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Mendeleev Commun., 1994, **4(4)**, 120–122

Mendeleev Communications

Circumambulatory Rearrangements of Dithioacyloxy Groups around the Cyclopentadiene Ring

Igor E. Mikhailov,[a] Galina A. Dushenko,*[a] Olga E. Kompan,[a] Yurii T. Struchkov,[b] Adolf Zschunke,[c] Clemens Mügge,[c] Viktor N. Drozd[d] and Vladimir I. Minkin[a]

[a] *Institute of Physical and Organic Chemistry, Rostov State University, 344104 Rostov-on-Don, Russian Federation. Fax: +7 863 228 5667*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085*
[c] *Institute of Analytical Chemistry, Humboldt University, 10115 Berlin, Germany. Fax: +49 30 284 68343*
[d] *K. A. Timiryazev Moscow Agricultural Academy, 127550 Moscow, Russian Federation.*

Circumambulatory rearrangements of dithioacyloxy groups around the cyclopentadiene ring have been found to occur by a 3,3-sigmatropic shift (hetero-Cope) mechanism with energy barriers in the range of 24–30 kcal mol^{-1}.

Circumambulatory 3,3-sigmatropic shifts of amidinyl[1] and acyloxy[2,3] groups along the perimeter of the cyclopentadiene ring (hetero-Cope rearrangements) have recently been found to occur with energy barriers $G^{\ddagger}_{90\,°\mathrm{C}}$ 18.5–22.7 kcal mol^{-1} and $G^{\ddagger}_{25\,°\mathrm{C}}$ 27.6–35.8 kcal mol^{-1}, respectively. Here we report on the extension of this type of rearrangement to another heteroallyl migrant, the dithioacyloxy group, in the cyclopentadiene derivatives (*S*)-(5-benzyl-1,2,3,4-tetraphenylcyclopentadienyl)ethoxydithiocarbonate **2** and (*S*)-(5-*p*-tolyl-1,2,3,4-tetraphenylcyclopentadienyl)dithiobenzoate **3**.

Dithiocarbonic esters **1–3**† were obtained in 35–40% yields upon stirring a solution of equimolar amounts of the respective 5-substituted 5-bromotetraphenylcyclopentadiene and the trimethylammonium salt of dithiocarbonic acid in acetonitrile–methylene dichloride (1:1) during 5 h at room temperature in an atmosphere of argon. All three possible isomers **a–c** have been chromatographically (neutral Al_2O_3, eluent CCl_4–hexane) isolated in the case of compounds **2** and **3**, their ratio being 85:5:10 and 5:1:80, respectively (Scheme 1).

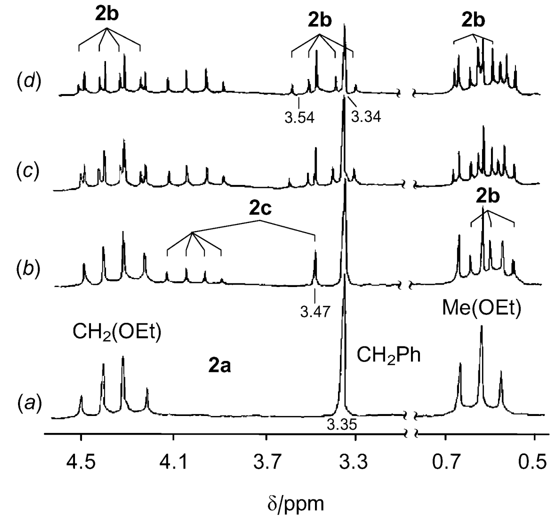

Fig. 1 Time-dependent ^{1}H NMR spectra (100 MHz) of compound **2a** in *o*-dichlorobenzene solution in the region δ 0.5–4.5 ppm, (*a*) at 25 °C, (*b*) after 5 min heating at 60 °C, (*c*) after 15 min heating at 60 °C, (*d*) after 25 min heating at 60 °C.

Fig. 1 shows the evolution of the ^{1}H NMR spectral pattern in time when a solution of compound **2a** in *o*-dichlorobenzene is heated at 60 °C.

The assignment of the emergent signals to isomers **2b** and **2c** has been carried out by taking into account the fact that diastereotopic splitting of the methylene proton peaks in **2b** must be substantially larger than that in **2c** because of the closer proximity of the prochiral and the emerging stereogenic centres in **2b** compared to **2c**. It was indeed found that while the methylene protons in **2b** displayed an AB-type spectral pattern (δ_1 3.34, δ_2 3.54 ppm, $^2J_{\mathrm{HH}}$ 8.0 Hz), no splitting at all was observed in **2c** (δ 3.47 ppm). The sequence of migratory

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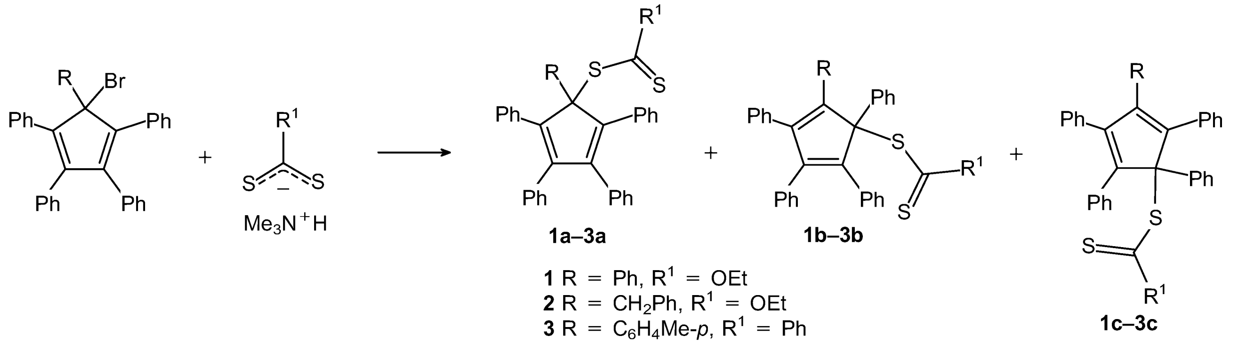
† Compound **1**: yellow crystals (from acetonitrile), m.p. 142–143 °C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.38 (3H, t, ^2J 7.1 Hz, Me), 4.66 (2H, q, ^2J 7.1 Hz, CH_2), 6.98–7.54 (25H, m, aromatic H). ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 14.3 (Me), 70.2 (CH_2), 77.1 (C^5-cp-ring); 126.8, 127.5, 127.6, 128.0, 128.2, 128.3, 129.2, 130.5, 130.7, 135.3, 135.5, 136.1 (C-ar-rings); 144.5, 147.4 (C^{1-4}-cp-ring); 210.4 (C=S). IR (Nujol) ν/cm^{-1} 1620, 1515, 1480, 1270, 1250, 1040. MS, *m*/*z* 566 (5%) $[C_5Ph_5SC(=S)OEt]^+$ = $[M]^+$, 521(1) $[M-OEt]^+$, 477(5) $[M-C(=S)OEt]^+$, 446(79) $[C_5Ph_5H]^+$, 445(99) $[C_5Ph_5]^+$, 367(29) $[C_5Ph_5-C_6H_6]^+$, 352(10) $[C_5Ph_5-C_7H_9]^+$, 289(32) $[C_5Ph_5-2C_6H_6]^+$, 267(17) $[C_5Ph_5-2C_6H_5-C_2]^+$, 265(19) $[C_5Ph_5-2C_6H_5-C_2H_2]^+$, 167(27) $[C_{13}H_{11}]^+$, 165(22) $[C_{13}H_9]^+$, 121(10) $[S–C(=S)OEt]^+$, 91(12) $[C_7H_7]^+$, 89(9) $[C(=S)OEt]^+$, 77(10) $[C_6H_5]^+$, 45(5) $[OEt]^+$, 29(100) $[Et]^+$.

Compound **2a**: yellow crystals (from acetonitrile), m.p. 128–129 °C. ^{1}H NMR (100 MHz, $C_6D_5NO_2$) δ 1.31 (3H, t, ^2J 7.1 Hz, Me), 3.46 (2H, s, benzyl CH_2), 6.88–7.58 (25H, m, aromatic H). IR (Nujol) ν/cm^{-1} 1615, 1505, 1490, 1250, 1010.

Compound **3c**: yellow crystals (from hexane), m.p. 101–102 °C. ^{1}H NMR (100 MHz, $C_6D_5NO_2$) δ 1.98 (3H, s, Me), 6.68–7.56 (29H, m, aromatic H). MS *m*/*z* 612 (3%) $[C_5Ph_4(4\text{-Tol})SC(=S)Ph]^+$ = $[M]^+$, 597 (0.5) $[M-Me]^+$, 535 (3) $[M-C_6H_5]^+$, 491 (0.5) $[M-C(=S)Ph]^+$, 461 (39) $[C_5Ph_4(4\text{-Tol})H]^+$, 460 (100) $[C_5Ph_4(4\text{-Tol})]^+$, 445 (0.5) $[C_5Ph_4(4\text{-Tol})-Me]^+$, 381 (27) $[C_5Ph_4(4\text{-Tol})-C_6H_6]^+$, 468 (3) $[C_5Ph_4(4\text{-Tol})-MeC_6H_5]^+$, 367 (5) $[C_5Ph_4(4\text{-Tol})-C_7H_9]^+$, 305 (7) $[C_5Ph_4(4\text{-Tol})H-2C_6H_6]^+$, 289 (13) $[C_5Ph_4(4\text{-Tol})-2C_6H_5-C_2H_2]^+$, 275 (4) $[C_5Ph_4(4\text{-Tol})-C_6H_5-C_2H_2]^+$, 165 (18) $[C_{13}H_9]^+$, 153 (9) $[S–C(=S)Ph]^+$, 91 (8) $[C_7H_7]^+$, 77 (9) $[C_6H_5]^+$.

Compounds **1–3** gave satisfactory elemental analyses.



1a–3a **1b–3b** **1c–3c**

1 R = Ph, R^1 = OEt
2 R = CH$_2$Ph, R^1 = OEt
3 R = C$_6$H$_4$Me-*p*, R^1 = Ph

Scheme 1

steps was elucidated through comparison of Figs. 1(*a*) and 1(*b*) which indicate that equilibration was attended by the initial appearance of the isomer **2c**, but not **2b**. Full equilibrium with the ratio of isomers **2a**:**2b**:**2c** = 45:25:30 was established at 60 °C in 25 min. It may, therefore, be concluded that an energy favourable mechanism for the displacement of the dithioacyloxy group in the cyclopentadiene ring is associated with either a 1,3- or 3,3- but not a 1,5(1,2)-sigmatropic shift characteristic of the migration of arylthio groups in the cyclopentadiene ring.[4,5]

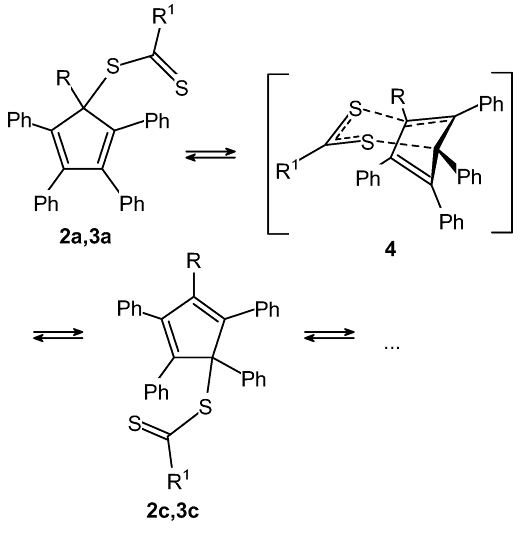
Whereas unambiguous choice between the 1,3- and 3,3-sigmatropic shift reaction pathways is rather complicated (isotopic labelling of one of the sulfur atoms in the migrant or implementation of dynamic ^{33}S NMR spectroscopy is required), the latter mechanism appears to be much more probable, based on the following arguments: i, the 3,3-sigmatropic shift mechanism proved to be the energetically favourable pathway for intramolecular migration of amidinyl[1,4] and acyloxy[2–4] groups around the cyclopentadiene ring; ii, in contrast to the 3,3-sigmatropic shift mechanism, that of suprafacial 1,3-sigmatropic shift is thermally forbidden by the Woodward–Hoffmann (W–H) rules;[6] and iii, theoretical modeling of the aforementioned reaction pathways for the circumambulatory rearrangement of dithioacyloxycyclopentadiene[4] by use of the semiempirical MINDO/3 technique is an accord with the expectations based on the W–H rules.

The same type of circumambulatory rearrangements (Scheme 2) **3a** ⇄ **3c** ⇄ **3b** were also observed in the case of (*S*)-(5-*p*-tolyl-1,2,3,4-tetraphenylcyclopentadienyl)dithiobenzoate **3**.

By heating **3c** in [^{2}H$_5$]nitrobenzene solution at 130 °C during 40 min an equilibrium mixture of isomers **3a**:**3b**:**3c** in a virtually statistical ratio (20:40:40) was obtained. Free energy barriers to 3,3-sigmatropic shifts in compounds **2** and **3** were calculated based on measurements of the temperature dependence of the intensities of the methylene (Fig. 1) and methyl (δ 1.86, 1.91 and 1.98 ppm for **3a**, **3b** and **3c**) proton signals, respectively. Table 1 contains kinetic parameters for separate 3,3-sigmatropic shifts of the *O*-ethyldithiocarbonate group in isomers of **2**. Averaged rate constants and activation parameters for migration of the dithiobenzoate group in **3** are as follows: $k_{130\,^{\circ}\mathrm{C}}$ $1.8 \times 10^{-4}\,\mathrm{s}^{-1}$, $G^{\ddagger}_{130\,^{\circ}\mathrm{C}}$ 30.7 kcal mol^{-1}, $H^{\ddagger}$ 28.9 ± 0.7 kcal mol^{-1}, $S^{\ddagger}$ -4.5 ± 0.9 e.u.

Table 1 Rate constants and free activation energy for individual 3,3-sigmatropic rearrangements of the isomers of **2** ([^{2}H$_5$]nitrobenzene).

Rate constants, free activation energy	3,3-sigmatropic shift			
	2a→2c	**2c→2a**	**2c→2b**	**2b→2c**
$k_{60\,^{\circ}\mathrm{C}} \times 10^4/\mathrm{s}^{-1}$	7.5	13.2	8.9	7.2
$G^{\ddagger}_{60\,^{\circ}\mathrm{C}}/\mathrm{kcal\ mol}^{-1}$	24.3	23.9	24.2	24.3



2a,3a **4** **2c,3c**

Scheme 2

High values of the energy barriers to dithioacyloxy migration in **2** and **3** explain why a five-fold degenerate rearrangement could not be detected by use of a dynamic ^{1}H NMR spectral technique for the closely congeneric compound **1**. The X-ray structure of **1**[‡] as shown in Fig. 2 indicates that

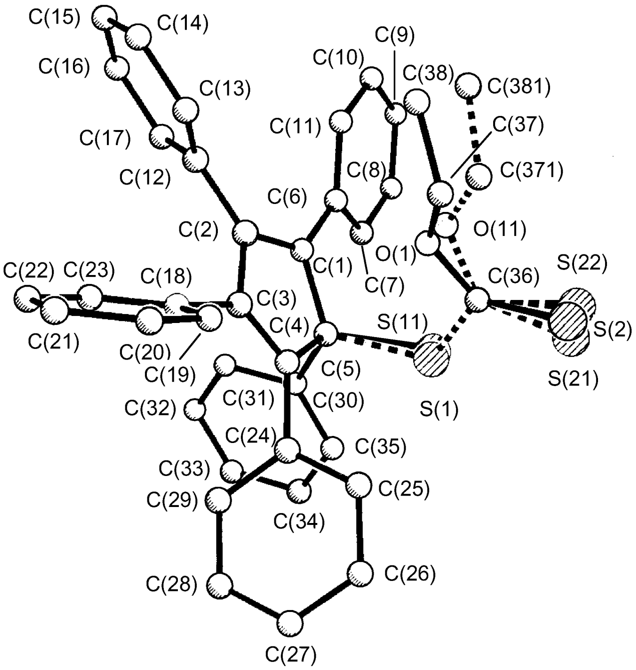


Fig. 2 The molecular structure of compound **1**. The average bond lengths (A) for the disordered positions of the dithioacyloxy moiety: S(1)–C(5) 1.855, S(1)–C(36) 1.74, C(36)–S(2) 1.62, C(36)–O 1.35 in two independent molecules. Torsion angles (°): C(1)C(5)S(1)C(36) 48.8–59.3 in molecule (*a*), 52.3–58.0 in (*b*); C(5)S(1)C(36)O 2.6 to −38.9 in (*a*), +5.1 to −23.2 in (*b*).

the molecule is not in the solid state, sterically prepared for the immediate 3,3-sigmatropic shift of the dithioacyloxy group. However, sulfur, oxygen and carbon centres within the potentially migrating moiety were found to be disordered on at least two positions. This fact points to low energy barriers against rotation about C–S bonds which would fit the molecule to a reactive transition-state like conformation of type **4** as predicted by calculations.[4]

We thank the Deutsche Forschungsgemeinschaft (project no. Zs13/2-1) and the International Science Foundation (grant no. RNI000) for financial support in carrying out the NMR study and organic synthesis.

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Received: Moscow, 26th January 1994
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[‡] Crystal data for $C_{38}H_{30}OS_2$, triclinic, space group $P1$, at +20 °C $a = 9.847(2)$, $b = 10.272(2)$, $c = 17.894(4)$ A, $\alpha = 95.25(2)$, $\beta = 96.51(2)$, $\gamma = 118.22(3)$, $V = 1562(2)$ A , $d_{calc} = 1.198$ g cm^{-3}, $Z = 2$. Data were measured on a Siemens R3m diffractometer with MoKα radiation ($\lambda = 0.7107$ A graphite monochromator) using a $\theta/2\theta$ scan technique ($2\theta \leq 50°$). The structure was solved by direct methods and refined anisotropically by a full-matrix least-squares procedure on 2643 reflectrions with $I > 4(\sigma)$. Due to a lack of reflections, phenyl ring atom positions were refined in an idealised geometry as rigid groups in both crystallographically independent molecules. All hydrogen atoms were located geometrically and a riding model was used for them. This model gave a final R-factor = 12.2%. Some peaks were found in the difference Fourier map near to the the dithioacyloxy groups in both molecules. After some trials the next model of disordering of the dithioacyloxy groups at both molecules was accepted: $J = 1/3$ for atoms S(2) and $J = 1/2$ for other atoms of this group. There is no clear description of the disordering but delocalised peaks of electron density would be approximated in the easiest way by this model. The final refinement converged at $R = 8.2\%$, $R_w = 7.6\%$, GOOF = 2.71. Atomic coordinates, bond lengths, angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, see Notice to Authors, *Mendeleev Commun.*, Issue 1, 1994.