.60 (m, 4 H, 2 CH_2); 2.63 (t, 2 H, CH_2S, *J* = 7.3)		1.12, 1.14 (both s, 6 H each, Me)		
5i	1.67, 1.84 (both m, 6 H each, 3 CH_2); 1.91 (m, 3 H, 3 CH)	2.13 (s, 3 H, Me)		1.17, 1.18 (both s, 6 H each, Me)		
5j	7.30—7.50 (m, 5 H, Ph)	2.28 (s, 3 H, Me)		1.30, 1.32 (both s, 6 H each, Me)		

propanes readily undergo isomerization with the ring opening to form the corresponding cycloheptadienes.[14]

The structures of products **8a** and **9** were established by ^{1}H and ^{13}C NMR spectroscopy without their isolation from the mixture. These spectra were very complicated. Hence, to make a reliable assignment of the signals and determine the structures of **8a** and **9**, we used the homo- and heteronuclear double resonance techniques and DEPT spectra.

The ^{1}H NMR spectrum of compound **8a** shows singlets of the *tert*-butyl and methyl groups at δ 1.19 and 1.59, respectively, an AB system with the spin-spin coupling

Table 4. The ^{13}C NMR spectra ($CDCl_3$, 50.32 MHz) and mass spectra of (alk-1-ynyl)organylthiocyclopropanes **5a—j**

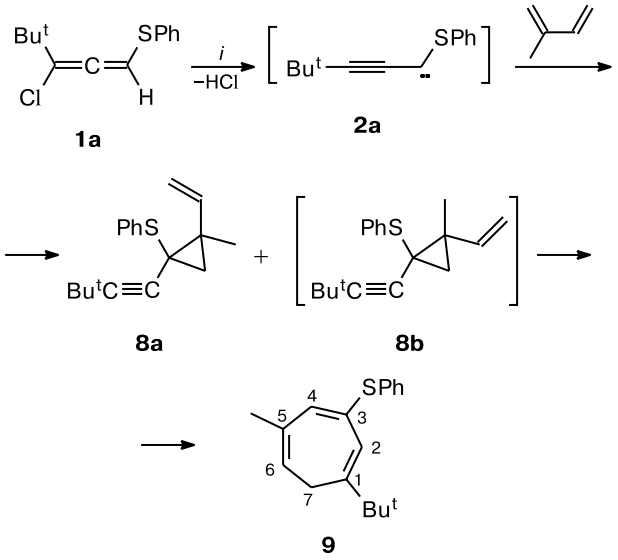
Compound	^{13}C NMR (δ)					MS, *m/z*
	C≡C	*cyclo*-C_3	R^1	R^2	R^3—R	
5a	77.7, 90.8	29.6 (2 $\underline{C}Me_2$); 34.3 ($\underline{C}$SMe)	27.7 ($\underline{C}Me_3$); 31.5 (3 Me)	14.9 (Me)	18.1, 20.2 (4 Me)	224 $[M]^+$
trans-**5b**	81.0, 86.7	22.3 (CH_2); 27.2 ($\underline{C}$SMe); 34.1 ($\underline{C}$HPh)	28.5 ($\underline{C}Me_3$); 30.9 (3 Me)	15.8 (Me)	126.5, 127.5, 128.9 (Ph); 135.8 (C(1), Ph)	244 $[M]^+$
cis-**5b**	75.2, 88.1	23.4 (CH_2); 23.8 ($\underline{C}$SMe); 35.2 ($\underline{C}$HPh)	28.2 ($\underline{C}Me_3$); 31.0 (3 Me)	16.2 (Me)	126.1, 127.3, 128.2 (Ph); 137.1 (C(1), Ph)	244 $[M]^+$
5c	78.6, 90.1	30.6 (2 $\underline{C}Me_2$); 33.7 ($\underline{C}$SMe)	27.6 ($\underline{C}Me_3$); 31.2 (3 Me)	124.8, 127.8, 128.3 (Ph); 137.3 (C_{ipso}, Ph)	18.8, 20.3 (4 Me)	286 $[M]^+$
5d	80.1, 88.9	26.2 ($\underline{C}$SPh); 27.5 ($\underline{C}Me_2$); 31.0 (CH_2)	27.3 ($\underline{C}Me_3$); 31.1 (3 Me)	125.2, 128.0, 128.4 (Ph); 137.1 (C_{ipso})	21.7, 23.9 (2 Me)	258 $[M]^+$
5e	78.9, 90.9	30.6 (2 $\underline{C}Me_2$); 34.0 ($\underline{C}$SMe)	27.7 ($\underline{C}Me_3$); 31.3 (3 Me)	21.1 (Me); 128.4, 129.1 (C(2), C(3), C(5), C(6)); 133.5, 134.7 (C(1), C(4))	18.8, 20.4 (4 Me)	300 $[M]^+$
5f	80.3, 88.6	27.2 ($\underline{C}Me_2$); 27.3 ($\underline{C}$STol); 31.0 (CH_2)	27.0 ($\underline{C}Me_3$); 31.1 (3 Me)	20.9 (Me); 128.7, 129.1 (C(2), C(3), C(5), C(6)); 133.1, 135.1 (C(1), C(4))	21.7, 23.9 (2 Me)	272 $[M]^+$
5g	77.6, 91.4	29.2 ($\underline{C}Me_2$); 29.3 ($\underline{C}$STol)	27.5 ($\underline{C}Me_3$); 31.0 (3 Me)	21.0 (Me); 128.3, 130.0 (C(2), C(3), C(5), C(6)); 133.7, 134.8 (C(1), C(4))	10.2, 18.0, 23.4, 32.2 (3 Me + CH)	286 $[M]^+$
5h	77.7, 91.2	29.1 (2 $\underline{C}Me_2$); 33.2 ($\underline{C}$SMe)	27.6 ($\underline{C}Me_3$); 31.4 (3 Me)	13.7 (Me); 22.1, 31.4, 31.6 (3 CH_2)	18.4, 20.1 (4 Me)	266 $[M]^+$
5i	78.0, 90.9	29.5 (2 $\underline{C}Me_2$); 34.3 ($\underline{C}$SMe)	28.1 (3 CH); 29.8 ($\underline{C}$C≡C); 36.2 (3 CH_2); 43.5 (3 CH_2)	14.9 (Me)	18.0, 20.3 (4 Me)	302 $[M]^+$
5j	81.8, 90.1	31.4 (2 $\underline{C}Me_2$); 34.7 ($\underline{C}$SMe)	124.1 (C(1)); 127.5, 128.2, 131.7 (Ph)	15.2 (Me)	18.2, 20.5 (4 Me)	244 $[M]^+$

constant of 5.3 Hz assigned to the methylene group in the cyclopropane ring, and a characteristic set of signals for the protons of the vinyl group at δ 5.1—6.2. The ^{13}C NMR spectrum of compound **8a** has signals for the carbon atoms of the triple bond at δ 79 and 90, signals of the vinyl fragment at δ 114.8 and 140.3, and signals of the *tert*-butyl, methyl, and phenyl groups.

We established the structure of compound **9** based primarily on the following characteristic signals in the ^1H NMR spectrum: a broadened singlet at δ 6.8 and a doublet with the spin-spin coupling constant of 1 Hz at δ 5.94, which correspond to the protons at the double bonds at positions 2 and 4 of the cycloheptatriene ring, respectively, and a triplet at δ 5.27 assigned to the proton at position 6, which is slightly broadened due to long-range spin-spin couplings. As expected, the signal of the methyl group in triene **9** is observed at substantially lower field (δ 1.9) compared to the analogous signal for cyclopropane **8a** (δ 1.59), and the signal of the methylene group is shifted to δ ~2.4 due to the influence of the double bonds.

According to the results of quantum-chemical calculations,[13] (alk-1-ynyl)alkylthiocarbenes prepared in the present study are in singlet states. Therefore, we characterized these species using the Moss method.[15]

Scheme 3



Reagent and conditions: *i.* Bu^{t}OK, hexane, –20 °C.

For this purpose, we determined the relative reactivities (k_i/k_0) of carbene **2d**, which was generated from halide **1d** under the action of Bu^{t}OK, with respect to a series of methyl-substituted olefins, by the competitive reaction method with the use of 2-methylpropene as the reference compound (k_i/k_0 = 1). The results of the present study and the analogous data for dichlorocarbene[16] are given in Table 5. The selectivity index calculated as the slope of the curve in the coordinates $X = \log(k_i/k_0) + 1$ for CCl_2 and $Y = \log(k_i/k_0) + 1$ for carbene **2d** is 0.59, which is indicative[15] of the electrophilic character of this carbene. The nature of the substituents at the triple bond and the sulfur atom would not have a considerable effect on the properties of carbenes **2**. Hence, other (alk-1-ynyl)organylthiocarbenes, most likely, will also exhibit electrophilic properties.

To summarize, we prepared previously unknown alk-1-ynyl(organylthio)carbenes **2** using an original procedure and demonstrated that these species can add at the double bond of olefins with different structures to form the corresponding cyclopropane adducts.

Table 5. Relative reactivities of 3,3-dimethylbut-1-ynyl(*p*-tolylthio)carbene **2d** and dichlorocarbene

Alkene	k_i/k_0	
	2d	Cl_2C[16]
2-Methylpropene	1.0	1.0
2-Methylbut-2-ene	2.05	3.05
2,3-Dimethylbut-2-ene	3.20	7.41

Experimental

The GLC analysis of the starting compounds and reaction products was carried out on a Hewlett—Packard 5890 Series II instrument equipped with a 30 m×0.153-mm capillary column and a Hewlett—Packard 3396A automatic integrator. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer in $CDCl_3$ with Me_4Si as the internal standard. The mass spectra were recorded on a Finnigan MAT INCOS-50 GLC-mass spectrometer.

The starting acetylenic sulfides **3** were prepared from the corresponding propargyl chlorides according to a known procedure.[17]

Synthesis of 1-substituted 1-chloro-3-organylthiopropa-1,2-dienes 1a—g (general procedure). *N*-Chlorosuccinimide (10.5 mmol) was added to a solution of sulfide **3** (10 mmol) in CCl_4 (10—15 mL). The reaction mixture was stirred at room temperature for 2—4 h, the course of the reaction being monitored by GLC. After completion of the reaction, the mixture was filtered, the solvent was removed *in vacuo*, and a pale-yellow liquid was obtained.

According to the ^{1}H NMR spectroscopic data (see Table 1), the reactions with sulfides **3c—g** afforded products, 75—85% of which are accounted for by the corresponding allenes **1a—g**. Under analogous conditions, the reaction of compound **3a** gave a mixture of allene **1a** and acetylene **4a** in a ratio of 1 : 1, whereas the reaction of **3b** produced a mixture of **1b** and **4b** in a ratio of 1 : 3.

1-Chloro-4,4-dimethyl-1-phenylthiopent-2-yne (4a). ^{1}H NMR, δ: 1.21 (s, 9 H, Bu^t); 5.86 (s, 1 H, CHCl); 7.20—7.70 (m, 5 H, Ph). ^{13}C NMR, δ: 27.6 (C$\underline{\text{C}}$Me$_3$); 30.4 (3 CH_3); 55.7 (CHCl); 74.3, 99.6 (C≡C); 128.4, 129.4, 129.6 (Ph); 131.2 (C(1), Ph).

1-Chloro-1-methylthio-3-phenylprop-2-yne (4b). ^{1}H NMR, δ: 2.50 (s, 3 H, SMe); 5.96 (s, 1 H, CHCl); 7.30—7.45 (m, 3 H, *m*-H, *p*-H, Ph); 7.62 (br.d, 2 H, *o*-H, Ph, J = 8.2 Hz). ^{13}C NMR, δ: 13.7 (SMe); 54.5 (CHCl); 83.9, 88.8 (C≡C); 121.5 (C(1), Ph); 128.3, 129.1, 131.7 (Ph).

Synthesis of 1-(alk-1-ynyl)-1-organylthiocyclopropanes 5a—j from 1-substituted 1-chloro-3-organylthiopropa-1,2-dienes 1a—f (general procedure). A solution of the starting halide (2 mmol) in hexane (1 mL) was added to a mixture of Bu^{t}OK (670 mg, 6 mmol), the starting alkene (6 mmol), and hexane (10 mL) at –20 °C. The reaction mixture was stirred for 30 min and allowed to warm to room temperature. Then the reaction mixture was treated with water, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, the solvent was evaporated, and the cyclopropane product was isolated from the residue by vacuum distillation (see Table 2). The yields, boiling points, and the ratios between the *cis* and *trans* isomers of cyclopropanes **5** are given in Table 2. The spectroscopic characteristics of cyclopropanes **5** are listed in Tables 3 and 4.

Reaction of (3,3-dimethylbut-1-ynyl)phenylthiocarbene (2a) with 2-but-1,3-diene. A solution of chloroallene **1a** (475 mg, 2 mmol) in hexane (1 mL) was added to a mixture of Bu^{t}OK (670 mg, 6 mmol), 2-methylbut-1,3-diene (410 mg, 6 mmol), and hexane (10 mL) at –20 °C. The reaction mixture was stirred for 30 min, allowed to warm to room temperature, and treated

with water. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, the solvent was evaporated, and a mixture of cyclopropane **8a** and cycloheptatriene **9** was isolated from the residue by vacuum microdistillation (1 Torr, the temperature of the bath was 140—150 °C) in a ratio of 1 : 0.8 (NMR spectroscopic data) in a total yield of 255 mg.

1-(3,3-Dimethylbut-1-ynyl)-2-methyl-1-phenylthio-2-vinylcyclopropane (8a). ^{1}H NMR, δ: 1.19 (s, 9 H, Bu^t); 1.40 (d, 1 H, CH_2, J = 5.3 Hz); 1.44 (d, 1 H, CH_2, J = 5.3 Hz); 1.59 (s, 3 H, Me); 5.18 (dd, 1 H, =CH_2, J = 10.7 Hz, J = 1.3 Hz); 5.25 (dd, 1 H, =CH_2, J_1 = 17.3 Hz, J_2 = 1.3 Hz); 6.10 (dd, 1 H, —CH=, J_1 = 10.7 Hz, J_2 = 17.3 Hz); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 19.7 (Me); 27.9 ($\underline{C}Me_3$); 30.7 (CH_2, *cyclo*-C_3H_2); 31.2 (3 Me); 32.2, 35.9 (2 C, *cyclo*-C_3H_2); 79.1, 90.1 (C≡C); 114.8 (=CH_2); 125.6, 128.3, 128.7 (Ph); 136.4 (C(1), Ph); 140.3 (—CH=).

1-*tert*-Butyl-5-methyl-3-phenylthiocyclohepta-1,3,5-triene (9). ^{1}H NMR, δ: 1.12 (s, 9 H, Bu^t); 1.91 (br.s, 3 H, Me); 2.43 (d, 2 H, CH_2, J = 6.7 Hz); 5.25 (br.t, 1 H, C(5)H, *cyclo*-C_7H_5, J = 6.7 Hz); 5.94 (d, 1 H, C(2)H or C(4)H, *cyclo*-C_7H_5, J = 1 Hz); 6.80 (d, 1 H, C(2)H or C(4)H, *cyclo*-C_7H_5, J = 1 Hz); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 20.8 (Me); 29.4 (3 Me); 35.9 ($\underline{C}Me_3$); 120.2 (C(6)); 120.6, 133.6 (C(2), C(4)); 122.0, 123.2 (C(1), C(4)); 125.9, 128.7, 129.7 (Ph); 136.1, 136.5 (C(3), C_{ipso}, Ph).

Determination of the relative reactivities of (3,3-dimethylbut-1-ynyl)-*para*-tolylthiocarbene (2d) generated from chloroallene 1d in the reaction with Bu^{t}OK. Potassium *tert*-butoxide (110 mg, 1 mmol) was added to a solution of weighed samples (10—15 mmol) of 2,3-dimethylbut-2-ene and 2-methylbut-2-ene in hexane (25 mL). The reaction mixture was cooled to a temperature from −10 to −20 °C, and 2-methylpropene (350—650 mg, 7—12 mmol) was condensed into this mixture. The flask was sealed with a rubber stopper and warmed to room temperature. Then a solution of chloride **1d** (1 mmol) in hexane (1—2 mL) was added. After 30 min, the reaction mixture was quenched with water and the organic layer was analyzed by GLC. Three experiments were carried out and the results of these experiments were averaged. The weight ratios of cyclopropanes were determined using a detector, which was preliminarily calibrated against pure samples. The ratios k_i/k_0 for carbene **2d** with respect to the corresponding alkene were calculated from these data according to the equation $k_i/k_0 = (n_i/n_0) \cdot (m_0/m_i)$, where n_i/n_0 is the ratio of the amounts of adducts of carbene **2c** with *i*-th alkene and 2-methylpropene and m_0/m_i is the molar ratio of 2-methylpropene to *i*-th alkene.

The ratios k_i/k_0 are given in Table 5.

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