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Hetero-Cope Rearrangement of *S*-(1,2,3-Triphenylcyclopropenyl)-*O*-ethyldithiocarbonate

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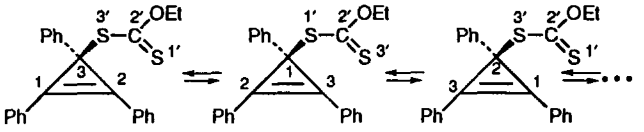
Rapid degenerate hetero-(*S*,*S*)-Cope rearrangement of *S*-(1,2,3-triphenylcyclopropenyl)-*O*-ethyldithiocarbonate has been studied by use of dynamic ^{1}H and ^{13}C NMR methods and semiempirical PM3 calculations.

It has recently been shown[1,2] that the 3,3-sigmatropic (hetero-Cope) rearrangement of amidinyl cyclopentadienes readily occurs in solution, the energy barriers ($\Delta G^{\ddagger}_{90\,^\circ\mathrm{C}}$ 18.5–22.7 kcal mol^{-1})[†] matching the ^{1}H NMR time scale. Here we report on the first example of the hetero-Cope rearrangement of a derivative of the unsaturated three-membered cyclic system, 1,2,3-triphenylcyclopropene. Whereas displacement of chlorine[3] and azido-group[4] along the perimeter of the cyclopropenyl ring proved to be governed by low-energy barrier ($\Delta G^{\ddagger}_{90\,^\circ\mathrm{C}}$ 13–15 kcal mol^{-1}) dissociation-recombination mechanisms, 3,3-sigmatropic shifts of allyl[5] and 3-indenyl groups in 1,2-diphenyl-3-allyl-3-methylcyclopropene[5] and 1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-3-methyl-1-phenylindene[6] require the overcoming of considerably higher (27–35 kcal mol^{-1}) activation energy barriers. From experimental[1,2] and computational[7] studies of Cope and hetero-Cope rearrangements in the cyclopentadiene series of compounds, it follows that one should expect a gradual decrease in the energy barrier compared with the 3,3-sigmatropic shift of an allyl-like group on moving from prototype hydrocarbon to acyloxy, amidinyl and dithioacyloxy migrants. In order to verify such a trend in the relevant cyclopropene series *S*-(1,2,3-triphenylcyclopropenyl)-*O*-ethyldithiocarbonate **1**[‡] has been synthesized and its propensity towards an NMR detectable rearrangement leading to displacements of the dithiocarbonate moiety in the cyclopropenyl ring studied by means of dynamic ^{1}H and ^{13}C NMR spectral techniques. Although the **1a**$\rightleftarrows$**1b**$\rightleftarrows$**1c** sequence of 3,3-sigmatropic shifts seems to be the most likely reaction pathway for the degenerate rearrangement, without special labeling it can not be unambiguously distinguished on experimental grounds from a competitive 1,3-sigmatropic shift mechanism.



1a **1b** **1c**

Therefore, in order to assess the energy preference for dithioacyloxy groups to migrate in a cyclopropenyl ring, semiempirical PM3[8] calculations have been performed for the rearrangement of a model cyclopropenyl dithioformiate **2**.

The low-field part of the ^{1}H NMR (300 MHz) spectrum of **1** in [^{2}H$_8$]toluene at room temperature consists of two multiplets (with intensity ratio 2:1) of the phenyl rings. On raising the temperature, the signals are broadened and coalesce forming a common sharp peak at 90 °C, thus indicating an occurrence of the rapid degenerate rearrangement. In the 75.5 MHz ^{13}C NMR spectra of **1** in [^{2}H$_8$]toluene an analogous pattern of reversible broadening and coalescence of signals at quaternary carbons as

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[†] 1 kcal = 4.184 J.

[‡] Characterization data for **1** [colourless crystals (from benzene)], T_m 160–161 °C, ^{1}H NMR (400MHz, CDCl$_3$, 25 °C) δ 1.17 (3H, *t*, ^3J 7.3 Hz, Me), 4.61 (2H, *q*, ^3J 7.3 Hz, CH$_2$), 7.19–7.91 (15H, *m*, aromatic H); ^{13}C NMR (100.6 MHz, CDCl$_3$ 25 °C) δ_c 13.48 (C–18), 42.79 (C–3), 69.66 (C–17), 117.87 (C–1, C–2), 126.31 (C–9), 126.61 (C–6), 126.62 (C–7, C–8), 128.26 (C–12), 129.13 (C–10, C–11), 130.03 (C–13, C–14, C–15), 143.50 (C–4, C–5), 214.31 (C–16); IR (Nujol) ν/cm^{-1}, 1610, 1480, 1460, 1385, 1305, 1280, 1240, 1120, 1095, 1020, 1015, 1010, 990, 920. **1** has been obtained by the reaction of 3-bromo-1,2,3-triphenylcyclopropene with potassium *o*-ethylxanthogenate in acetonitrile at room temperature for 40 h. Satisfactory elemental analyses were obtained for compound **1**.

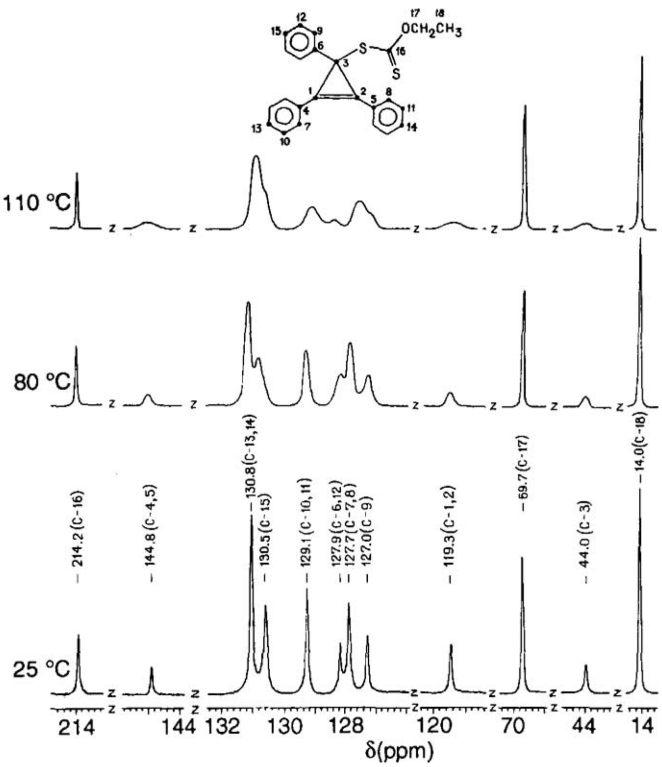
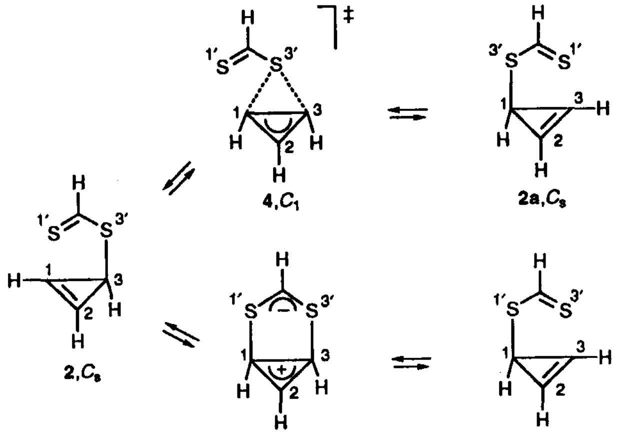
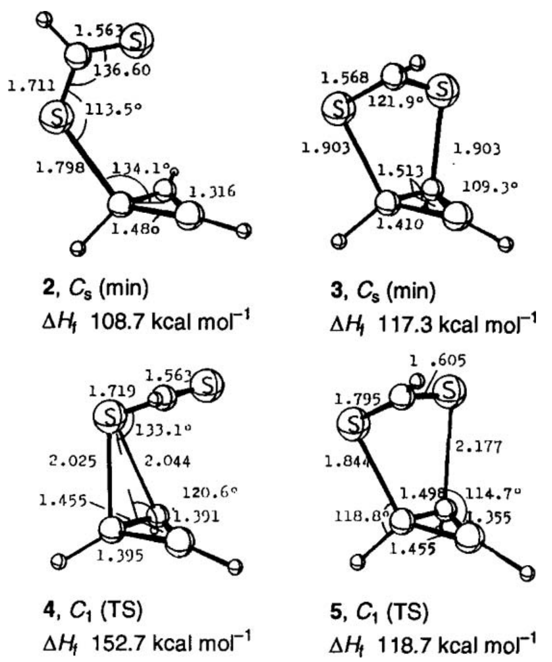


Fig. 1 75.5 MHz ^{13}C NMR spectra of *S*-(1,2,3-triphenylcyclopropenyl)-*O*-ethyldithiocarbonate in [^{2}H$_8$]toluene solution at temperatures +25 °C (*a*), +80 °C (*b*) and +110 °C (*c*). The signals have been assigned by use of monoresonance ^{13}C NMR spectra. The solution signals are removed from the spectra.



well as those related to *ortho*-, *meta* and *para*-sites of two kinds of groups is observed as a feature in Fig. 1.

From line shape analysis of the ^{13}C NMR spectra at temperature interval 25–110 °C, the following kinetic parameters of the degenerate rearrangement have been calculated: $\Delta G^{\ddagger}_{298}$ 17.8 kcal mol^{-1}, $\Delta H^{\ddagger}$ 14.8±0.2 kcal mol^{-1}, $\Delta S^{\ddagger}$ −10±0.3 e.u., k_{298} 0.43 s^{-1}. These are not measurably affected by the solution concentration (0.01–0.3 mol dm^{-3}). Such an observation is in line with the intramolecular character of the migration of the dithioacyloxy group between the cyclopropenyl ring carbon centres. To distinguish the two competitive migration mechanisms (3,3- and 1,3-sigmatropic shift pathways) the use of ^{33}S dynamic NMR techniques is conceivable. However, considering the relatively high activation energy barrier and the large chemical shift difference to observe a coalescence of two signals (for thioether and thiocarbonyl sulfur signals[9]), one might hardly expect an unambiguous selection of the mechanistic possibilities. In order to elucidate the problem computationally, semiempirical PM3[8] MO calculations of energy barriers to both 1,3- and 3,3-shift rearrangements have been performed for the model compound **2**. According to calculations, there exist two stable ground state (*endo* and *exo*) conformations of C_s symmetry, the *exo*-form being 0.7 kcal mol^{-1} energy preferable. The transition state structure **4** of η^2-type has been located for the 1,3-sigmatropic shift rearrangement, calculated activation barriers being estimated as 44.7 kcal mol^{-1}. Much lower is the energy barrier predicted by calculations for the 3,3-sigmatropic shift pathway. It was estimated to be equal to 10.8 kcal mol^{-1}; this value is sufficiently close to the experimental one obtained for the rearrangement of **1**. Geometric parameters of the ground state **2** and intermediate **3** and transition state structures **4** and **5** predicted by PM3 calculations are given in Fig. 2.



2, C_s (min)
ΔH_f 108.7 kcal mol^{-1}

3, C_s (min)
ΔH_f 117.3 kcal mol^{-1}

4, C_1 (TS)
ΔH_f 152.7 kcal mol^{-1}

5, C_1 (TS)
ΔH_f 118.7 kcal mol^{-1}

Fig. 2 Geometric characteristics and heats of formations of the ground state structures of **2** and intermediate **3**, and transition state structures **4** and **5** calculated by PM3 method. The bond lengths are in Å. Arrows show the direction of the components of the transition vectors.

Analogous PM3 calculations performed for 3-allylcyclopropene give 70 and 42 kcal mol^{-1} for the activation barriers of the 1,3- and 3,3-sigmatropic shift rearrangements, respectively. The latter value is in good agreement with the experimental data.[5] Thus, on the basis of the experimental data obtained for **1** and theoretical calculations for its model **2** we can conclude that the fast, intramolecular degenerate sigmatropic rearrangement of *S*-(1,2,3-triphenylcyclopropenyl)-*O*-ethyldithiocarbonate occurs *via* a hetero-(*S*,*S*')-Cope rearrangement.

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