Organic Chemistry

Fast and reversible migrations of N,S-centered groups around the perimeter of cyclopropene and cycloheptatriene rings

V. I. Minkin,[a] I. E. Mikhailov,[a] G. A. Dushenko,[a]* O. E. Kompan,[a] and A. Zschunke[b]*

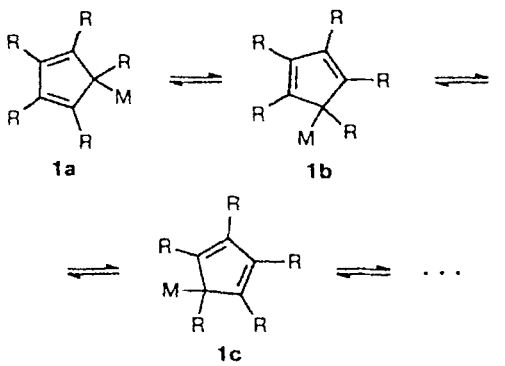
[a]Scientific-Research Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.
Fax: +7 (863 2) 28 5667. E-mail: minkin@ipoc.rnd.runnet.ru; mikhail@ipoc.rnd.runnet.ru
*[b]Institute of Chemistry, Humboldt University, D-10115 Berlin, Germany.**
Fax: +49 (030) 2093 7343. E-mail: adolf.zschunke@bam-berlin.de

The kinetics and mechanism of circumambulatory rearrangements of N-centered (NCS) and S-centered (SPh, SC_3Ph_3, SC(OEt)=S) groups in corresponding derivatives of 1,2,3-triphenylcyclopropene and cycloheptatriene were studied by dynamic ^1H and ^{13}C NMR spectroscopy. Migrations of the isothiocyanate group occur by the dissociation-recombination mechanism with intermediate formation of a tight ionic pair. Migrations of the phenylthio group around the perimeter of cyclopropene and cycloheptatriene rings occur by the 1,2-shift mechanism. It was found that rearrangements of the *O*-ethyl dithiocarbonate group in *S*-(1,2,3-triphenylcyclopropen-3-yl)-*O*-ethyl dithiocarbonate occur by the 3,3-sigmatropic shift mechanism. The molecular and crystal structure of *O*-ethyl *S*-(1,2,3-triphenylcyclopropen-3-yl) dithiocarbonate was studied by X-ray analysis.

Key words: cyclopropene, cycloheptatriene, tautomeric rearrangements; dynamic NMR, organic reaction mechanisms; X-ray analysis.

The ideas of structural flexibility, *i.e.*, the capability of some compounds to undergo fast and reversible rearrangements on a characteristic time scale of NMR spectroscopy (with energy barriers below 100 kJ mol^{-1}), were introduced into organic chemistry with the discovery[1] of circumambulatory (merry-go-round, walk) rearrangements of organometallic cyclopentadiene derivatives of the type **1**.

Early reports on the circumambulatory rearrangements, in which the migrating groups consisted of atoms of Group IIIA—VA elements of the Periodic system,

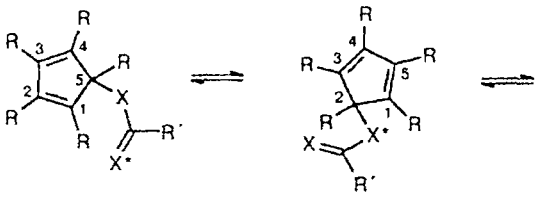


M = Fe(η^5-Cp)(CO)$_2$, Hg(η^1-Cp), Cr(η^5-Cp)(NO)$_2$, Cu(PEt_3); R = H

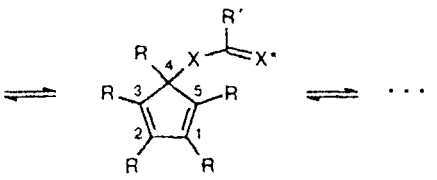
* Institut für Chemie, Humboldt Universität, D-10115 Berlin, Deutschland.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 913—923, May, 1998.

date back to the seventies (see Refs. 2, 3). Later, rearrangements of cyclopentadiene **1** derivatives with N-, O-, S-, Se, Te-, and Hal-centered groups were also studied.[4–8] As in the case of organometallic derivatives, the 1,5-sigmatropic (1,2-) shift of migrating group around the perimeter of the ring is the preferential mechanism of rearrangements. However, a dissociation-recombination rearrangement mechanism with intermediate formation of ionic pairs was revealed for several arylazocyclopentadienes containing electron-withdrawing groups in the cycle (R = COOMe).[9,10] The rearrangements of cyclopentadienes of the type **2** containing heteroallylic migrants (M = X—C(R′)=X, where X = O, S, and NR″) should be particularly mentioned. In these cases, the 1,5-sigmatropic shift competes with the 3,3-sigmatropic shift which is known to be the preferential mechanism for migrations of amidinyl (X = NAr, R = COOMe),[11] acyloxy (X = O, R = COOMe),[12] and dithioacyloxy groups (X = S, R = Ph).[13]



2a **2b**



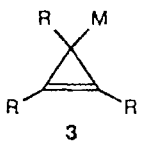
2c

Thus, circumambulatory rearrangements of cyclopentadiene derivatives are one of the best studied areas of the dynamic stereochemistry of structurally flexible compounds. Analogous rearrangements in the series of derivatives of the preceding and successive members of the family of conjugated carbocyclic structures (cyclopropene (**3**) and cycloheptatriene (**4**), respectively) are much less studied. For compounds of this type, one can expect that electronic interactions between the migrating group and the carbocyclic fragment will considerably differ from those for the cyclopentadiene **1** derivatives, where stabilization of both the transition state of the reaction of 1,5-sigmatropic shift and the intermediate ionic pair in the dissociation of the C—M bond is favored by electron-withdrawing groups in the five-membered ring. On the contrary, "aromatization" of the cycle in compounds **3** and **4** requires charge transfer to the migrant.

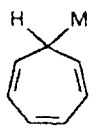
In fact, the circumambulatory rearrangements of cyclopropenes (**3**: R = H, Cl; M = Cl [14] or R = Bu^t, M = N_3 [15]) and cycloheptatrienes (**4**: M = NCS or N_3)[16,17] known by the time we began our studies were restricted to examples of randomization of the position of the migrating group in the ring occurring by the dissociation-recombination mechanism favored by the anionoid nature of the migrant.

The shift of the migrant around the perimeter of the seven-membered cycle by the mechanism of 1,2- and 3,3-sigmatropic shift was only observed for **4** (M = N_3)[16] along with the ionic equilibrium.

In this work, the structure, kinetics, and mechanism of circumambulatory rearrangements were studied for a wider series of triphenylcyclopropene and cycloheptatriene derivatives (**3a—e** and **4a,b**, respectively) with N- and S-centered groups. Some preliminary results of these investigations have been reported earlier.[18–22]



3



4

3: R = Ph; M = SPh (**a**), SC_3Ph_3 (**b**), NCS (**c**), SCN (**d**), SC(OEt)=S (**e**)

4: M = SPh (**a**), SC(OEt)=S (**b**)

Experimental

The ^{1}H NMR spectra of compounds under study were recorded on a Bruker-AM 300 spectrometer operating at 300 MHz. The concentrations of the substances were equal to 0.05 mol L^{-1}. The ^{13}C and ^{13}C APT NMR spectra were recorded on a Bruker-AM 300 spectrometer operating at 75.47 MHz with $SiMe_4$ as internal standard. The concentrations of the substances were equal to 0.5 mol L^{-1}. IR spectra were recorded on a Specord IR-75 spectrophotometer in Vaseline oil (thin layer). Mass spectra were obtained on a HP 5995 A spectrometer (direct inlet, EI, 70 eV, 60 °C).

Quantum-chemical calculations were carried out by the MNDO/PM3 semiempirical method[23] and MOPAC 6.0 program package[24] with full optimization of geometry for all structures and identification of the structures of transition states by analyzing the corresponding Hessians. The solvation effect was taken into account by a method based on the polarized continuum model.[25]

1,2,3-Triphenyl-3-phenythiocyclopropene (3a). Powder-like sodium thiophenoxide (0.264 g, 2 mmol) was added with stirring to a solution of 3-bromo-1,2,3-triphenylcyclopropene (0.694 g, 2 mmol) in 20 mL of anhydrous MeCN in an argon atmosphere at 0 °C. The temperature was raised to ~20 °C and the mixture was stirred for 2 h at ~20 °C and then refluxed for 0.5 h. The reaction mixture was filtered, the precipitate was washed with 20 mL of hot MeCN, the combined filtrate was evaporated *in vacuo*, and the residue was twice recrystallized from MeCN to give **3a** as white crystals (0.640 g, 85%). MS, *m/z* (I_{rel} (%)): 376 $[M]^+$ (0.6), 267 $[M-SPh]^+$ (100), 189 $[Ph_3C_3-C_6H_6]^+$ (5.8), 165 $[Ph_3C_3-C_6H_6-C_2]^+$ (13.9), 109 $[C_6H_5S]^+$ (13.2), 77 $[Ph]^+$ (8.6), 65 $[HS_2]^+$ (14.1).

Bis(1,2,3-triphenylcyclopropenyl) sulfide (3b). Anhydrous Na_2S (0.156 g, 2 mmol) was added with stirring to a solution of

Table 1. Data of elemental analysis and IR spectra of compounds **3a—c,e** and **4a,b**

Compound	M.p. /°C	Found / Calculated (%)			Empirical formula	IR (Vaseline oil), ν/cm^{-1}
		C	H	S		
3a	122—123	86.24 86.13	5.41 5.35	8.40 8.52	$C_{27}H_{20}S$	1835, 1615, 1585, 1500, 1480, 1320, 1160, 1080, 1060, 1030, 870, 790, 770, 700
3b	182—183	89.12 89.01	5.28 5.33	5.60 5.66	$C_{42}H_{30}S$	1840, 1610, 1580, 1500, 1480, 1320, 1170, 1080, 1070, 1040, 930, 860, 770, 700
3c	141—142	81.00 81.20	4.77 4.65	9.68 9.85	$C_{22}H_{15}NS$ [a]	2190—1980, 1840, 1610, 1500, 1460, 1320, 1170, 1080, 1040, 970, 920
3e	161—162	74.02 74.19	5.27 5.19	16.38 16.50	$C_{24}H_{20}OS_2$	1610, 1480, 1460, 1385, 1305, 1280, 1240, 1120, 1095, 1020, 1015, 1010, 990, 920
4a	—[b]	62.79 62.87	4.80 4.87	12.79 12.91	$C_{13}H_{12}S$	1630, 1610, 1260
4b	—[b]	56.48 56.57	5.60 5.70	30.32 30.20	$C_{10}H_{12}OS_2$	1635, 1620—1605, 1180

[a] Found: N, 4.22%. Calculated: N, 4.30%.
[b] Oil.

3-bromo-1,2,3-triphenylcyclopropene (1.388 g, 4 mmol) in 50 mL of dry MeCN in an argon atmosphere. The reaction mass was stirred for 3 h at ~20 °C and then refluxed for 1 h. The precipitate was filtered off, washed with 50 mL of hot MeCN, the combined filtrate was evaporated *in vacuo*, and the solid residue was crystallized from MeCN to give **3b** as colorless crystals (0.906 g, 80%). MS, *m/z* (I_{rel} (%)): 566 $[M]^+$ (12.1), 534 $[M-S]^+$ (17.7), 489 $[M-Ph]^+$ (1.8), 388 $[M-C_2Ph_2]^+$ (24.5), 267 $[M-SC_3Ph_3]^+$ (9.3), 189 $[Ph_3C_3-C_6H_6]^+$ (3.9), 178 $[Ph_2C_2]^+$ (8.5), 165 $[Ph_3C_3-C_6H_6-C_2]^+$ (9.5), 122 $[C_7H_6S]^+$ (8.8), 121 $[C_7H_5S]^+$ (100), 77 $[C_6H_5]^+$ (6.0).

3-Isothiocyanato-1,2,3-triphenylcyclopropene (3c). Powder-like 3-bromo-1,2,3-triphenylcyclopropene (1.388 g, 4 mmol) was added with intense stirring to a solution of potassium thiocyanate (0.097 g, 4 mmol) in 20 mL of water at 5 °C. At this temperature, the reaction mass was stirred for 0.5 h, the precipitate of product **3c** was filtered off, washed with water (10×2 mL), dried in a vacuum desiccator, and the product was crystallized from MeCN to give **3c** as colorless crystals (1.131 g, 87%). MS, *m/z* (I_{rel} (%)): 325 $[M]^+$ (21.9), 299 $[M-CN]^+$ (0.4), 298 $[M-HCN]^+$ (0.4), 293 $[M-S]^+$ (0.8), 292 $[M-HS]^+$ (1.1), 291 $[M-H_2S]^+$ (1.9), 267 $[M-NCS]^+$ (or $[M-CNS]^+$) (100), 266 $[M-HNCS]^+$ (10.2), 248 $[M-Ph]^+$ (2.3), 247 $[M-C_6H_6]^+$ (0.5), 222 $[M-PhCN]$ (5.4), 221 $[M-C_6H_6-CN]^+$ (9.8), 214 $[M-Ph-H_2S]^+$ (1.1), 213 $[M-C_6H_6-H_2S]^+$ (1.5), 190 $[Ph_2C_3]^+$ (3.0), 178 $[Ph_2C_2]^+$ (5.6), 115 $[PhC_3H_2]^+$ (6.0), 113 $[PhC_3]^+$ (7.7), 103 $[PhC_2H_2]^+$ (31.2), 101 $[PhC_2]^+$ (2.1), 89 $[C_7H_5]^+$ (10.9), 77 $[Ph]^+$ (14.2), 76 $[C_6H_4]^+$ (18.9), 59 $[HNCS]^+$ (4.6), 32 $[S]^+$ (4.2), 27 $[HCN]^+$ (9.3).

***O*-Ethyl *S*-(1,2,3-triphenylcyclopropene-3-yl) dithiocarbonate (3e).** Potassium *O*-ethylxanthate (0.640 g, 4 mmol) in 20 mL of anhydrous MeCN was added to a solution of 3-bromo-1,2,3-triphenylcyclopropene (1.388 g, 4 mmol) in 30 mL of anhydrous MeCN at 22 °C. The mixture was kept for 72 h at ~20 °C, the precipitated KBr was filtered off, the filtrate was evaporated *in vacuo*, and the residue was recrystallized from benzene and filtered while hot. After the second crystallization from benzene, compound **3e** was isolated as colorless crystals (1.411 g, 91%). MS, *m/z* (I_{rel} (%)): 388 $[M]^+$ (0.7), 359 $[M-Et]^+$ (0.7), 343 $[M-OEt]^+$ (0.1), 328 $[MH-Et-S]^+$ (0.3), 312 $[MH-OEt-S]^+$ (3.0), 300 $[MH-C(=S)OEt]^+$ (0.4), 299 $[M-C(=S)OEt]^+$ (0.9), 295 $[M-Et-2S]^+$ (0.3), 283 $[M-Et-CS_2]^+$ (1.4), 268 $[MH-SC(=S)OEt]^+$ (23.4), 267 $[M-SC(=S)OEt]^+$ (100), 222 $[M-C(=S)OEt-Ph]^+$ (0.5), 221 $[M-C(=S)OEt-C_6H_6]^+$ (2.0), 190 $[Ph_2C_3]^+$ (0.8), 189 $[Ph_2C_3-H]^+$ (4.1), 178 $[Ph_2C_2]^+$ (2.5), 121 $[SC(=S)OEt]^+$ (32), 115 $[PhC_3H_2]^+$ (1.4), 113 $[PhC_3]^+$ (1.4), 93 $[SC(=S)OH]^+$ (3.2), 89 $[C_7H_5]^+$ (3.0), 77 $[Ph]^+$ (12.1), 29 $[Et]^+$ (22.7).

7-Phenylthiocyclohepta-1,3,5-triene (4a). Powder-like sodium thiophenoxide (0.660 g, 5 mmol) was added with stirring to a solution of tropylium tetrafluoroborate (0.890 g, 5 mmol) in 50 mL of anhydrous MeCN in an argon atmosphere at 22 °C. The reaction mass was stirred for 24 h at ~20 °C, the precipitated $NaBF_4$ was filtered off, the filtrate was evaporated *in vacuo*, and the oily residue was chromatographed on Silochrom (with benzene—hexane (1 : 3) as eluent), R_f 0.50. Compound **4a** was obtained as a colorless oil (1.054 g, 85%).

***S*-(Cyclohepta-1,3,5-triene-7-yl) *O*-ethyl dithiocarbonate (4b).** Potassium *O*-ethyl xanthate (0.800 g, 5 mmol) in 20 mL of anhydrous MeCN was added dropwise with stirring to a solution of tropylium tetrafluoroborate (0.890 g, 5 mmol) in 20 mL of anhydrous MeCN in an argon atmosphere at 0 °C. At this temperature, the reaction mass was stirred for 4 h, the precipitated KBF_4 was filtered off, the filtrate was evaporated *in vacuo*, and the oily residue was chromatographed on Silochrom (with benzene—hexane (1 : 2) as eluent), R_f 0.80. Compound **4b** was obtained as a light-yellow oil (1.00 g, 95%). The melting points, data of elemental analysis, ^1H and ^{13}C NMR and IR spectra of compounds **3a—c,e** and **4a,b** are given in Tables 1 and 2.

X-ray study of compound 3e.* Crystals of **3e** ($C_{24}H_{20}OS_2$) are monoclinic, a = 9.875(6) Å, b = 15.572(10) Å, c = 13.537(7) Å, β = 93.64(6)°, V = 2078(3) Å^3, d_{calc} = 1.23 g cm^{-3}, space group $P2_1/n$, Z = 4. The cell parameters and intensities of 3345 reflections with $I > \sigma(I)$ were measured on an automatic Siemens-R3m diffractometer (Mo-Kα radiation, ω-scan, 2θ < 28°). The structure was solved by direct methods and refined anisotropically by the least squares method using 2219 reflections with $F^2 > 2.5\sigma(F^2)$. The positions of the

* X-ray analysis of compound **3e** was carried out at the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (Moscow).

Table 2. ^{1}H and ^{13}C NMR spectral parameters of compounds **3a—c,e** and **4a,b**

Compound	Solvent	^{1}H NMR (300 MHz), δ (*J*/Hz)	^{13}C NMR (75.47 MHz, at 25 °C), δ[a]			
			C(1)—C(3(7)) of cyclopolyene ring	C(Ph) (quaternary)	C arom.	C(OEt)
3a	$CDCl_3$	6.92—7.60 (m, 20 H, 1-, 2-, 3-Ph, SPh)	42.6 (C(3)); 118.5 (C(1), C(2))	127.1, 134.7, 144.2	126.3, 127.1, 127.3, 128.2, 128.2, 129.3, 128.8, 129.7, 134.4	
3b	$CDCl_3$	6.48—7.07 (m, 30 H, Ph)	38.8 (C(3), C(3)); 120.1 (C(1), C(2))	127.6, 145.0	125.9, 127.8, 127.8, 128.5, 128.7, 129.6	
3c	C_6D_6	6.95—7.16 (m, 9 H); 7.39—7.44 (m, 6 H, Ph)[b]	47.1 (C(3)); 114.6 (C(1), C(2)); 131.3 (NCS)	125.1, 139.6[c]	125.5, 127.4, 129.0, 129.4, 130.1, 130.3[c]	
	$CDCl_3$	7.39 (br.m, 9 H); 7.63 (br.m, 6 H, Ph)[b]	46.6 (C(3)); 114.1 (C(1), C(2)); 130.3 (NCS)	124.9, 139.3	125.0, 127.1, 128.8, 129.1, 129.9, 130.0	
3e	$CDCl_3$	1.17 (t, 3 H, Me, ^3J = 7.3); 4.61 (q, 2 H, CH_2, ^3J = 7.3); 7.19—7.91 (m, 15 H, Ph)[b]	42.8 (C(3)); 117.9 (C(1), C(2)); 214.3 (C=S)	126.6, 143.5	126.3, 126.6, 128.3, 129.1, 130.0	13.5 (CH_3); 69.7 (CH_2)
	$C_6D_5CD_3$	—	44.0 (C(3)); 119.3 (C(1), C(2)); 214.2 (C=S)	127.9, 144.8[d]	127.0, 127.7, 127.9, 129.1, 130.5, 130.8[d]	14.0 (CH_3); 69.7 (CH_2)
4a	C_6D_6	3.74 (t, 1 H, H(7)); 5.38 (m, 2 H, H(1), H(6)); 5.97 (m, 2 H, H(2), H(5)); 6.34 (m, 2 H, H(3), H(4), $^3J_{H(1),H(7)}$ = 6.8, $^3J_{H(1),H(2)}$ = 8.4, $^3J_{H(2),H(3)}$ = 3.5); 6.91—7.35 (m, 5 H, Ph)[b]	45.8 (C(7)); 124.8 (C(1), C(6)); 126.8 (C(2), C(5)); 131.6 (C(3), C(4))	136.3	126.6, 129.0, 131.0	
4b	C_6D_6	0.75 (t, 3 H, Me, ^3J = 7.1); 4.14 (q, 2 H, CH_2, ^3J = 7.1); 4.95 (t, 1 H, H(7)); 5.61 (m, 2 H, H(1), H(6)); 6.01 (m, 2 H, H(2), H(5)); 6.27 (m, 2 H, H(3), H(4), $^3J_{H(1),H(7)}$ = 7.9, $^3J_{H(1),H(2)}$ = 9.1, $^3J_{H(2),H(3)}$ = 3.9)[b]	47.7 (C(7)); 122.7 (C(1), C(6)); 129.1 (C(2), C(5)); 132.1 (C(3), C(4)); 214.9 (C=S)			13.6 (CH_3); 69.6 (CH_2)
	$C_6D_5CD_3$	0.99 (t, 3 H, Me, ^3J = 7.1); 4.28 (q, 2 H, CH_2, ^3J = 7.1); 4.94 (t, 1 H, H(7)); 5.59 (m, 2 H, H(1), H(6)); 6.04 (m, 2 H, H(2), H(5)); 6.32 (m, 2 H, H(3), H(4), $^3J_{H(1),H(7)}$ = 7.9, $^3J_{H(1),H(2)}$ = 9.4, $^3J_{H(2),H(3)}$ = 3.6)[b]	47.5 (C(7)); 122.6 (C(1), C(6)); 128.9 (C(2), C(5)); 131.9 (C(3), C(4)); 214.5 (C=S)			13.6 (CH_3); 69.4 (CH_2)

[a] The signals were assigned using monoresonant ^{13}C NMR spectra (for **3c** in C_6D_6 and **3e** in $C_6D_5CD_3$) and the APT technique.
[b] At 25 °C.
[c] For the assignment of signals, see Fig. 1, *a*.
[d] For the assignment of signals, see Fig. 3, *a*.

hydrogen atoms were calculated geometrically and refined isotropically. All calculations for structure **3e** were carried out using the SHELXTL PLUS program package. The final values of reliability factors are R = 0.043, R_w = 0.043, GOOF = 0.92. The coordinates of non-hydrogen atoms and their equivalent thermal parameters are listed in Table 3, and the bond lengths and bond angles are listed in Tables 4 and 5, respectively.

Results and Discussion

The reaction of 3-bromo-1,2,3-triphenylcyclopropene with potassium thiocyanate results in the isothiocyanate derivative **3c**, the structure of which in both solution and the crystalline state was confirmed by ^{13}C NMR and IR spectroscopy.[19] The ^{13}C NMR spectrum of compound **3c** at room temperature is shown in Fig. 1. The signals of **3c** are broadened as the temperature increases and coalesce at 50—80 °C. The observed dynamic pattern of the NMR spectrum is explained by fast and reversible migration of the isothiocyanate group around the perimeter of the cyclopropene ring. In this case, the patterns of dynamic ^{1}H and ^{13}C NMR spectra are independent of the solution concentration (0.01 to 0.50 mol L^{-1}), which indicates the intramolecular character of the rear-

Table 3. Atomic coordinates ($\times 10^4$) and their equivalent thermal parameters* ($U_{eq} \times 10^3$) in structure **3e**

Atom	*x*	*y*	*z*	U_{eq}/Å^2	Atom	*x*	*y*	*z*	U_{eq}/Å^2
S(1)	1911(1)	8483(1)	4296(1)	56(1)	C(12)	521(6)	5535(3)	1386(3)	80(2)
S(2)	253(1)	9928(1)	3574(1)	89(1)	C(13)	−850(6)	5655(3)	1375(3)	84(2)
O	−622(3)	8347(2)	3804(2)	83(1)	C(14)	−1401(5)	6117(3)	2103(4)	80(2)
C(1)	2808(3)	6795(2)	4210(2)	45(1)	C(15)	−571(4)	6480(2)	2855(3)	61(1)
C(2)	1689(3)	6744(2)	3654(2)	45(1)	C(16)	922(3)	7093(2)	5419(2)	41(1)
C(3)	1651(3)	7345(2)	4525(2)	42(1)	C(17)	306(4)	7676(2)	6015(3)	58(1)
C(4)	4156(3)	6528(2)	4550(2)	47(1)	C(18)	−364(4)	7409(3)	6824(3)	72(2)
C(5)	4733(4)	6830(3)	5448(3)	66(1)	C(19)	−424(4)	6557(3)	7061(3)	68(2)
C(6)	6010(5)	6552(4)	5782(4)	89(2)	C(20)	189(4)	5974(3)	6491(3)	67(1)
C(7)	6712(5)	5995(4)	5232(4)	92(2)	C(21)	848(4)	6232(2)	5678(3)	53(1)
C(8)	6163(5)	5698(3)	4345(4)	78(2)	C(22)	359(4)	8912(2)	3852(3)	55(1)
C(9)	4885(4)	5957(2)	4001(3)	59(1)	C(23)	−2013(8)	8619(7)	3543(7)	152(4)
C(10)	819(3)	6376(2)	2867(2)	46(1)	C(24)	−2900(7)	8337(6)	4173(5)	135(4)
C(11)	1362(4)	5888(3)	2131(3)	64(1)					

* The equivalent thermal parameters were defined as 1/3 of the spur of the orthogonalized $U(i,j)$ tensor.

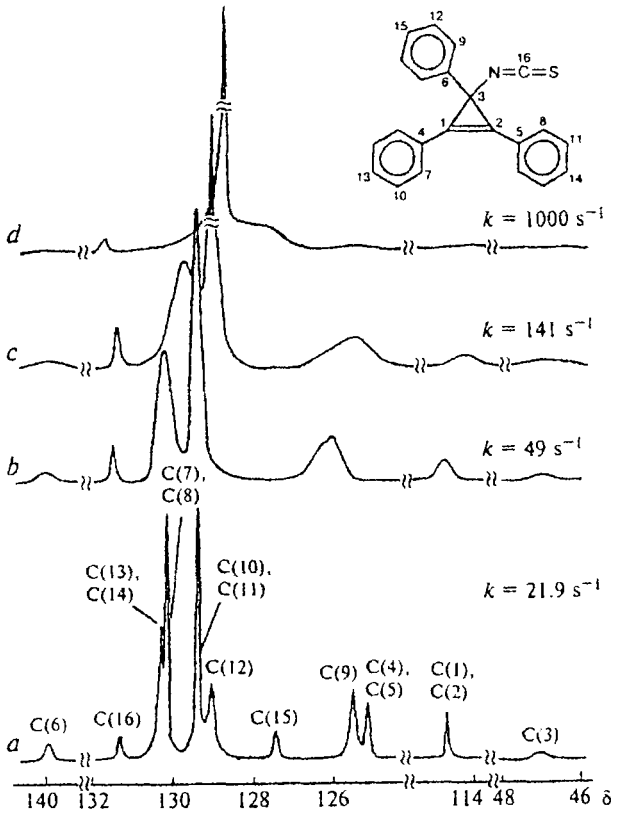


Fig. 1. ^{13}C NMR spectrum (75.47 MHz) of 3-isothiocyanato-1,2,3-triphenylcyclopropene (**3c**) in C_6D_6 at 25 °C (*a*), 35 °C (*b*), 49 °C (*c*), and 80 °C (*d*). The solvent signals were removed from the spectrum.

rangement. The kinetic parameters of degenerate rearrangements of the isothiocyanate group around the perimeter of the cyclopropene ring were calculated for the temperature interval 10—80 °C using the lineshape analysis of indicator signals in dynamic ^{13}C NMR spectra.

Solvent	$\Delta G^{\neq}_{298}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	k_{298}
	kJ mol^{-1}		J mol^{-1} deg^{-1}	s^{-1}
C_6D_6	65.2	59.8±1.2	−18.4±1.6	21.9
$CDCl_3$	60.6	44.7±1.2	−53.5±1.6	139.0

The rearrangement mentioned above can occur by one of the three plausible mechanisms described in Scheme 1.

The pathway of reaction (1) is associated with dissociation of the C—N bond and generation of the ionic pair **5** whose recombination occurs through equiprobable formation of a covalent bond with any of the carbon atoms of the ring. Reaction (2) occurs as 1,3-sigmatropic shift of the isothiocyanate group through transition state **6** (TS). The pathway (3) is the 3,3-sigmatropic shift with the intermediate formation of 3-thiocyanato-1,2,3-triphenylcyclopropene **3d**. This compound was not detected in the equilibrium with compound **3c** in solution; however, traces of **3d** (0.4%) were detected in the gas phase as a peak with *m/z* 299 $[C_3Ph_3SCN-CN]^+$, characteristic of fragmentation of the thiocyanate group.

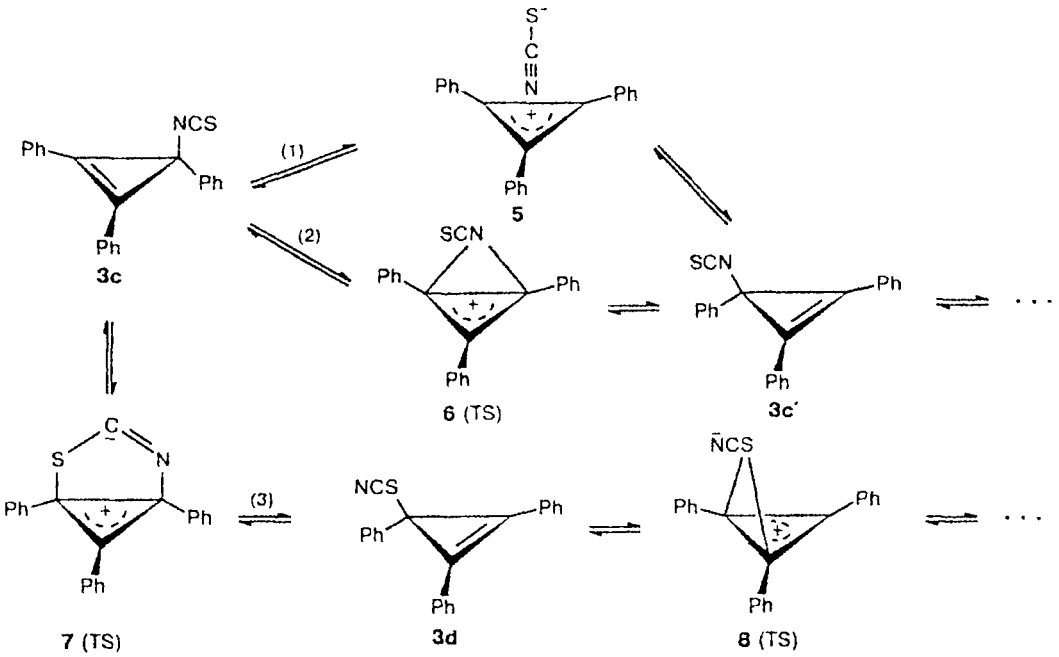
Table 4. Bond lengths (*d*) in structure **3e**

Bond	*d*/Å	Bond	*d*/Å
S(1)—C(3)	1.821(3)	C(7)—C(8)	1.367(8)
S(1)—C(22)	1.743(4)	C(8)—C(9)	1.378(6)
S(2)—C(22)	1.628(4)	C(10)—C(11)	1.388(5)
O—C(22)	1.307(4)	C(10)—C(15)	1.382(5)
O—C(23)	1.458(8)	C(11)—C(12)	1.378(6)
C(1)—C(2)	1.299(4)	C(12)—C(13)	1.367(8)
C(1)—C(3)	1.511(4)	C(13)—C(14)	1.362(7)
C(1)—C(4)	1.442(4)	C(14)—C(15)	1.386(6)
C(2)—C(3)	1.507(4)	C(16)—C(17)	1.381(5)
C(2)—C(10)	1.444(4)	C(16)—C(21)	1.390(5)
C(3)—C(16)	1.499(4)	C(17)—C(18)	1.379(6)
C(4)—C(5)	1.392(5)	C(18)—C(19)	1.366(7)
C(4)—C(9)	1.389(5)	C(19)—C(20)	1.358(6)
C(5)—C(6)	1.382(6)	C(20)—C(21)	1.374(6)
C(6)—C(7)	1.360(8)	C(23)—C(24)	1.330(1)

Table 5. Bond angles (ω) in structure **3e**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(3)—S(1)—C(22)	107.5(2)	S(1)—C(3)—C(16)	118.1(2)	C(2)—C(10)—C(11)	120.6(3)	C(17)—C(16)—C(21)	117.0(3)
C(22)—O—C(23)	120.0(5)	C(1)—C(3)—C(16)	119.4(3)	C(2)—C(10)—C(15)	120.4(3)	C(16)—C(17)—C(18)	121.2(4)
C(2)—C(1)—C(3)	64.3(2)	C(2)—C(3)—C(16)	120.4(3)	C(11)—C(10)—C(15)	119.0(3)	C(17)—C(18)—C(19)	120.6(4)
C(2)—C(1)—C(4)	154.4(3)	C(1)—C(4)—C(5)	120.0(3)	C(10)—C(11)—C(12)	120.1(4)	C(18)—C(19)—C(20)	119.3(4)
C(3)—C(1)—C(4)	140.6(3)	C(1)—C(4)—C(9)	120.8(3)	C(11)—C(12)—C(13)	120.3(4)	C(19)—C(20)—C(21)	120.6(4)
C(1)—C(2)—C(3)	64.7(2)	C(5)—C(4)—C(9)	119.2(3)	C(12)—C(13)—C(14)	120.3(4)	C(16)—C(21)—C(20)	121.3(3)
C(1)—C(2)—C(10)	153.5(3)	C(4)—C(5)—C(6)	119.6(4)	C(13)—C(14)—C(15)	120.2(4)	S(1)—C(22)—S(2)	119.6(2)
C(3)—C(2)—C(10)	141.3(3)	C(5)—C(6)—C(7)	120.5(5)	C(10)—C(15)—C(14)	120.1(4)	S(1)—C(22)—O	113.1(2)
S(1)—C(3)—C(1)	112.8(2)	C(6)—C(7)—C(8)	120.6(4)	C(3)—C(16)—C(17)	123.5(3)	S(2)—C(22)—O	127.2(3)
S(1)—C(3)—C(2)	117.4(2)	C(7)—C(8)—C(9)	120.1(4)	C(3)—C(16)—C(21)	119.4(3)	O—C(23)—C(24)	113.3(7)
C(1)—C(3)—C(2)	51.0(2)	C(4)—C(9)—C(8)	120.0(4)				

Scheme 1



The choice between the possibilities considered can be made on the basis of results of quantum-mechanical calculations by the MNDO/PM3 method (Table 6). The experimental results indicating that the isothiocyanate isomer **3c** is energetically preferential as compared to the thiocyanate isomer **3d** (the heat of formation of the latter is 17.5 kJ mol^{-1} larger than that of **3c**) are well reproduced by the calculations. The reaction pathway through transition state **7** *via* the 3,3-sigmatropic shift followed by the migration of the thiocyanate group seems to be the least realistic because of the high calculated energy barrier to the first stage (206.7, 208.8, and 211.3 kJ mol^{-1} in the gas phase, benzene, and chloroform, respectively).[19] As follows from Table 6, taking into account the solvation effect makes the tight ionic pair **5** energetically preferential as compared to the structure of transition state **6** for the alternative mechanism of rearrangement (1,3-sigmatropic shift). This fact is evidence for the dissociation-recombination mechanism **3c** ⇌ **5** ⇌ **3c'** ⇌ .... The energy barrier of 64.4 kJ mol^{-1} obtained for solution in chloroform (estimated as the relative energy of the ionic pair) is close to the experimental value of 61.5 kJ mol^{-1}.

Because of the low relative content of the thiocyanate isomer **3d** in the equilibrium with **3c**, the migration of the S-centered group around the perimeter of the three-membered cycle cannot be observed experimentally despite the fact that the energy barriers to 1,3-sigmatropic shift and dissociation-recombination mechanism calculated by the MNDO/PM3 method are rather close for both isomers. We detected the circumambulatory rearrangement of S-centered groups taking 1,2,3-triphenyl-3-phenylthiocyclopropene **3a** and bis(1,2,3-triphenylcyclopropenyl)sulfide **3b** as examples. In both compounds, the bond between the carbon atoms of the cyclopropene ring and the S atom is of covalent character

Table 6. Energy barriers (ΔE) to the circumambulatory rearrangement in the gas phase and in solution (ΔH_f(**3c**) = 752.3 kJ mol^{-1}, ΔH_f(**3d**) = 769.9 kJ mol^{-1}) calculated for compound **3c** by the MNDO/PM3 method

Medium	ε*	ΔE/kJ mol^{-1}	
		1,3-sigmatropic shift	Ionic pair
Gas	—	197.5	—
Benzene	2.28	117.6	107.5
Chloroform	4.81	79.1	64.4
DMSO	46.70	43.9	24.3

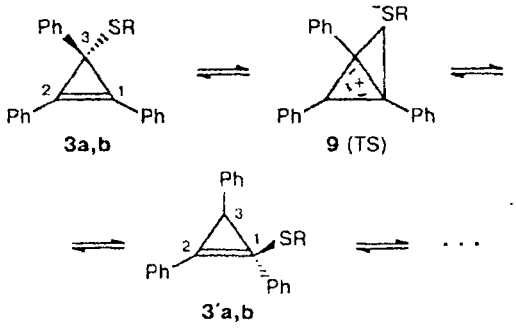
* Dielectric constant.

in both solution (ν(C=C) 1830 and 1835 cm^{-1} for **3a** and **3b**, respectively) and the crystalline state (ν(C=C) 1835 and 1840 cm^{-1} for **3a** and **3b**, respectively).

It was found that the ^{1}H and ^{13}C NMR spectra of compounds **3a,b** in the interval 70—145 °C are temperature-dependent. Thus, an increase in the temperature of solutions ($C_2D_2Cl_4$) in both cases leads to a reversible broadening of the signals of the atoms of the cyclopropene fragment in the ^{1}H and ^{13}C NMR spectra followed by (130—135 °C) coalescence of the proton signals of indicator aryl substituents in positions 3 and 1, 2. In this case neither concentration dependence of the dynamics of ^{1}H and ^{13}C NMR spectra nor temperature dependence of the signals of protons and carbon atoms of the phenylthio substituent in compound **3a** are observed. This spectral behavior is due to fast reversible intramolecular 1,3-sigmatropic shifts of the phenylthio and cyclopropenylthio groups around the perimeter of the 1,2,3-triphenylcyclopropene ring (Scheme 2).

The free activation energies ($\Delta G^{\neq}_{298}$) of migration of the phenylthio (**3a**) and cyclopropenylthio (**3b**) groups around the perimeter of the 1,2,3-triphenylcyclopropene ring calculated from the lineshape analysis of indicator signals in dynamic ^{13}C NMR spectra are equal to 102.1 and 100.8 kJ mol^{-1}, respectively. MNDO/PM3 calculations lead to greatly overestimated values of energy barriers to 1,3-sigmatropic shift with transition state

Scheme 2



of the type **9** and the formation of tight ionic pair (163.0 and 181.6 kJ mol^{-1}, respectively). However, it is important that in contrast to rearrangement **3c** ⇌ **3c'** ⇌ ..., the calculations reveal no pronounced dependence of the energy barriers on the solvent polarity. Additionally, the structure of transition state **9** (R = Ph) for the mechanism of 1,3-sigmatropic shift of the phenylthio group in media of different polarity is always more favorable energetically (by 16—22 kJ mol^{-1}) than the tight ionic pair structure. Thus, there are sufficient grounds to assume that, unlike compounds **3c,d**, circumambulatory rearrangements of cyclopropenyl derivatives **3a,b** occur by the non-dissociative mechanism. It should be noted that the found value of the energy barrier to the shift of the phenylthio group around the perimeter of the cyclopropene ring in molecule **3a** is 20—40 kJ mol^{-1} higher than barriers to migration of this group in the cyclopentadiene system.[4] This is explained by the fact that the conditions of delocalization of the positive charge in the allylic fragment of transition state of the thiabicyclo[3.1.0.]hexenyl type required for the phenylthio group to migrate around the cyclopentadiene ring are more favorable than those in structure **9**.[19,26] The third possible mechanism for the circumambulatory rearrangement in the series of cyclopropene derivatives, *viz.*, the 3,3-sigmatropic shift (or the hetero-Cope rearrangement), occurs most likely in the case of *O*-ethyl *S*-(1,2,3-triphenylcyclopropene-3-yl) dithiocarbonate (**3e**).

The structure of molecule **3e** has been confirmed by X-ray difraction analysis (Fig. 2, see Table 3—5). The molecule has a covalent structure; the C(3)—S(1) bond length (1.821 Å) is typical of the upper limit of the lengths of the C—S bond (which indicates its lability). The molecule is sterically strained. The phenyl rings at the C=C bond of the three-membered cycle are conjugated with this bond: the C(1)—C(4) and C(2)—C(10) bonds (1.442(4) Å and 1.444(4) Å, respectively) are shorter than the C(3)—C(16) bond (1.499(4) Å). However, despite the conjugation, a small rotation of conjugated phenyl rings relative to the C(1)C(2)C(3) cycle (by 14° and 20°) is observed. In addition, the above Ph rings are out of the plane of the three-membered cycle (the distances between the C(4) and C(10) atoms and the plane of the cyclopropene ring are equal to 0.12 and 0.11 Å, respectively) towards the phenyl substituent at the sp^3-hybridized carbon atom. Thus, a prerequisite is created in the form of empty space for the migration of the *O*-ethyl dithiocarbonate group around the cyclopropene rings. The molecule has an *exo*-conformation of the dithioacyloxy group with respect to the three-membered cycle (corresponding torsion angles about the C(3)—S(1) and S(1)—C(22) bonds are equal to 82.8° and 180°, respectively). According to calculations, this conformation is more favorable energetically than the *endo*-form, the transition to which is needed for the migration event to occur. Since the barrier to rotation about the C(3)—S(1) bond in solutions is less than

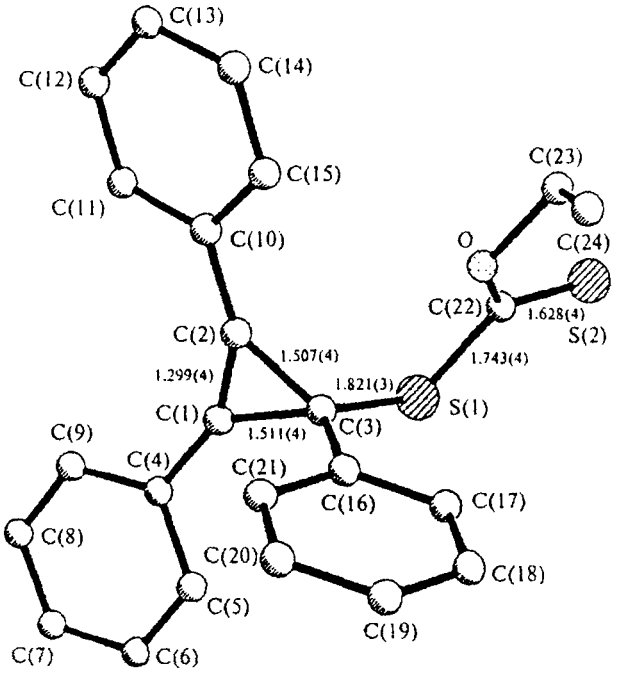


Fig. 2. The molecular structure of compound **3e** (bond lengths/Å are indicated).

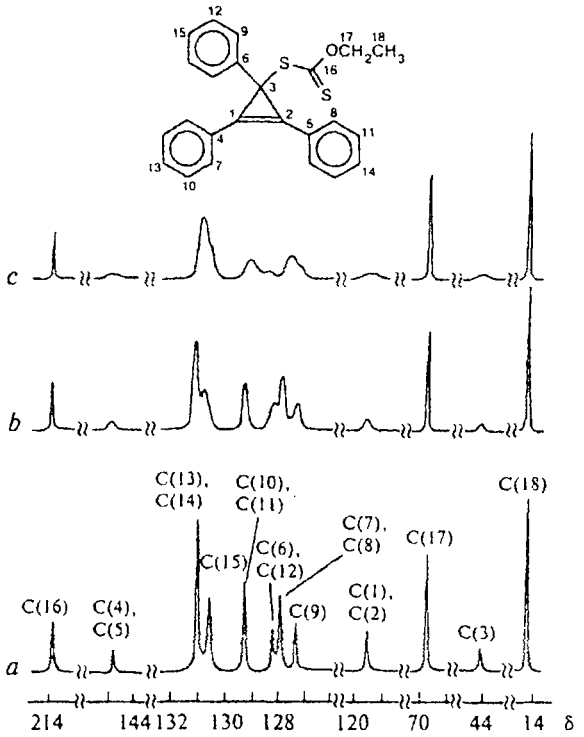


Fig. 3. ^{13}C NMR spectrum (75.47 MHz) of *O*-ethyl *S*-(1,2,3-triphenylcyclopropen-3-yl) dithiocarbonate (**3e**) in deuterotoluene at 25 °C (*a*), 80 °C (*b*), and 110 °C (*c*).

48 kJ mol^{-1} (according to NMR spectroscopy), this mutual conversion of the two forms occurs with ease in solutions.

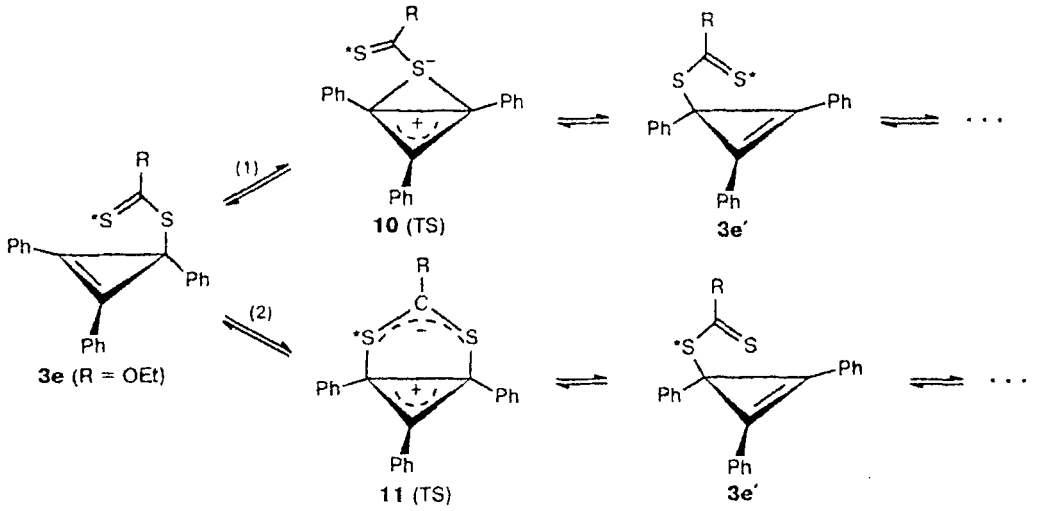
The dynamic process observed in solutions of compound **3e** is illustrated by the temperature dependence of the ^{13}C NMR spectrum of this compound in deuterotoluene (Fig. 3). The low-field part of the ^{1}H NMR spectrum (300 MHz) of compound **3e** at room temperature consists of two multiplets of the phenyl ring protons with ratio of intensities equal to 2 : 1. These signals are broadened and coalesce to give one narrow peak at 90 °C as the temperature of solution increases, which indicates a fast degenerate rearrangement. An analogous reversible broadening and coalescence of signals is also observed in the ^{13}C NMR spectra (75.47 MHz) of compound **3e** in deuterotoluene for quaternary carbon atoms as well as for carbon atoms in *ortho*-, *meta*-, and *para*-positions of two types of phenyl groups. The kinetic and activation parameters of these degenerate rearrangements were calculated from the analysis of the experimental lineshape of indicator signals in the ^{13}C NMR spectra in the temperature interval 25—110 °C using the DNMR-5 program: $\Delta G^{\neq}_{298}$ = 74.4 kJ mol^{-1}, $\Delta H^{\neq}$ = 61.9±0.8 kJ mol^{-1}, $\Delta S^{\neq}$ = −41.8±1.2 kJ mol^{-1} deg^{-1}, and k_{298} = 0.43 s^{-1}. These parameters are independent of both the solution concentration (0.01 to 0.30 mol L^{-1}) and the polarity of the solvent used. This makes it possible to rule out the dissociation-recombination mechanism. Since the found barrier to migration of the S-centered dithioacyloxy group is more than 25 kJ mol^{-1} lower than the barriers to migrations of other similar groups in cyclopropene derivatives **3a,b**, one can assume that the circumambulatory rearrangement **3e** ⇌ **3e′** ⇌ ... occurs by a mechanism that differs from the 1,3-sigmatropic shift (Scheme 3, pathway (1)) characteristic of compounds **3a,b**, namely, by the 3,3-sigmatropic rearrangement (pathway (2)).

An unambiguous experimental distinction between two possible directions of sigmatropic reaction could be made by ^{33}S NMR spectroscopy.

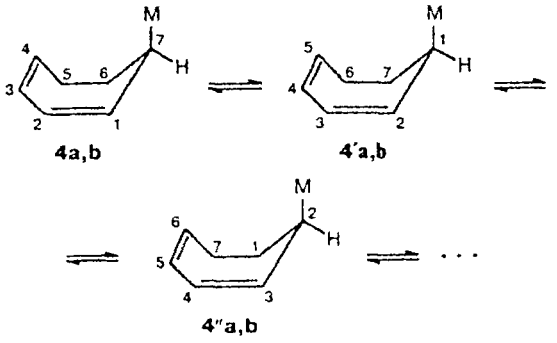
The results of MNDO/PM3 calculations of the energy barriers for compounds simulating structures **3e**, **10**, and **11** (R = H) provide additional evidence in favor of the mechanism of 3,3-sigmatropic shift.[18] The calculated barrier to the 3,3-sigmatropic shift of the dithioacyloxy group with transition state **11** (R = H) is considerably lower than the calculated barrier to the 1,3-sigmatropic shift with transition state of the type **10** (R = H) (45.2 kJ mol^{-1} *vs.* 183.7 kJ mol^{-1}, respectively).

In contrast to compound **3e**, migration of the *O*-ethyl dithiocarbonate group around the perimeter of the seven-membered ring in *S*-(cyclohepta-1,3,5-triene-7-yl) *O*-ethyl dithiocarbonate (**4b**) occurs by the mechanism of 1,7-sigmatropic (1,2-) shift (Scheme 4).

Scheme 3



Scheme 4



M = SPh (**a**), S(OEt)=S (**b**)

The value of the $^3J_{H(1),H(7)}$ spin-spin coupling constant (7.9 Hz) indicates that the *O*-ethyl dithiocarbonate group is in a quasi-axial position. This is also confirmed by the value of the $^3J_{H(1),H(7)}$ constant in the analogous triphenylstannyl derivative (**4**: M = $SnPh_3$) whose structure was established by X-ray analysis.[27] The dynamic process of averaging of the proton signals of the seven-membered cycle is illustrated in Fig. 4. The temperature-dependent ^{1}H NMR spectrum of compound **4b** indicates an asymmetrical picture of averaging, which is evidence against the dissociation-recombination mechanism with intermediate formation of a tight ionic pair between the tropylium cation and the *O*-ethyl dithiocarbonate anion. A synchronous broadening of the signals corresponding to the H(7), H(1), H(6) and H(2), and H(5) protons is observed first as the solution temperature increases; the broadening of the signals corresponding to the H(3) and H(4) protons occurs at a halved rate (see Fig. 4). Similar changes are also observed for the signals of the ^{13}C nuclei in corresponding positions of the seven-membered cycle in the dynamic ^{13}C NMR spectrum of solution of compound **4b**. This temperature-dependent spectral behavior is evidence in favor of the mechanism of circumambulatory rearrangements with successive 1,2- (1,7-sigmatropic) shift around the perimeter of the cycloheptatriene ring. The predominant 1,2-shift of the *O*-ethyl dithiocarbonate group is also confirmed by the ^{1}H 2D EXSY NMR spectrum

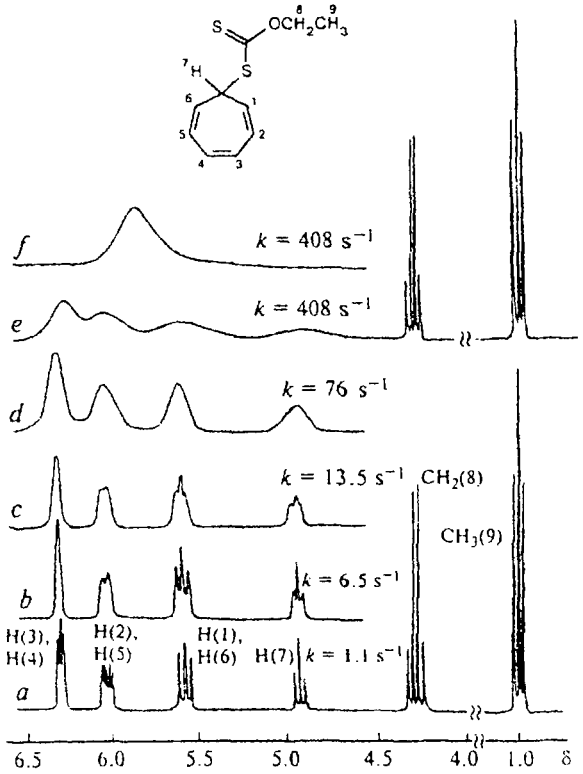


Fig. 4. ^{1}H NMR spectrum (*a*—*e*, at 300 MHz; *f*, at 80 MHz) of compound **4b** in deuterotoluene at 24 °C (*a*), 45 °C (*b*), 55 °C (*c*), 80 °C (*d*), and 108 °C (*e*, *f*).

of compound **4b**, in which the exchange cross peaks between the pairs of signals H(7)—H(1), H(6) and H(2), H(5)—H(3), H(4) are detected even at 27 °C. The following kinetic and activation parameters of degenerate migrations of the *O*-ethyl dithiocarbonate group around the perimeter of the cycloheptatriene ring were obtained from the lineshape analysis of proton and carbon signals of the cycloheptatriene ring performed using the DNMR-5 program:

Solvent	$\Delta G^{\neq}_{298}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	k_{298}
	kJ mol^{-1}		/J mol^{-1} deg^{-1}	/s^{-1}
C_6D_6	74.8	70.6±1.3	−13.8±1.6	0.45
$C_6D_5CD_3$	72.7	64.4±0.8	−27.6±1.2	1.1

The rate of the observed dynamic process is independent of the solution concentration within the limits 0.007—0.700 mol L^{-1}. Since only the type of permutation mechanism can be revealed in mechanistic studies using the dynamic NMR, an alternative 2,3-sigmatropic shift accompanied by a successive or simultaneous 1,3-shift of hydrogen cannot be ruled out *a priori*. However, it seems to be very unfavorable energetically as follows from a comparison between the calculated energy barriers to different pathways of circumambulatory rearrangements of heteroallylic groups in the cyclopentadiene ring.[28]

The fact that the mechanism of the 3,3-sigmatropic shift of the dithioacyloxy group, more energetically favorable for the cyclopropene derivative **3e**, is not observed for compound **4b** can be explained by unfavorable spatial orientation of the C=C bond in the boat-like conformation of the latter, which most likely impedes the formation of the structure of a transition state similar to **11**.

The boat-like conformation of the seven-membered cycle with quasi-axial orientation of the phenythio group is also more preferential for phenythiocycloheptatriene **4a**. The $^3J_{H(1),H(7)}$ constant is equal to 6.8 Hz. As in the case considered above, the analysis of both the dynamic ^{1}H and ^{13}C NMR spectra and ^{13}C 2D EXSY NMR spectra indicates the mechanism of successive 1,2-shifts of the phenythio group around the perimeter of the seven-membered cycle (see Scheme 4). As is shown in Fig. 5, a reversible broadening of the proton signals of the seven-membered cycle occurs as the temperature of solution of compound **4a** in [$^2H_5$]-nitrobenzene increases to 160 °C, whereas the signals of the aromatic ring protons remain unchanged.

The asymmetrical pattern of averaging of the proton signals of the cycloheptatriene ring, which is similar to that described above for compound **4b**, makes it possible to rule out the dissociation-recombination mechanism established earlier for the migration of the isothiocyano group in the seven-membered cycle.[29] Changes in the temperature-dependent ^{13}C NMR spectrum of compound **4a** are similar to those observed in the ^{1}H NMR spectrum. Moreover, the exchange cross peaks that correlate positions 7—1, 6 and 1, 6—2, and 5 of the

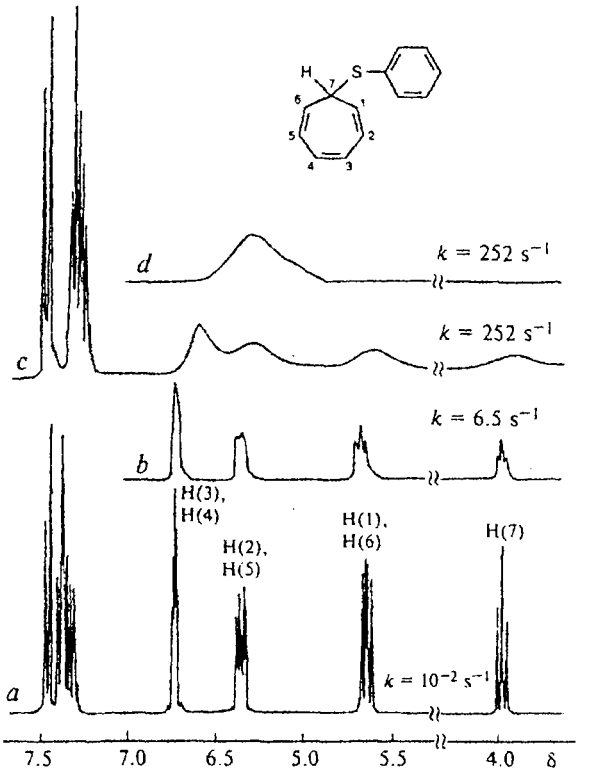


Fig. 5. ^{1}H NMR spectrum (*a*—*c*, at 300 MHz; *d*, at 80 MHz) of compound **4a** in deuteronitrobenzene at 20 °C (*a*), 100 °C (*b*), and 160 °C (*c*, *d*).

cycloheptatriene ring are detected in the ^{1}H and ^{13}C 2D EXSY NMR spectra of compound **4a** even at 15 °C. The rate of the process is independent of the solution concentration (0.006 to 0.800 mol L^{-1}). These facts indicate fast intramolecular 1,2- (1,7-sigmatropic) shifts of the phenythio group around the perimeter of the seven-membered cycle. Migration of a similar type in the cycloheptatriene ring of $(\sigma\text{-}C_7H_7)Re(CO)_5$ was reported previously.[30] On the contrary, the hydrogen atom,[31] methoxy,[32] and triphenylstannyl[33] groups migrate around the perimeter of the cycloheptatriene ring through successive 1,5-sigmatropic shifts. The kinetic and activation parameters of degenerate rearrangements of the phenythio group were calculated from the lineshape analysis of indicator signals in the dynamic ^{1}H and ^{13}C NMR spectra in the temperature interval 24—160 °C using the DNMR-5 program.

Solvent	$\Delta G^{\neq}_{298}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$k_{298} \cdot 10^2$
	kJ mol^{-1}		/J mol^{-1} deg^{-1}	/s^{-1}
C_6D_6	81.5	76.5±1.6	−16.7±1.6	2.9
$C_6D_5NO_2$	84.0	77.3±1.9	−23.0±1.6	1.1

The authors express their gratitude to R. M. Minyaev and I. V. Dorogan for their help in performing quantum-chemical calculations.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09559) and the Grant Center for Natural Science at the Saint Petersburg State University (Grant 95-0-9.4-162).

References

1. G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, 1956, **2**, 32.
2. R. F. Childs, *Tetrahedron*, 1982, **38**, 507.
3. P. Jutzi, *Chem. Rev.*, 1986, **86**, 983.
4. I. E. Mikhailov, V. I. Minkin, A. A. Klenkin, G. A. Dushenko, O. E. Kompan, Yu. T. Struchkov, A. I. Yanovsky, L. P. Olekhnovich, and N. I. Borisenko, *Zh. Org. Khim.*, 1988, **24**, 2301 [*J. Org. Chem. (USSR)*, 1988, **24** (Engl. Transl.)].
5. V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, I. D. Sadekov, A. A. Maksimenko, and Yu. E. Chernysh, *Dokl. Akad. Nauk*, 1992, **322**, 706 [*Dokl. Chem.*, 1992 (Engl. Transl.)].
6. I. E. Mikhailov, G. A. Dushenko, Yu. A. Zhdanov, L. P. Olekhnovich, and V. I. Minkin, *Dokl. Akad. Nauk SSSR*, 1984, **375**, 1431 [*Dokl. Chem.*, 1984 (Engl. Transl.)].
7. V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, I. A. Yudilevich, R. M. Minyaev, A. Zschunke, and K. Mugge, *J. Phys. Org. Chem.*, 1991, **4**, 31.
8. G. I. Borodkin, E. R. Susharin, and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1687 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1537 (Engl. Transl.)].
9. O. E. Kompan, M. Yu. Antipin, Yu. T. Struchkov, I. E. Mikhailov, G. A. Dushenko, L. P. Olekhnovich, and V. I. Minkin, *Zh. Org. Khim.*, 1985, **21**, 2032 [*J. Org. Chem. (USSR)*, 1985, **21** (Engl. Transl.)].
10. I. E. Mikhailov, G. A. Dushenko, V. I. Minkin, and L. P. Olekhnovich, *Zh. Org. Khim.*, 1984, **20**, 2306 [*J. Org. Chem. (USSR)*, 1984, **20** (Engl. Transl.)].
11. V. I. Minkin, I. E. Mikhailov, and G. A. Dushenko, *J. Chem. Soc., Chem. Commun.*, 1988, 1181.
12. I. E. Mikhailov, G. A. Dushenko, I. A. Kamanetskaya, O. E. Kompan, Yu. T. Struchkov, and V. I. Minkin, *Mendeleev Commun.*, 1991, 83.
13. G. A. Dushenko, I. E. Mikhailov, O. E. Kompan, Yu. T. Struchkov, A. Zschunke, C. Mugge, V. N. Drozd, and V. I. Minkin, *Mendeleev Commun.*, 1994, 120
14. R. Breslow, G. Ryan, and J. T. Groves, *J. Am. Chem. Soc.*, 1970, **92**, 988.
15. R. Curci, *J. Org. Chem.*, 1973, **38**, 3149.
16. H. Kessler and M. Feigel, *Acc. Chem. Res.*, 1982, **15**, 2.
17. M. Feigel, H. Kessler, D. Liebfritz, and A. Walter, *J. Am. Chem. Soc.*, 1979, **101**, 1943.
18. I. E. Mikhailov, G. A. Dushenko, I. V. Dorogan, R. M. Minyaev, V. V. Negrebetskii, A. Zschunke, and V. I. Minkin, *Mendeleev Commun.*, 1994, 9.
19. G. A. Dushenko, I. E. Mikhailov, I. V. Dorogan, R. M. Minyaev, A. Zschunke, and V. I. Minkin, *Mendeleev Commun.*, 1995, 213.
20. G. A. Dushenko, I. E. Mikhailov, A. Zschunke, N. Hakam, C. Mugge, and V. I. Minkin, *Mendeleev Commun.*, 1995, 133.
21. G. A. Dushenko, I. E. Mikhailov, A. Zschunke, N. Hakam, C. Mugge, and V. I. Minkin, *Mendeleev Commun.*, 1997, 50.
22. G. A. Dushenko, I. E. Mikhailov, A. Zhunke, and V. I. Minkin, *Zh. Org. Khim.*, 1996, **32**, 1112 [*Russ. J. Org. Chem.*, 1996, **32** (Engl. Transl.)].
23. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
24. J. J. P. Stewart, *MOPAC 6.0. QCPE*, 1990, 455.
25. J. Tomasi, R. Cammi, and P. J. Olivarez del Valle, *J. Mol. Struct. (Theochem.)*, 1991, **234**, 401.
26. V. I. Minkin, R. M. Minyaev, and I. A. Yudilevich, *J. Mol. Struct. (Theochem.)*, 1989, **186**, 293.
27. A. Padwa, D. M. Cordona, and M. J. Pulwer, *J. Org. Chem.*, 1991, **56**, 4747.
28. I. A. Yudilevich, R. M. Minyaev, I. E. Mikhailov, and V. I. Minkin, *Zh. Org. Khim.*, 1991, **27**, 1805 [*J. Org. Chem. (USSR)*, 1991, **27** (Engl. Transl.)].
29. M. Feigel, H. Kessler, and A. Walter, *Chem. Ber.*, 1978, **111**, 2947.
30. D. M. Heinekey and W. A. G. Graham, *J. Am. Chem. Soc.*, 1979, **101**, 6115.
31. Ch. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.
32. R. W. Hoffmann, K. R. Eicksen, H. J. Luthardt, and B. Dittrich, *Tetrahedron Lett.*, 1969, 3789.
33. R. B. Larrabee, *J. Am. Chem. Soc.*, 1971, **93**, 1510.

Received October 15, 1997