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# Structural Effects on Thermal Rearrangement of Fulleroids to Methanofullerenes. The Prominent Role of Cyclopropyl vs Aryl Substituent

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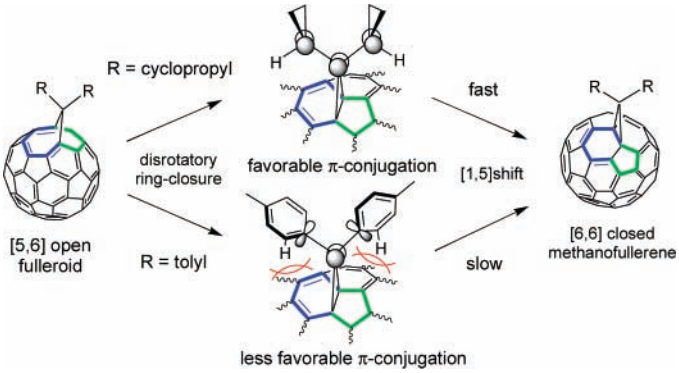
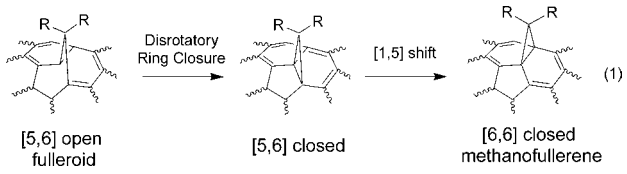
## ABSTRACT




**The kinetics of the thermal rearrangement of a series of novel cyclopropyl-substituted [5,6] open fulleroids to the [6,6] closed methanofullerenes have been investigated in comparison with the aryl-substituted homologues. The cyclopropyl group markedly accelerated the rates due to the stereoelectronically favorable $\pi$-conjugative effects in the radical-like [1,5] shift of the transient [5,6] closed isomers, overriding the geometrically constrained aryl group.**

The reaction of diazoalkanes with $C_{60}$ is well-known to give pyrazolines as the primary adducts, and the following nitrogen evolution provides the [5,6] open fulleroids and the [6,6] closed methanofullerenes, depending on the identities of the diazoalkanes.[1] Due to the mechanistic and structural interests, continuous studies have been made for the rearrangement of fulleroids to methanofullerenes under the thermal,[2] photochemical,[3] and electrochemical conditions[4] or under acid catalysis.[5] In particular, thermal rearrangement of fulleroids has attracted considerable attention and has been proposed to occur through a stepwise mechanism involving a disrotatory ring closure to the transient [5,6] closed valence isomer and the following [1,5] shift to the [6,6] closed structure (eq 1).[2]




(1)

This rearrangement is strongly dependent on the substituents at the methano-bridged carbon. Although the effects

(1) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301. (b) Schick, G.; Hirsch, A. *Tetrahedron* **1998**, *54*, 4283. (c) Kitamura, H.; Kokubo, K.; Oshima, T. *Org. Lett.* **2007**, *9*, 4045.

(2) (a) Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 391. (b) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492. (c) Li, Z.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 1149. (d) Hall, M. H.; Lu, H.; Shevlin, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 1349.

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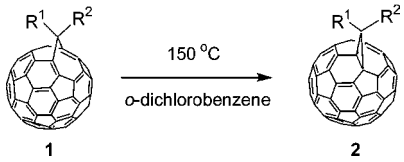
of the radical stabilizing groups such as double bonds and aryl substituents were systematically investigated to evaluate the mechanistic aspects of rearrangement,[2d] similar $\pi$-resonating cyclopropyl group which has the advantage of functioning as a mechanistic probe (as radical clock)[6] has not been hitherto employed.[7] In this study, we wish to report a kinetic study of the thermal rearrangement of a series of novel cyclopropyl-substituted fulleroids and explain the remarkable rate-acceleration in terms of the stereoelectronic effects of the cyclopropyl group on the radical-like [1,5] shift in comparison with the results of aryl-substituted fulleroids.

The cyclopropyl substituted fulleroids **1b**−**e** were synthesized and purified according to our previous report.[1c] Trifluoromethyl-substituted **1f** was synthesized from the reaction of $C_{60}$ with the diazoalkane generated in situ by heating the corresponding tosylhydrazone with NaH at 60 °C in *o*-dichlorobenzene (ODCB). Dicyclopropyl-substituted **1g** was synthesized by the reaction of $C_{60}$ with dicyclopropyldiazomethane generated in situ from the corresponding hydrazone with $Ag_2O$ at room temperature in ODCB. The fulleroids **1h**−**j** were prepared by the literature methods.[8]

Thermal rearrangement of the [5,6] open isomers **1b**−**j** was carried out in the dark at 80−150 °C in ODCB. The rearranged products for the cyclopropyl-substituted **1c**-**g** had the intact cyclopropyl groups as confirmed by $^1$H NMR for the diagnostic methine proton (tt, 1H) and were assigned as the [6,6] closed isomers on the basis of the $^{13}$C NMR and UV−vis spectra.[9] Kinetic studies of the rearrangement of the [5,6] open fulleroids **1b**−**j** were performed by monitoring the decrease of **1b**−**j** by $^1$H NMR or by HPLC on a Buckyprep column. Since these rearrangements provided only the [6,6] closed isomers as the rearranged products, the first-order rate constants ($k$/s$^{-1}$) were obtained by plotting logarithmic values of the relative signal intensities of the methyl protons for $^1$H NMR and of the relative absorption peak intensity (310 nm) of a constant aliquot (10 $\mu$L) of a reaction solution for HPLC.

The rate constants $k$ thus obtained for **1b**−**j** were collected along with the dimethyl-substituted **1a** as reference (Table 1).[2b] The noticeable points are as follows: (1) except very slow **1b**, the cyclopropyl-substituted **1c**−**g** rearranged 10 times faster than **1a**, attaining the largest 1550-fold acceleration for the dicyclopropyl-substituted **1g**; (2) the diastereomeric pair of **1c** and **1d** exhibited almost the same reactivity; (3) the replacement of the Me group of **1c** by $CF_3$ resulted in a fair acceleration (3.6-fold) as found for **1f**; (4) unexpectedly, however, the highly $\pi$-resonating aryl groups exerted considerably diminished effects as found for the relative rate ratios of 3−28 for the mono- and the diaryl-substituted **1h**−**j**; (5) generally, the less bulky substituents like H and Me markedly reduced the reactivity (**1a**, **1b**, and **1h**).

**Table 1.** Rate Constants of Thermal Rearrangement of Fulleroids to Methanofullerenes at 150 °C in *o*-Dichlorobenzene




| 1 | $R^1$ | $R^2$ | $10^5\,k$/s$^{-1}$ ($k_{rel}$) |
|---|---|---|---|
| **1a** | Me | Me | 0.231[a] (1.0) |
| **1b** | cyclopropyl | H | 0.133 (0.6) |
| **1c** | cyclopropyl | Me | 2.77 (12) |
| **1d** | Me | cyclopropyl | 3.12 (14) |
| **1e** | cyclopropyl | *p*-tolyl | 4.91 (21) |
| **1f** | cyclopropyl | $CF_3$ | 11.1 (48) |
| **1g** | cyclopropyl | cyclopropyl | 359[b] (1550) |
| **1h** | *p*-tolyl | Me | 0.770 (3.3) |
| **1i** | *p*-tolyl | *p*-tolyl | 6.40 (28) |
| **1j** | Ph | Ph | 4.25 (18) |

[a] Cited from ref 2b. [b] Extrapolated from the $k$ at other temperatures; $10^5$ $k$ = 0.717 s$^{-1}$ (at 80 °C), 2.03 (90 °C), 5.40 (100 °C), and 14.2 (110 °C).

How can these structural effects on the rates be understood? To gain some insight into this question, we evaluated the effects on each step of the first ring-closure and the second [1,5] shift processes. The PM3 semiempirical method indicated that the [5,6] closed isomers are $\Delta H$ = 14.1−15.9 kcal mol$^{-1}$ higher in energy than the corresponding [5,6] open isomers (Table 2).[10] The smallest $\Delta H$ is provided by the dicyclopropyl-substituted **1g**, while the largest by the dimethyl-substituted **1a**. It was also found that the fulleroids bearing two bulkier substituents such as cyclopropyl and aryl groups tend to advantageously lower the $\Delta H$ (**1e**, **1g**, **1i**, and

**Table 2.** PM3 Heats of Formation ($H$/kcal mol$^{-1}$) of [5,6] Isomers and Experimental $\Delta G^{\ddagger}$/kcal mol$^{-1}$ and Corrected $\Delta G^{\ddagger}_{corr}$/kcal mol$^{-1}$

| | $H$, [5,6] isomers | | $\Delta H$ | | |
|---|---|---|---|---|---|
| 1 | open | closed | (closed − open) | $\Delta G^{\ddagger}$ | $\Delta G^{\ddagger}_{corr}$[a] |
| **1a** | 801.58 | 817.46 | 15.88 | 36.70 | 20.81 |
| **1b** | 831.47 | *b* | | | |
| **1c** | 831.72 | 847.39 | 15.67 | 34.56 | 18.89 |
| **1d** | 831.69 | 847.05 | 15.37 | 34.46 | 19.10 |
| **1e** | 859.45 | 873.92 | 14.47 | 34.07 | 19.60 |
| **1f** | 693.71 | 708.19 | 14.49 | 33.37 | 18.89 |
| **1g** | 864.75 | 878.84 | 14.08 | 30.39 | 16.31 |
| **1h** | 828.61 | 843.83 | 15.22 | 35.66 | 20.44 |
| **1i** | 856.63 | 870.98 | 14.35 | 33.85 | 19.49 |
| **1j** | 875.52 | 889.89 | 14.37 | 34.20 | 19.83 |

[a] $\Delta G^{\ddagger}_{corr} = \Delta G^{\ddagger} - \Delta H$. [b] Instead, converged as the [5,6] open isomer.

(3) Janssen, R. A. J.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 544.
(4) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364.
(5) González, R.; Hummelen, J. C.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 2618.
(6) Beckwith, A. L. J.; Vowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710.
(7) Only the thermolysis of *p*-anisyl- and cyclopropyl-substituted fulleroid is reported; see ref 2d.
(8) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186. (b) Shi, S.; Khemani, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656.
(9) Unfortunately, a detailed structure of the rearranged product for **1b** was not confirmed due to the poor solubility.

**1j**) as compared with the fulleroids bearing at least one less bulky Me group (**1a**, **1c**, **1d** and **1h**).[11] Here, we assumed that the first ring-closure is more effectively controlled by the enthalpy change ($\Delta H$) than by the entropy change ($\Delta S$) because of the apparent structual similarity between the [5,6] open fulleroid and [5,6] closed isomer.

As to the latter [1,5] shift, we employed the corrected $\Delta G^{\ddagger}_{corr}$ by subtracting the above $\Delta H$ from the $\Delta G^{\ddagger}$ derived from the observed $k$ values (Table 2). When $\Delta G^{\ddagger}_{corr}$ was plotted against $\Delta H$, a fairly well correlated line with the slope of 0.82 (including **1a**) was obtained for the aryl-substituted fulleroids (filled circle) as shown in Figure 1. This means

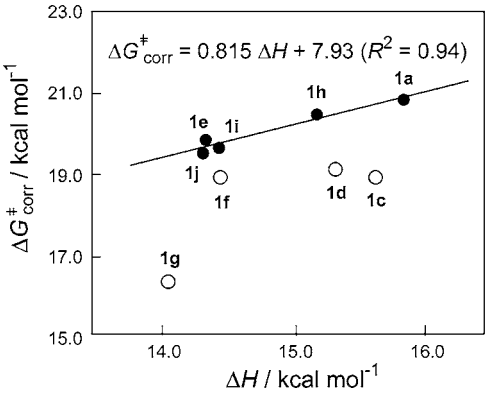



**Figure 1.** Plots of $\Delta G^{\ddagger}_{corr}$ vs $\Delta H$ for the rearrangement of fulleroids **1**.

that the aryl group exerts the promoting effects both on the ring-closure and the [1,5] shift, although the efficiency is slightly larger in the former process. On the other hand, the cyclopropyl-substituted fulleroids gave the scattered plots (open circle) well below the aryl line. The lower deviation is increased with the increasing number of cyclopropyl group (**1a** < **1d** ≤ **1c** < **1g**), demonstrating the additivity of cyclopropyl contribution (vide infra). This is also the case for the tolyl-substituted fulleroids (**1h** < **1i**), although the efficacy is considerably reduced. Accordingly, the substituent effect of cyclopropyl group on the [1,5] shift is found to be more effective than that of aryl group.

Mechanistically, the [1,5] shift is invoked to proceed via radical species by Shevlin et al. on the basis of the captodative effects in aryl-substituted fulleroids as well as the dramatic rate enhancement by the prealigned $\pi$-resonating substituents.[2d] It may be also possible that the present [1,5] shift is similar to the norcaradiene-type rearrangement, so-called "walk rearrangement", in which the proposed diradical species rapidly recombines with the stereoinversion.[12] Our results are also compatible with the radical process in view of the captodative acceleration in the case of $CF_3$- and cyclopropyl-substituted **1f**[13] as well as the poor dependency of rate on the solvent polarity (as $E_T$[14]) for **1g** at 90 °C; i.e., $10^5 k/s^{-1}$ = 1.35 (toluene, $E_T$ = 33.9), 2.03 (ODCB, 38.0), and 4.25 (1,1,2,2-tetrachloroethane, 39.4). Absence of the $\beta$-scission products of a cyclopropyl group of **1c**−**g** may be ascribed to the rapid recombination of the possible biradical intermediate like in norcaradiene walk rearrangement.[15] However, a question is raised as to why the far more intrinsically potent aryl groups did not contribute to the stabilization of radical intermediate as compared to the cyclopropyl groups.[16] This can be explained by considering the geometrically controlled stereoelectronic effects of the relevant substituents.

As depicted in Figure 2, the cyclopropyl group will promote the homolytic-cleavage of the methano-bridged bond

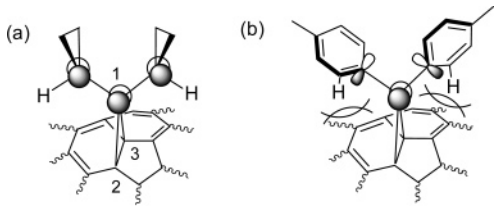



**Figure 2.** (a) Favorable $\pi$-conjugation of **1g** with the bisected cyclopropyl group; (b)less favorable $\pi$-conjugation of **1i** with the hindered aryl group.

(C1−C2 or C1−C3) by $\pi$-resonating stabilization of the generating spin center in the bisected conformation (a) typically represented for **1g**. By contrast, such an orbital interaction is severely inhibited in case of the aryl-substituted fulleroids due to the congested steric repulsion between the peri-hydrogen and the fullerene cage (b). This geometrical explanation is supported by the activation parameters for thermal rearrangement of dicyclopropyl-substituted **1g**. The plot of ln $k$ vs $1/T$ yielded the extrapolated $\Delta H^{\ddagger}$ (25.4 kcal mol$^{-1}$) and $\Delta S^{\ddagger}$ (−10.3 cal mol$^{-1}$ T$^{-1}$) at 170 °C. Compared with the rearrangement of bis($p$-anisyl)-substituted fulleroid (22.9 kcal mol$^{-1}$ and −24.2 cal mol$^{-1}$ T$^{-1}$, respectively),[2d] **1g** takes advantage of the far more favorable $\Delta S^{\ddagger}$, reflecting the facile prealignment of the two cyclopropyl groups for the bisected conformation (a).

However, at present, we cannot thoroughly rule out the possibility that the homolytic bond cleavage takes place in

(10) Minimum energy of the possible monocyclopropyl-substituted [5,6] closed isomer was not obtained as in the case of the unsubstituted [5,6] closed isomer; see ref 2a. This may be one of the reasons for the very slow or negligible rearrangement of these [5,6] open fulleroids.

(11) Such a steric bulk effect is well recognized in the valence equilibration between 7-substituted cycloheptatriene and norcaradiene: Takahashi, K.; Takase, K.; Toda, H. *Chem. Lett.* **1981**, 979.

(12) Kless, A.; Nendel, M.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4524.

(13) (a) Creary, X.; M.-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 2664. (b) Creary, X.; Sky, A. F.; M.-Mohammadi, M. E. *Tetrahedron Lett.* **1988**, *29*, 6839.

(14) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

(15) Based on the caluculated $\beta$-scission rate constant ($3.11 \times 10^9$ s$^{-1}$) at 150 °C for the comparable dimethyl cyclopropyl carbinyl radical (ref 6) and the limits of detectability (< 2 %) by $^1$H NMR mesurements, the lifetimes of biradical intermediate from **1c** and **1d** were estimated to be shorter than 6.4 ps.

(16) The cyclopropyl group is less effective in radical stabilization than the phenyl group: Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7102.

such a way of intermingling with a slightly charged species in view of the donor (cyclopropyl) and acceptor ($C_{60}$)-substituted methano-bridged bond.[17] In addition, it is also conceivable that the $\pi$-electron donation of the cyclopropyl substituent to the Walsh-type LUMO of the $C_{60}$-fused cyclopropane ring results in the lengthening of the C1−C2 and C1−C3 bonds, facilitating the bond cleavage.[18]

In summary, we investigated kinetics of the thermal rearrangement of a series of novel cyclopropyl-substituted fulleroids and found the remarkable rate-acceleration due to the favorable stereoelectronic effects and the pronounced $\pi$-electron-donating effects of the cyclopropyl group on the radical-like [1,5] shift as compared with the restricted aryl group. Further study on the stereoelectronic and the $\pi$-electron donating effects in the rearrangement of fulleroids to methanofullerenes is now in progress.

**Supporting Information Available:** Experimental details and characterization data for **1f**, **1g**, **2c** (= **2d)**, **2f**, **2g**, and cyclopropyl trifluoromethyl ketone tosylhydrazone. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Cyclopropyl group is more effective in cation stabilization than phenyl group: Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1977**, *99*, 1712.

(18) Gûnther, H. *Tetrahedron Lett.* **1970**, *11*, 5173.