Structural Manifestations of the Retro Diels–Alder Reaction
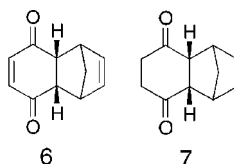
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ABSTRACT

6   7

**Examination of selected cyclohexene derivatives which are fixed into the boat conformation reveals structural deviations from "normal" C–C bond distances consistent with the early stages of the retro Diels–Alder reaction.**

According to the structure-correlation principle,[1] structural changes which occur along a reaction coordinate can sometimes manifest in the ground state of the reactant as measurable deviations of bond distances and angles from "normal values" along the reaction coordinate. This is especially true if the molecule in question is highly reactive.[2,3] For example, β-trimethylsilyl esters (**1**) undergo unimolecular solvolyses at rates as much as 10^{12} times faster than those of the corresponding silicon-free analogues.[4] We have found that crystal structures of a number of β-trimethylsilyl esters and ethers reveal significant lengthening of the C–O(ester) bond distance compared with silicon-free model compounds with concommitent lengthening (but to a lesser extent) of the C–Si(Me)$_3$ distance.[5–7]

The lengthening of the C–O(ester) bond represents the early stages of heterolysis of the labile C–O(ester) bond, while lengthening of the C–Si(Me)$_3$ represents the beginnings of hyperconjugation (σ-π) between the C–Si bond and the developing carbenium ion p orbital (Scheme 1).
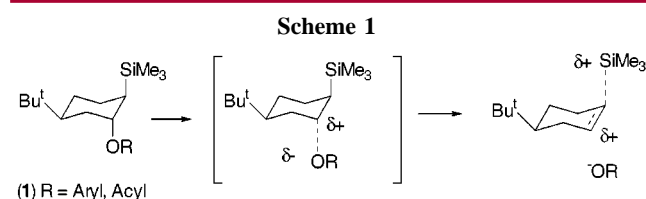
We were interested in investigating whether the retro Diels–Alder reaction would be manifest in the ground-state structure of crystalline cyclohexene derivatives. The retro Diels–Alder reaction is unimolecular, and because it involves the breaking of two C–C single bonds, there was the strong possibility that lengthening these C–C bonds distances would be observable in the ground state. The structural changes which occur along the rDA reaction coordinate (Scheme 2)

Scheme 2
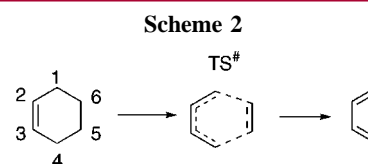
which might manifest in the ground-state structure are lengthening of the C1–C6, C4–C5, and C2–C3 bonds and

(1) Burgi, H. B.; Dunitz, J. D. A*cc. Chem. Res.* **1983**, *16*, 153.
(2) Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. *J. Am. Chem. Soc.* **1984**, *106*, 6200.
(3) Amos, R. D.; Handy, N. C.; Jones, P. G.; Kirby, A. J.; Parker, J. K.; Percy, J. M.; Su, M. D. *J. Chem. Soc., Perkin Trans. 2* **1992**, 549.
(4) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.
(5) White, J. M.; Robertson, G. B. *J. Org. Chem.* **1992**, *57*, 4638.
(6) Chan V. Y.; Clark, C. I.; Giordano, J.; Green, A. J.; Karalis, A.; White, J. M. *J. Org. Chem.* **1996**, *61*, 5227.
(7) Giordano, J.; Green, A. J.; White, J. M. *Aust. J. Chem.* **2000**, *53*, 285.

Scheme 1

(**1**) R = Aryl, Acyl

shortening of the C1−C2, C3−C4, and C5−C6 bonds compared to standard values for single C−C and double C=C bonds.

Because the Diels−Alder reaction must give rise to cyclohexene derivatives initially in the boat conformation[8] (Scheme 3), the retro Diels−Alder reaction should manifest

Scheme 3
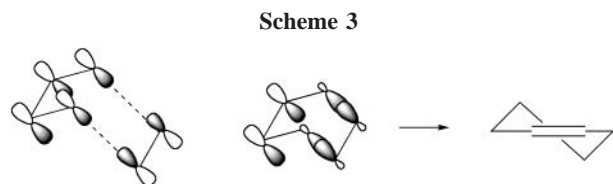
itself only in the structures of cyclohexene derivatives which are in the boat conformation rather than the preferred half-chair conformation. Thus, we narrowed our study to those cyclohexenes which were constrained to adopt the boat conformation.

Initially we carried out a systematic search of the Cambridge Crystallographic Database[9] for organic molecules containing the bicyclic cyclohexene fragments **2** and **3**, which are formally Diels−Alder cycloadducts between ethylene and various substituted cyclopentadienes and cyclohexadienes.

(2)   (3)   (4)   (5)
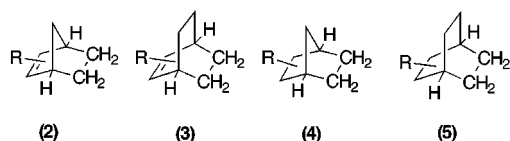
For comparison purposes, the saturated bicyclic fragments **4** and **5** which cannot undergo the retro Diels−Alder reaction were also extracted from the CSD. Only those structures with *R* factors < 5% and with esd's of the C−C distances between 0.001 and 0.005 Å were retained. The results of these searches are summarized in Table 1. The structural data in

Table 1. C−C Bond Distances for Bicyclic Cylcohexenes **2**−**5** from the Cambridge Crystallographic Database

| structure	hits	av. C1−C6; C4−C5 (Å)
2	17	1.555(1)
3	24	1.540(1)
4	74	1.535(1)
5	16	1.531(1)

Table 1 clearly show that the C−C bonds of fragments **2** and **3** which are broken in the retro Diels−Alder reaction are indeed significantly longer than the corresponding C−C

(8) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley and Sons: New York, 1989.

(9) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, T.; Kennard, O.; Motherwell, W. D. S.; Rogers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331.

bond distances for the saturated fragments **4** and **5**. There were, however, no other significant structural features evident in the structures of **2** and **3**.

To further examine the structural features apparent in these derivatives, we decided to determine the X-ray crystal structures of the benzoquinone cyclopentadiene adduct **6** and its saturated analogue **7** at low temperature.[10] Compound **6**

6   7
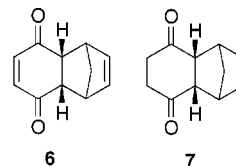
undergoes a particularly facile retro Diels−Alder reaction; indeed crystals of **6** become tacky upon standing for a day or two at room temperature and develop the distinct odor of cyclopentadiene. Hydrogenation of **6** under ca. 3 atm of hydrogen and Pd−C gave the saturated analogue **7** in low yield. The crystal structures of **6** and **7** were determined at 200 and 130 K, respectively. Selected structural parameters for **6** and **7** are summarized in Table 2 while a numbering scheme for both structures is presented in Figure 1.

Table 2. Selected Structural Parameters for **6** and **7**

	compound **6**		compound **7**	
	uncorr.	corr.	uncorr.	corr.
C(1)−C(10)	1.571(2)	1.581	1.537(2)	1.542
C(6)−C(7)	1.575(2)	1.576	1.553(2)	1.558
C(1)−C(6)	1.551(2)	1.556	1.563(2)	1.569
C(8)−C(9)	1.327(3)	1.330	1.553(2)	1.559
C(2)−C(1)−C(6)	117.03(12)		117.7 (1)	
C(2)−C(1)−C(10)	111.76(12)		115.3(1)	
C(6)−C(1)−C(10)	102.69(11)		102.9(1)	
C(1)−C(6)−C(7)	102.61(11)		102.7(1)	
C(9)−C(10)−C(1)	105.68(12)		109.4(1)	
C(8)−C(7)−C(6)	106.26(12		109.1(1)	
C(10)−C(1)−C(6)−C(7)	1.23(14)		−3.53(12)	
C(2)−C(1)−C(6)−C(5)	1.79(18)		−7.85(16)	

Corrections to the bond distances for rigid body thermal motion were made to both structures using the program THMA14.[11] In both molecules the conformations about the C(6)−C(7) and C(1)−C(10) bonds are essentially identical. However, the bond distances differ significantly. The C(6)−C(7) and C(1)−C(10) bonds in **6** are both clearly longer than
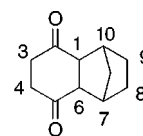
Figure 1. Numbering scheme for **6** and **7**.

the corresponding distances in **7**. The lengthening of these bonds in **6** is consistent with the expected structural effects arising from the interaction between the π orbital of the double bond C(8)−C(9) and the σ^* orbitals of both the C(1)−C(10) and C(6)−C(7) bonds and between the σ orbitals of both the C(1)−C(10) and C(6)−C(7) bonds with the π^* orbital of the C(8)−C(9) bond. These are the orbitals which are involved in the early stages of the retro Diels−Alder reaction.[11,12]

The observation of significant structural effects along the retro Diels−Alder reaction coordinate in the cyclohexene

derivatives studied in this paper opens up many interesting possibilities: (i) that the rate of the retro Diels−Alder reaction might be correlated with the C−C bond distances in the ground state and (ii) that other unimolecular pericyclic fragmentations (e.g., cheleotropic reactions) might also show significant effects in the ground state.

Supporting Information Available: Perspective diagrams and details of crystallographic analysis of compounds **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystal data for **6**. $C_{11}H_{10}O_2$, $M = 174.19$, orthorhombic, *Pbca*, $a = 11.7130(10)$, $b = 12.4643(10)$, $c = 11.9420(10)$ Å, $V = 1743.5(3)$ Å^3, $Z = 8$, $D_{calc} = 1.327$ g cm^{-3}, μ(Cu Kα) $= 0.736$ mm^{-1}, 2686 reflections measured ($2\theta_{max} = 75°$), 1777 unique ($R_{int} = 0.0346$), 1425 having $I > 2\sigma(I)$, full matrix least squares on F^2, $R_1 = 0.0406$, wR$_2 = 0.1022$, GOF = 1.023, maximum shift/esd 0.001, maximum and minimum difference peak and hole 0.239, −0.241 e Å^3, respectively. Crystal data for **7**. $C_{11}H_{12}O_2$, $M = 176.21$, orthorhombic, *Pbca*, $a = 10.863(3)$, $b = 10.452(2)$, $c = 15.973(5)$, $V = 1813.6(8)$ Å^3 $Z = 8$, $D_{calc} = 1.29$ g cm^{-3}, μ(Mo Kα) 0.088 mm^{-1}, 2854 reflections measured measured ($2\theta_{max} = 27.5°$), 2074 unique ($R_{int} = 0.022$), 1655 having $I > 2\sigma(I)$, full matrix least squares on F^2, $R_1 = 0.0396$, wR$_2 = 0.0938$, GOF = 1.033, maximum shift/esd 0.000, maximum and minimum difference peak and hole 0.26, −0.18 e Å^3, respectively.

(11) Trueblood, K. N.; Maverick, E. F. *THMA14c*, A TLS thermal motion analysis based on experimentally measured anisotropic displacement parameters available from the WEB site www.chem.gla.ac.uk/∼louis/thma14/.

(12) Enraf Nonius CAD-4Machs single-crystal diffractometer (Nickel filtered, $\lambda = 1.5418$ Å) for **6** and (graphite monochromator, $\lambda = 0.71069$) for **7**. At 130 K for **6** and 200 K for **7** (using an Oxford Cryostream cooling device) in the $\omega - 2\theta$ scan mode, $2\theta_{max} = 75°$. Solution by direct methods (SHELXS86[13]) and refinement using SHELXL97.[14] Thermal ellipsoid plots were drawn using the program ZORTEP.[15]

(13) SHELXS-86: Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M.

(14) SHELXL-97: Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Göttingen, Germany, 1997.

(15) ZORTEP: Zsolnai, L. *An Interactive ORTEP Program*; University of Heidelberg, Germany, 1994.