# Observation of Both Thermal First-Order and Photochemical Zero-Order Kinetics in the Rearrangement of [6,5] Open Fulleroids to [6,6] Closed Fullerenes

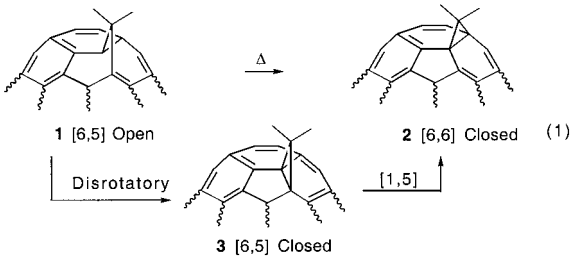
**Melvin H. Hall, Huajun Lu, and Philip B. Shevlin***

*Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849*

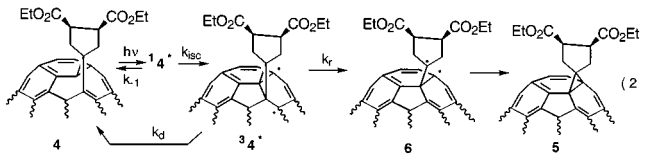
*Received August 15, 2000*

**Abstract:** A series of [6,5] open fulleroids with radical stabilizing groups on the methano bridge were synthesized and their rearrangements to the more stable [6,6] closed fullerenes studied. These [6,5] open fulleroids all rearrange both by a zero-order photochemical process and by a higher energy unimolecular pathway involving disrotatory closure to the [6,5] closed fullerene, which subsequently rearranges to the [6,6] closed fullerene via a biradical-like intermediate.

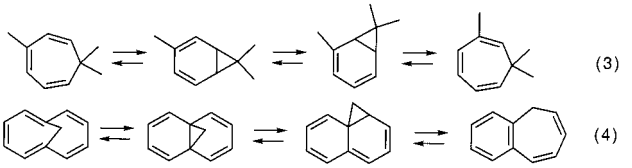
Although there are four possible ways to add a one carbon bridge across a carbon−carbon bond in $C_{60}$, only the [6,5] open methanofulleroids, **1**, and the [6,6] closed methanofullerenes, **2**, have been experimentally observed. Addition of carbene transfer reagents such as diazo compounds to $C_{60}$ often generates the [6,5] open fulleroid, **1**, as the kinetically controlled product, while the thermodynamically controlled product is the [6,6] closed methanofullerene, **2**.[1] When the [6,5] open isomers are isolated, they have been reported to rearrange to [6,6] closed methanofullerenes thermally,[2] photochemically,[3] electrochemically, or under acid catalysis.[5] Although the thermal rearrangement has been proposed to proceed by disrotatory ring closure to the [6,5] closed isomer, **3**, followed by a [1,5] shift (eq 1),[6]




several studies report zero-order kinetics which are inconsistent with this mechanism.[2,5b,7] We have postulated that a photochemical step in the thermal rearrangement is responsible for the observed zero-order kinetics.[7] Thus, the rearrangement of [6,5] open fulleroid, **4**, to [6,6] closed fullerene, **5**, occurs in 8 h in the presence of ambient light at 153 °C with zero-order kinetics. However, heating **4** at 153 °C for 24 h in the dark produced no rearrangement. The inhibitory effect of oxygen led us to propose the triplet mechanism in eq 2, in which the rate of rearrangement at a given temperature is dependent only on the intensity of the light. In this mechanism, the opening of triplet **4** to biradical **6** is the step requiring thermal activation.




It is interesting to consider the reason that the two-step thermal process in eq 1 is not operable in this system even at temperatures as high as 180 °C. The first step in eq 1 is simply an example of the cycloheptatriene−norcaradiene tautomerism which would be expected to be facile.[8] However, as Wudl et al. point out,[5] the second step may be thought of as a Berson−Wilcott rearrangement, and this is the probable source of the high barrier. The original example of this rearrangement[9] (eq 3) requires temperatures in excess of 300 °C, while a closer




analogy to the present process reported by Vogel[10] (eq 4) requires FVP conditions at 500 °C. Since the 1,5 shift in

(1) . For reviews, see: (a) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317−323. (b) Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc. Rev.* **1994**, 243−255. (c) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: Stuttgart, 1994. (d) Taylor, R. *Lecture Notes on Fullerene Chemistry*; Imperial College Press: London, 1999.

(2) 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*, 5492−5502.

(3) (a) Janssen, R. A. J.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 544−545. (b) Ceroni, P.; Conti, F.; Corvaja, C.; Maggini, M.; Paolucci, F.; Roffia, S.; Scorrano, G.; Toffoletti, A. *J. Phys. Chem. A* **2000**, *104*, 156−163.

(4) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364−8365.

(5) (a) González, R.; Hummelen, J. C.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 2618−2620. (b) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wlikins, C. L. *J. Org. Chem.* **1995**, *60*, 532−538.

(6) (a) Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc., Perkin Trans. 2* **1994**, 391−394. (b) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301−7302.

(7) Li, Z.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 1149−1150.

(8) Roth, W. R.; Klärner, F.-G.; Siepert, G.; Lennartz, H.-W. *Chem. Ber.* **1992**, *125*, 217−224.

(9) Berson, J. A.; Wilcott, M. R., III. *J. Am. Chem. Soc.* **1966**, *88*, 2494−2502.

(10) Vogel, E. *Aromaticity*; Special Publication No. 21; Chemical Society: London, 1967; pp 113−147.

10.1021/ja003042w CCC: $20.00 
Published on Web 01/26/2001

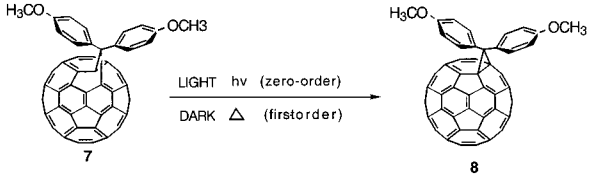
norcaradienes is thought to proceed via a transition state that has a great deal of biradical character,[11,12] it is expected that radical-stabilizing substitutents on the methano bridge of **1** may lower the barrier to thermal rearrangement and permit the observation of a first-order process in the absence of light.

In this study, we report an investigation of a series of [6,5] open methanofulleroids which undergo both a thermal first-order rearrangement and a photochemical rearrangement with zero-order kinetics.

## Results and Discussion

**The Effect of Aryl Substitutents.** To examine the effect of radical-stabilizing groups on the rate of the fulleroid−fullerene rearrangement, a series of [6,5] open fulleroids with one or two aryl groups on the methano bridge were synthesized. These compounds are conveniently prepared by the addition of the corresponding diazo compound and/or tosylhydrazone salt to $C_{60}$.[13] When an unsymmetrically substituted methano bridge is added to $C_{60}$, two isomers of the [6,5] open compound result. In these cases, the isomer with the larger group over the five-membered ring predominates,[14] and the isomers are easily identified by NMR spectroscopy.[15] To maximize the yield of the [6,5] isomer, it is necessary to rigorously protect the sample from light during the synthesis. Despite these precautions, a small amount [6,6] isomer was always present. Since we can conveniently follow the kinetics of the clean rearrangement of [6,5] to [6,6] isomer by NMR spectroscopy, it was not necessary to remove the small amount of [6,6] isomer present initially.

As shown in Table 1, a number of these aryl-substituted fulleroids rearrange by both photochemical and thermal mechanisms. A representative example is the rearrangement of the [6,5] open bis-(*p*-methoxyphenyl)fulleroid, **7**,[16] to the corresponding [6,6] closed isomer, **8**.




A degassed solution of **7** in *o*-dichlorobenzene-$d_4$, when exposed to ambient light, rearranged at 35 °C with a zero-order rate constant of $1.4 \times 10^{-6}$ M s$^{-1}$ in about 40 min (Figure 1). The rate of this reaction increases with temperature, and a four-point plot of ln($K$/$T$) vs 1/$T$ between 35 and 100 °C yields an apparent activation enthalpy of 9.6 ± 2.4 kcal/mol and an activation entropy of −41.1 ± 7 cal mol$^{-1}$ deg$^{-1}$.[17] The inhibitory effect of oxygen was also observed (at 35 °C, $K_o = 3.26 \times 10^{-7}$ M s$^{-1}$), supporting a triplet intermediate. At room temperature in the absence of light, a solution of **7** undergoes no detectable rearrangement to **8**. These facts are consistent with the kinetics of the light-catalyzed reactions of fulleroids reported earlier.[7]

When a degassed solution of **7** was rigorously protected from light and heated in a NMR tube at 130 °C, a clean first-order rearrangement to **8** ($K_1 = 1.63 \times 10^{-5}$ s$^{-1}$) was observed in 27 h (Figure 2). This first-order reaction rate also increases with temperature, and kinetic measurements from 120 to 170 °C give an activation energy of 22.9 ± 0.3 kcal/mol and an entropy of activation of −24.2 ± 0.8 cal mol$^{-1}$ deg$^{-1}$ for the rearrangement of **7** to **8**. As expected, the first-order thermal rearrangement proceeds by a higher energy pathway than the photochemical reaction.

**Table 1.** Rate Constants for the Thermal (170 °C) First-Order and Photochemical (35 °C) Zero-Order Rearrangement of [6,5] Open Fulleroids to [6,6] Closed Fullerenes

| [6,5] open fulleroid | thermal rate constant (s$^{-1}$) | photochemical rate constant (M s$^{-1}$) |
|---|---|---|
| **7** | $2.27 \times 10^{-4}$ | $1.38 \times 10^{-6}$ |
| **12a**, $R_1 = OCH_3$, $R_2 = Ph$ | $1.14 \times 10^{-4}$ | $4.08 \times 10^{-7}$ |
| **12b**, $R_1 = OCH_3$, $R_2$ = cyclopropyl | $8.47 \times 10^{-5}$ | *a* |
| **12c**, $R_1 = OCH_3$, $R_2 = CH_3$ | $2.29 \times 10^{-5}$ | $9.06 \times 10^{-7}$ |
| **12d**, $R_1 = H$, $R_2 = CH_3$ | $1.03 \times 10^{-5}$ | *a* |
| **12e**, $R_1 = NO_2$, $R_2 = CH_3$ | $1.56 \times 10^{-5}$ | $2.23 \times 10^{-7}$ |
| **12f**, $R_1 = OCH_3$, $R_2 = H$ | $1.37 \times 10^{-5}$ | $2.66 \times 10^{-6}$ |
| **14a** | $2.02 \times 10^{-6}$ | $3.49 \times 10^{-8}$ |
| **15a** | $1.74 \times 10^{-6}$ | *a* |

[a] Although a clean photochemical conversion of [6,5] to [6,6] isomer was observed, kinetics were not measured.

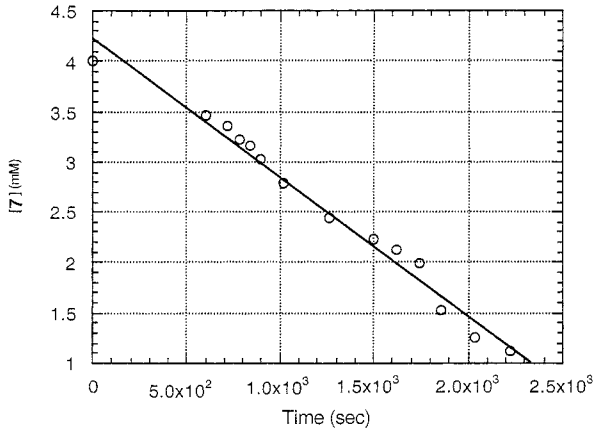



**Figure 1.** Kinetics of the light-promoted rearrangement of **7** at 35 °C under ambient light, $k_o = 1.38 \times 10^{-6}$ M/s.

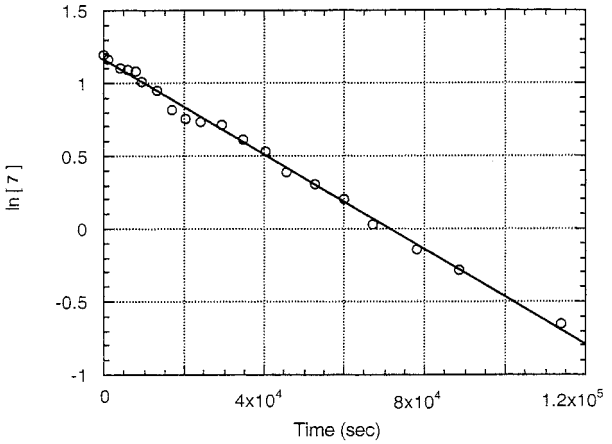
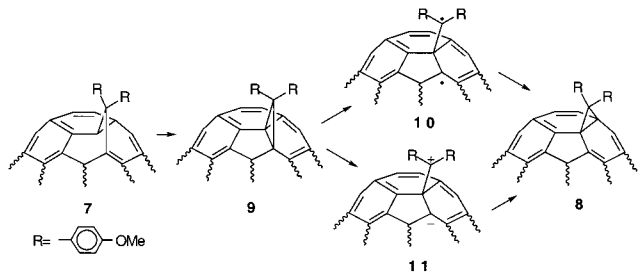



**Figure 2.** Kinetics of the thermal rearrangement of **7** at 130 °C in the absence of light, $k_1 = 1.63 \times 10^{-5}$ s$^{-1}$.

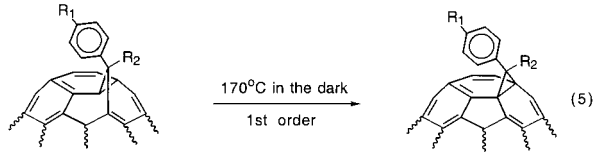
(11) Jarzecki, A. A.; Gajewski, J.; Davidson, E. R. *J. Am. Chem. Soc.* **1999**, *121*, 6928−6935.
(12) Kless, A.; Nendel, M.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4524−4525.
(13) Li, Z.; Bouhadir, K. H.; Shevlin, P. B. *Tetrahedron Lett.* **1996**, *36*, 4651−4654.
(14) Schick, G.; Hirsch, A. *Tetrahedron* **1998**, *54*, 4283−4296.
(15) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479−8480.
(16) (a) Shi, S.; Khemani, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656−10657. (b) Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, R. S.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388−6394.
(17) The enthalpic and entropic values derived from examining the rate of the photochemical rearrangement as a function of temperature are actually $\Delta H^{\ddagger}_r - \Delta H^{\ddagger}_d$ and $\Delta S^{\ddagger}_d - \Delta S^{\ddagger}_r$ in eq 2.[7]

The fact that the thermal first-order rearrangement of **7** to **8** occurs at a reasonable rate, while the corresponding **4** to **5** rearrangement cannot be detected, provides evidence for an initial disrotatory closure to the [6,5] closed isomer **9**, followed by cleavage to biradicaloid intermediate **10**. Although the




intermediacy of **10** is reasonable given the propensity of both fullerenes and aryl groups to stabilize radicals,[18] the ability of fullerenes to stabilize anions[19] is well documented, and zwitterion **11** must also be considered a possible intermediate.

To distinguish between these two possible intermediates, we have measured the rate of rearrangement of a series of aryl-substituted [6,5] open fulleroids in eq 5 and in Table 1. As we

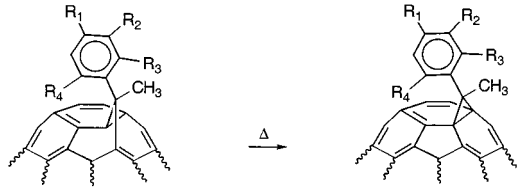



(5)

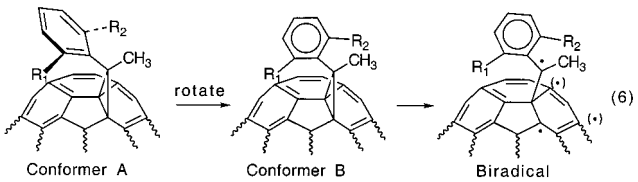
**12a**; $R_1$=$OCH_3$; $R_2$=Ph
**12b**; $R_1$=$OCH_3$; $R_2$=cyclopropyl
**12c**; $R_1$=$OCH_3$; $R_2$=$CH_3$
**12d**; $R_1$=H; $R_2$=$CH_3$
**12e**; $R_1$=$NO_2$; $R_2$=$CH_3$
**12f**; $R_1$=$OCH_3$; $R_2$=H

go from **7** to **12a**−**d** in this series, we expect a decreasing ability to stabilize either a biradical intermediate corresponding to **10** or a zwitterionic species similar to **11**, and the rate of rearrangement decreases as predicted. However, comparison of the rates of rearrangement of **12c**, **12d**, and **12e** provides evidence in favor of a biradical intermediate in that a *p*-nitrophenyl group on the methano bridge accelerates the reaction as compared to an unsubstituted phenyl group. While this behavior is not consistent with the development of a positive charge on the bridge carbon as in zwitterion **11**, the formation of a biradical intermediate similar to **10** would be accelerated by replacement of *p*-H by $NO_2$. A rate acceleration on the ring opening of a phenyl-substituted methylenecyclopropane is observed when a nitro group is substituted for a *p*-hydrogen.[20] The rather large variation in rates with changing substituents on the methano bridge appears to preclude a concerted [1,5] sigmatropic rearrangement via the [6,5] closed fullerene corresponding to **9**.

An examination of the rate of rearrangement of [6,5] open fulleroids **14a** and **15a** reveals an interesting stereoelectronic effect. Thus, **14a** with three methoxy substituents rearranges

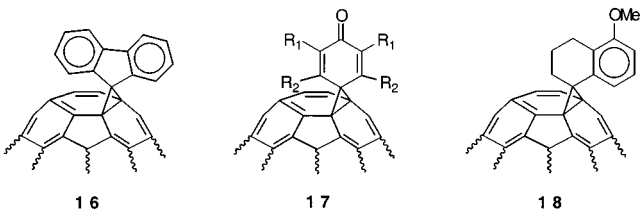



more slowly than **12c** with one *p*-methoxy substituent by a factor of over 100. Furthermore, fulleroid **15a** with two o-methoxy substituents rearranges even more slowly. We attribute these dramatic decreases in rate to difficulty in achieving a conformation of the aryl group in which stabilization of the forming radical can occur. In order for this stabilization to be operative, the aromatic p orbitals must become parallel to the bonds connecting the methano bridge to the fullerene. In this way, the unpaired electron on the erstwhile methano bridge can be stabilized by delocalization onto the aromatic ring. These stereoelectronic interactions, which are shown in eq 6, require a rotation of the aromatic ring from conformation A to conformation B, in which the ortho substituents are pointing into the fullerene cage. When these substituents are larger than H, steric interactions make this rotation difficult.




(6)

The negative entropy of activation observed for these rearrangements is a reflection of the fact that the [6,5] open fulleroid must assume the specific conformation B for ring opening to occur. We thus expect fulleroids in which the $\pi$ system is prealigned in a conformation to stabilize a biradical intermediate to undergo the [6,5] to [6,6] rearrangement quite rapidly. In accordance with this expectation, we note that attempts to prepare such compounds generally result in the isolation of only the [6,6] closed fullerene. Examples include the preparation of methanofullerenes **16**−**18**, whose [6,5] open analogues have not been reported.[20−23] The failure to isolate [6,5] open fulleroids in these systems is presumably due to the fact that they rearrange rapidly to the [6,6] isomers.




**Effect of a Spiro Conjugated Double Bond on the Rate of Rearrangement.** To explore the stereoelectronic effect of a double bond which is prealigned to stabilize the biradical, we

(18) (a) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *J. Am. Chem. Soc.* **1991**, *113*, 6274−6275. (b) Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* **1991**, *254*, 1183−1185.

(19) (a) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050−1051. (b) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978−3980. (c) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075−1120.

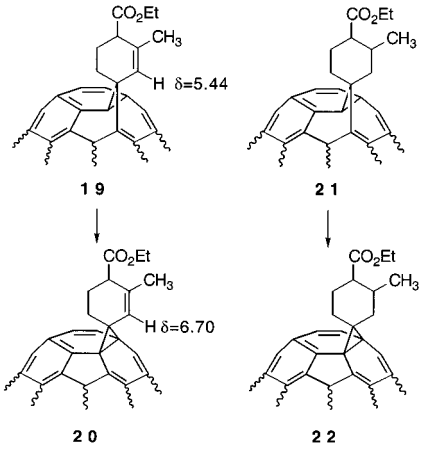
(20) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254−3263.

(21) Knight, B.; Martín, N.; Ohno, T.; Ortí, E.; Rovira, C.; Veciana, J.; Vidal-Gancedo, J.; Viruela, P.; Viruela, R.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 9871−9882.

(22) Ohno, T.; Martín, N.; Knight, B.; Wudl, F.; Suzuki, T.; Yu, H. *J. Org. Chem.* **1996**, *61*, 1306−1309.

(23) Li, Z. Ph.D. Thesis, Auburn University, August, 1997.

have examined the rates of rearrangements of fulleroids **19** and **21**. Fulleroid **19** contains a double bond whose p orbitals are aligned with the exocyclic cyclopropane C−C bonds and is thus expected to rapidly undergo first-order rearrangement. When we used our standard procedure for the preparation of **19**, by refluxing $C_{60}$ with the tosylhydrazone salt in toluene at 110 °C in the dark, only one product was obtained. The NMR spectra of this product and the fact that it did not rearrange upon thermolysis or photolysis indicated that it was the [6,6] closed fullerene **20**. Monitoring the progress of the reaction by NMR




showed only **20**. However, when the synthesis was carried out at 70 °C, a 1.1:1 mixture of **19** and **20** was obtained. These results indicate that the difficulty in preparing **19** results from the fact that it simply rearranges to **20** at the normal temperatures for fulleroid preparation.

To assess the reactivity of **19**, we have measured the rate of the conversion of a 1.1:1 mixture of **19** and **20** to **20** in the absence of light by integrating the respective NMR peaks at $d = 5.44$ and 6.70 ppm. As expected, this is a clean first-order rearrangement at six different temperatures from 57 to 100 °C. An examination of the rate of rearrangement as a function of temperature gives an activation enthalpy of 21.2 ± 0.5 kcal/mol and an activation entropy of −16.0 ± 1.5 cal·mol $K^{-1}$.

The preparation of the saturated fulleroid **21** from the corresponding tosylhydrazone and $C_{60}$ is straightforward. Refluxing the mixture for 1 h at 110 °C gives a greater than 10:1 mixture of **21** and **22**. As expected, the rearrangement of **21** to **22** is much slower than that of **19** to **20** and requires far higher temperatures. Although the elevated temperatures and long reaction times required for the rearrangement precluded determination of the activation parameters, a clean first-order rearrangement of **21** to **22** was observed at 177 °C over 156 h ($k_1 = 2.4 \times 10^{-6}$ $s^{-1}$). When the activation parameters for the rearrangement of **19** to **20** are used to estimate the rate of this rearrangement at 177 °C, the reaction is found to proceed $6.4 \times 10^4$ times faster than the **21** to **22** rearrangement. This large rate acceleration may again be taken as evidence for an intermediate having a great deal of biradical character which is stabilized by the adjacent double bond and the fullerene cage.

Both **19** and **21** were observed to undergo clean zero-order rearrangement in the presence of light. However, the two [6,5] fullerenes rearrange photochemically at vastly different rates which depend on the intensity of the light, and the rearrangement of **19** is conveniently followed at lower light intensity than that of **21**. For this reason, a comparison of zero-order rate constants is difficult. When solutions of **19** and **21** were exposed to the same light intensity at room temperature, a 1:1 mixture of **19** and **20** was converted to **20** in approximately 35 s, while the conversion of **21** to **22** took 12 h. The fact that **19** undergoes photochemical rearrangement considerably faster than **21** again reflects the stabilizing effect of the double bond on the corresponding biradical which is now generated by cleavage of the triplet in a process analogous to that shown in eq 1.

**Table 2.** PM3 Heats of Formation (kcal/mol) of Fulleroids and Methanofullerenes

| starting fulleroid | [6,5] isomers open | [6,5] isomers closed | [6,6] isomer, closed | $\Delta H^0$ for the rearrangement of [6,5] open to [6,6] closed |
|---|---|---|---|---|
| **7** | 799.38 | 813.83 | 791.98 | −7.48 |
| **12a** | 837.44 | 851.76 | 830.08 | −7.36 |
| **12b** | 830.82 | 845.25 | 823.57 | −7.25 |
| **12c** | 799.98 | 815.16 | 793.72 | −6.24 |
| **12d** | 838.06 | 853.30 | 831.86 | −6.20 |
| **12e** | 830.01 | 845.46 | 824.03 | −5.98 |
| **12f** | 801.30 | 819.76 | 798.77 | −2.53 |
| **14a** | 734.55 | 748.59 | 727.53 | −7.01 |
| **15a** | 771.81 | 784.52 | 763.34 | −8.48 |
| **19** | 730.84 | 746.41 | 724.28 | −6.56 |
| **21** | 710.81 | 726.40 | 704.62 | −6.18 |

That unsaturated **19** rearranges more rapidly than saturated **21** both thermally and photochemically is certainly expected in view of the postulated biradical-like intermediates. More striking is the fact that **19** rearranges faster than **7** or any of the other phenyl-substituted fulleroids studied. A comparison of the activation parameters for the thermal rearrangement of **19** and **7** reveals that both the enthalpy ($\Delta H^{\ddagger}_{7} - \Delta H^{\ddagger}_{19} = 2.6$ kcal/mol) and entropy ($\Delta S^{\ddagger}_{7} - \Delta S^{\ddagger}_{19} = -8.8$ cal·mol $K^{-1}$) of activation contribute to this rate difference, which is a factor of $10^5$ at 110 °C. These data are nicely accounted for by our postulated stereoelectronic effect on rearrangement rates. Since the double bond in **19** is aligned to stabilize the transition state as it is formed, this compound enjoys an enthalpic and entropic advantage over **7**, which must undergo a rotation to a higher energy conformer for transition state stabilization to occur. If stabilization of the biradicaloid transition state were the only factor, one would expect the two *p*-methoxyphenyl groups in **7** to exert far more stabilization than the double bond in **19**.

All of the [6,5] open fulleroids reported herein rearrange both by a zero order photochemical process and by a higher energy unimolecular pathway involving disrotatory closure to the [6,5] closed fullerene which subsequently rearranges to the [6,6] closed fullerene via a biradical like intermediate. This thermal reaction requires first-order kinetics.

Although the size of the molecules involved precludes an accurate quantum mechanical evaluation of the reaction coordinates, the PM3[24] semiempirical method appears to provide a reasonable estimate of the energetics of this rearrangement. As shown in Table 2, the starting fulleroids are all calculated to be 12.7−18.5 kcal/mol lower in energy than their corresponding [6,5] closed isomers, and all rearrangements are calculated to be exothermic by 2.5−8.5 kcal/mol.

The PM3 method also provides a reasonable estimate of the energy surface connecting the isomeric fullerenes. Thus, an activation energy of 35 kcal/mol is calculated for the **7** → **8** rearrangement, in reasonable agreement with our experimental measurement of 23 kcal/mol. In this rearrangement, the [6,5] closed isomer is calculated to be of minimal stability, with **9** lying in an energy minimum only 0.8 kcal deep.

## Conclusions

These experiments demonstrate that the rearrangement of [6,5] open fulleroids to [6,6] closed fullerenes can be induced

(24) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220.

to follow a unimolecular pathway at reasonable temperatures if radical stabilizing groups are attached to the one-carbon bridge. It appears that these rearrangements involve a biradical intermediate which achieves a major part of its radical stabilization from the fullerene ring.

## Experimental Section

**Instrumentation and Materials.** $^1$H and $^{13}$C NMR spectra were recorded on Bruker AC 250 and AM 400 spectrometers using *o*-dichlorobenzene-$d_4$ (ODCB-$d_4$) and 1:2 $CDCl_3$:$CS_2$ as solvents. FAB mass spectra were measured on a VG 7070 spectrometer with *m*-nitrobenzyl alcohol (NBA) as the matrix. Commercial reagents were used as received from Aldrich. Solvents were distilled before use. Fullerene-60 (99.5%) was purchased from MER Corp. The diazo compounds and the tosylhydrazones were prepared by standard procedures. Flash column chromatography was preformed using 60−200 mesh Fisher silica gel.

**General Procedure for the Reaction of C60 with Diazo Compounds.** In all reactions, flasks and columns were protected with aluminum foil to exclude as much light as possible. To 72 mL of a 1.4 mM solution of $C_{60}$ in toluene contained in a 250-mL flask at 0 °C was added 1 equiv (0.1 mmol) of the diazo compound. The solution was stirred for 1 h under $N_2$. The reaction was monitored by TLC in toluene for the product spot appearing just below that of the $C_{60}$. The solvent was removed from the reaction mixture under reduced pressure at room temperature, and the reaction mixture was loaded onto a silica gel column and eluted with toluene or hexane/toluene (4:1). Compounds **7** and **12a** were synthesized by this procedure.

**Compound 7** [41.0 mg (57%) yield]: $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ = 7.98 (d, $J$ = 8.7 Hz, 2H), 7.30 (d, $J$ = 8.8 Hz, 2H), 7.02 (d, $J$ = 8.7 Hz, 2H), 6.75 (d, $J$ = 8.8 Hz, 2H), 3.82 (s, 3H), 3.73 (s, 3H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 159.44, 159.29, 149.32, 148.29, 147.18, 146.06, 145.64, 145.54, 145.19, 144.87, 144.71, 144.62, 144.53, 144.47, 144.15 144.00, 143.91, 143.56, 143.03, 142.94, 142.77, 142.23, 141.55, 141.09, 139.83, 138.95, 138.38, 137.82, 136.69, 131.96, 130.86, 127.89, 114.66, 114.29, 113.80, 66.02, 55.26, 55.08; FABMS (NBA) $m/z$ 947 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 12a** [0.045 g, 49% yield], $^1$H NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz), major isomer (80%), $\delta$ = 8.08 (d, $J$ = 7.3 Hz, 2H), 8.03 (d, $J$ = 8.8 Hz, 2H), 7.51 (m, 2H), 7.31 (m, 1H), 6.76 (d, $J$ = 8.8 Hz, 2H), 3.74 (s, 3H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 149.49, 149.33, 147.77, 147.58, 145.55, 145.34, 144.89, 144.48, 144.11, 143.99, 143.78, 143.28, 143.20, 143.11, 142.93, 142.85, 142.41, 142.28, 142.23, 142.06, 141.49, 141.03, 140.70, 140.61, 140.60, 140.28, 139.94, 139.11, 138.55, 138.23, 137.73, 135.57, 134.69, 132.18, 131.12, 130.90, 130.00, 129.22, 128.91, 128.49, 128.16, 127.35, 114.69, 114.38, 113.88, 68.16, 55.34, 55.15; FABMS (NBA) $m/z$ 917 ((M + 1)$^+$), 720 ($C_{60}^+$).

**General Procedure for the Reaction of C60 with Tosylhydrazone Lithium Salts.** To a solution of tosylhydrazone (0.1 mmol) in 3 mL of hexane at 0 °C under $N_2$ in a 250-mL flask was added MeLi (1.4 M, 0.107 mL, 0.15 mmol) using a syringe. A previously prepared $C_{60}$ solution in toluene (72 mL, 1.40 mM, 0.1 mmol) was added to the flask. The flask was heated at reflux for 20−30 min and monitored by TLC in toluene or hexane:toluene (4:1). The solvent was reduced in vacuo to 20 mL and was then loaded on a silica gel column and eluted with toluene or hexane:toluene. The yields were generally between 37 and 57%. The product was always recovered as a mixture of two or three isomers. The [6,5] open compound with the bulkier group over the five-membered ring was always the major isomer,[14] comprising between 70 and 90% of the total. Compounds **7**, **12a**−**12f**, **14**, **15**, **19**, and **21** were synthesized by this procedure. The NMR spectral data for compounds **12c** and **12f** agree with those in the literature.[15]

**Compound 12b** [0.039 g, 45% yield] (mixture of isomers): $^1$H NMR ($CDCl_3$, 400 MHz), major isomer (75%), $\delta$ = 7.76 (d, $J$ = 8.6 Hz, 2H), 7.03 (d, $J$ = 8.6 Hz, 2H), 3.88 (s, 3H), 0.35 (m, 1H), 0.31 (m, 2H), 0.03 (m, 2H), minor isomer (15%), $\delta$ = 7.01 (d, $J$ = 8.7 Hz, 2H), 6.76 (d, $J$ = 8.7 Hz, 2H), 3.69 (s, 3H), 2.65 (m, 1H), 2.51 (m, 2H), 2.3 (m, 2H); $^{13}$C NMR (2:1 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 159.92, 145.44, 144.76, 144.65, 144.24, 144.10, 144.00, 143.81, 143.23, 142.85, 142.41, 142.13, 141.03, 139.48, 139.09, 138.70, 137.92, 134.81, 133.28, 130.27, 113.86, 113.67, 112.95, 67.98, 59.34, 55.52, 55.34, 52.66, 30.01, 24.60, 14.14, 4.01, 3.65, 2.56; FABMS (NBA) $m/z$ 881 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 12c** [0.036 g, 42% yield].

**Compound 12d** [0.041 g, 50% yield]: $^1$H NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz), [6,5] open (95%), $\delta$ = 8.00 ($\delta$, $J$ = 7.4 Hz, 2H), 7.58 (m, 2H), 7.44 (m, 1H), 1.37 (s, 3H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 149.69, 148.91, 148.41, 147.91, 147.50, 146.88, 146.67, 146.32, 145.12, 144.00, 143.77, 143.64, 143.09, 142.26, 141.98, 141.39, 139.66, 138.75, 138.25, 138.01, 136.98, 136.80, 135.13, 129.41, 129.02, 128.67, 128.20, 127.52, 125.41, 56.92, 25.64; FABMS (NBA) $m/z$ 825 ((M + 1)$^+$), 720 ($C_{60}^+$). This compound contained a small amount of $C_{60}$.

**Compound 12e** [0.032 g, 37% yield]: $^1$H NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz), [6,5] open (95%), $\delta$ = 8.21 (d, $J$ = 8.7 Hz, 2H), 8.00 (d, $J$ = 8.7 Hz, 2H) 1.23 (s, 3H, $CH_3$); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 156.84, 147.55, 145.72, 145.45, 145.11, 144.49, 144.34, 144.19, 143.89, 143.48, 143.17, 142.86, 142.63, 142.40, 141.60, 139.73, 139.11, 138.31, 137.35, 136.05, 133.43, 132.18, 131.65, 130.23, 129.68, 128.58, 128.03, 124.58, 124.28, 123.82, 56.09, 25.31; FABMS (NBA) $m/z$ 870 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 12f** [0.047 g, 55% yield].

**Compound 14a** [0.031 g, 35% yield]: $^1$H NMR (ODCB-$d_4$, 400 MHz) (95%) $\delta$ = 7.67 (d, $J$ = 8.7 Hz, 1H), 6.71 (d, $J$ = 8.7 Hz, 1H), 4.02 (s, 3H), 3.87 (s, 3H), 3.75 (s, 3H), 1.35 (s, 3H); $^{13}$C NMR (ODCB-$d_4$, 400 MHz) $\delta$ = 153.82, 147.47, 145.35, 144.98, 144.61, 144.41, 144.02, 143.90, 143.74, 143.49, 143.36, 143.08, 142.98, 142.67, 142.36, 142.29, 142.18, 141.85, 141.28, 140.60, 140.42, 140.31, 139.93, 139.45, 139.10, 138.93, 138.76, 138.10, 137.97, 136.61, 134.95, 129.26, 128.45, 124.78, 107.01, 61.30, 60.95, 56.27, 52.925, 23.90; FABMS (NBA) $m/z$ 915 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 15a** [0.035 g, 40% yield]: $^1$H NMR (ODCB-$d_4$, 400 MHz), major isomer (>95%), $\delta$ = 7.24 (t, 1H), 6.64 (d, $J$ = 8.3 Hz, 2H), 3.78 (s, 6H), 1.29 (s, 3H); $^{13}$C NMR (ODCB-$d_4$, 400 MHz) $\delta$ = 158.71, 147.64, 145.44, 144.81, 144.38, 143.94, 143.65, 143.19, 143.11, 143.04, 142.91, 142.75, 142.13, 141.94, 141.51, 141.26, 140.53, 140.38, 140.23, 139.35, 139.16, 138.94, 138.35, 137.62, 137.48, 137.06, 135.14, 105.69, 104.99, 56.26, 51.35, 20.60; FABMS (NBA) $m/z$ 885 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 19** was prepared by heating the reaction mixture at 70 °C for 5 h [0.022 g, 25% yield]: $^1$H NMR (ODCB-$d_4$, 250 MHz) $\delta$ = 5.44 (s, 1H), 4.19 (q, 2H), 3.92 (m, 1H), 3.79 (m, 1H), 3.15 (m, 1H), 2.56−2.49 (m, 2H), 1.79 (s, 3H), 1.23 (t, 3H).

**Compound 21** was isolated as a mixture of stereoisomers [0.018 g, 20% yield]: $^1$H NMR (ODCB-$d_4$, 250 MHz) $\delta$ = 4.34−4.03 (m, area = 9.6), 3.97 (m, area = 1.8), 3.76 (m, area = 1.7), 3.50 (m, area = 1.4), 2.16 (m, 1H), 2.65 (m, area = 3.5), 2.56 (m, area = 2.8), 2.35 (m, area = 3.7), 1.75 (m, area = 9.7), 1.27 (d and t, area = 16.7), 0.96 (d, area = 4.4). The doublet at 0.96 ppm is assumed to result from the isomer with the ring methyl over the six-membered ring,[15] indicating that this compound makes up 35% of the [6,5] open isomer mixture. Kinetics were followed by monitoring the disappearance of the multiplets at 3.76 and 3.50 ppm.

**Conversion of [6,5] Open Isomers to [6,6] Closed Isomers.** All the [6,5] open isomers were quantitatively converted to the [6,6] closed isomers by heating in the presence of ambient light and by heating in the dark. The NMR spectral data for compounds **13c** and **13f** agree with those in the literature.[15]

**Compound 8:** $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ = 8.00 (d, $J$ = 8.7 Hz, 4H), 7.01 (d, $J$ = 8.7 Hz, 4H), 3.85 (s, 6H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 159.61, 148.88, 145.68, 145.3, 145.24, 144.82, 144.75, 144.42, 143.96, 143.09, 142.43, 142.26, 141.07, 138.47, 134.40, 114.55, 114.49, 114.43, 80.08, 57.69, 55.18; FABMS (NBA) $m/z$ 947 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 13a:** $^1$H NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 8.10 (d, $J$ = 7.5 Hz, 2H), 8.00 (d, $J$ = 8.7 Hz, 2H), 7.57 (m, 2H), 7.43 (m, 1H), 7.02 (d, $J$ = 8.7 Hz, 2H), 4.24 (s, 3H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 159.23, 148.29, 145.24, 145.20, 144.90, 144.83, 144.41, 144.33, 144.05, 143.98, 143.54, 142.70, 142.67, 142.65, 141.97, 141.85, 140.67, 139.72, 138.13, 138.01, 114.06, 79.87, 58.23, 54.74; FABMS (NBA) $m/z$ 917 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 13b:** $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ = 7.72 (d, $J$ = 8.6 Hz, 2H), 7.06 (d, $J$ = 8.6 Hz, 2H), 3.85 (s, 3H), 1.25 (m, 1H), 0.87

(m, 2H), 0.61 (m, 2H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 159.40, 149.28, 148.44, 145.92, 145.03, 144.96, 144.89, 144.75, 144.47, 144.39, 144.21, 144.15, 143.75, 143.60, 143.50, 142.80, 142.72, 142.12, 141.93, 140.70, 140.57, 138.03, 137.39, 134.55, 133.32, 125.10, 113.54, 113.38, 81.49, 54.76, 30.02, 13.93, 3.45; FABMS (NBA) *m*/*z* 881 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 13d:** $^1$H NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 8.00 (d, *J* = 7.4 Hz, 2H), 7.60 (m, 2H), 7.40 (m, 1H), 2.56 (s, 3H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 149.14, 148.17, 146.11, 145.36, 145.26, 145.18, 145.10, 144.93, 144.76, 144.52, 144.46, 144.06, 143.93, 143.79, 143.09, 142.49, 142.25, 140.90, 140.20, 139.56, 138.88, 138.20, 137.60, 135.70, 135.29, 81.25, 27.92, 22.8; FABMS (NBA) *m*/*z* 825 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 13e:** $^1$H NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 8.20 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 2H), 2.44 (s, 3H); $^{13}$C NMR (1:2 $CDCl_3$:$CS_2$, 400 MHz) $\delta$ = 147.61, 147.34, 146.89, 146.53, 145.37, 144.87, 144.70, 144.39, 144.18, 144.13, 143.85, 143.40, 143.33, 142.73, 142.67, 141.96, 141.81, 141.69, 140.75, 140.64, 137.92, 137.11, 123.63, 79.92, 46.41, 21.78; FABMS (NBA) *m*/*z* 870 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 14b:** $^1$H NMR (ODCB-$d_4$, 400 MHz) $\delta$ = 7.50 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 4.25 (s, 3H), 3.89 (s, 3H), 3.74 (s, 3H), 2.47 (s, 3H); $^{13}$C NMR (ODCB-$d_4$, 400 MHz) $\delta$ = 154.29, 153.72, 152.63, 150.10, 149.71, 148.56, 148.41, 146.01, 145.42, 144.90, 144.81, 144.75, 144.43, 144.17, 144.08, 143.61, 143.57, 143.43, 142.80, 142.71, 142.21, 142.50, 141.91, 141.75, 141.13, 140.82, 140.52, 137.89, 136.61, 125.04, 124.23, 106.98, 106.25, 80.01, 61.52, 60.33, 55.45, 46.00, 20.66; FABMS (NBA) *m*/*z* 915 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 15b:** $^1$H NMR (ODCB-$d_4$, 400 MHz) $\delta$ = 7.23 (t, 1H), 6.62 (d, J = 8.2 Hz, 2H), 3.83 (s, 6H), 2.39 (s, 3H); $^{13}$C NMR (ODCB-$d_4$, 400 MHz) $\delta$ = 159.39, 152.25, 149.41, 147.42, 145.72, 145.44, 145.41, 145.29, 145.22, 144.95, 144.87, 144.79, 144.62, 144.22, 144.05, 144.01, 143.30, 143.14, 143.04, 142.89, 142.30, 142.19, 141.33, 141.10, 138.38, 136.09, 135.24, 114.88, 105.42, 105.11, 81.99, 56.88, 38.99, 18.42; FABMS (NBA) *m*/*z* 885 ((M + 1)$^+$), 720 ($C_{60}^+$).

**Compound 20:** $^1$H NMR (ODCB-$d_4$, 250 MHz) $\delta$ = 6.73 (s, 1H), 4.28 (q, 2H), 3.42 (m, 1H), 3.1ñ2.3 (m, 4H), 2.11 (s, 3H), 1.31 (t, 3H).

**Compound 22** was isolated as a mixture of cis and trans isomers: $^1$H NMR (ODCB-$d_4$, 250 MHz) $\delta$ = 4.26 (m, 2H), 2.97 (m, 3H), 2.62 (m, 3H), 2.31 (m, 1H), 2.16 (m, 1H), 1.32 (d and t, 6H).

**Kinetic Studies of the Rearrangement of the [6,5] Open to the [6,6] Closed Isomer: General Procedure.** A 5-mm NMR tube, wrapped with aluminum foil, was charged with the [6,5] open isomer and 0.5 mL of ODCB-$d_4$ (ca. 3.4 mM) at room temperature. At this temperature in the dark, the rearrangement does not proceed. The NMR tube was attached to a vacuum line, degassed with three freeze−thaw cycles, and sealed. In the light-promoted reaction, the NMR tube was removed from the aluminum foil and exposed to ambient light for a measured amount of time at a given temperature. The kinetics were followed by NMR spectroscopy. The first-order kinetics were measured with the NMR tube completely wrapped with the aluminum foil while heating. At intervals, the tube was cooled to room temperature and the NMR spectrum measured.

**Acknowledgment.** We thank the National Science Foundation (CHE-9901068) for support of this research.

**Supporting Information Available:** Kinetic data for the rearrangements of **7**, **12a**−**f**, **14**, **15**, **19**, and **21** (PDF). This material is available free of charge via the Internet at http://www.acs.org.

JA003042W