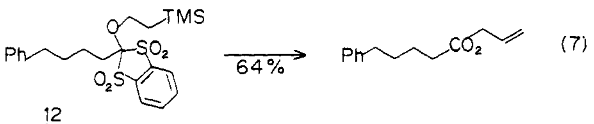
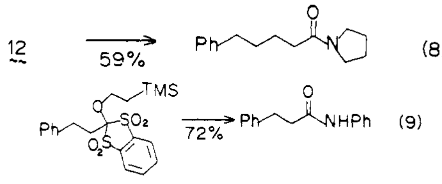
can be employed (cf. eq 7), but trichloroethanol failed.



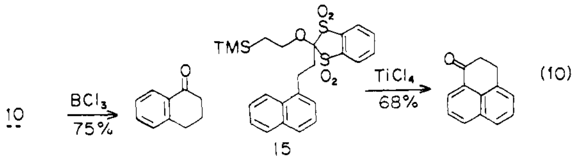
12

Direct amide formation proceeds equally well. For example, reacting **12** or **13** with boron trichloride (2.4 equiv) followed by excess amine led to the amides as in eq 8 and 9.



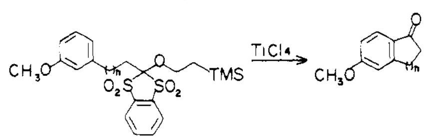
13

The question of intramolecular trapping by carbon nucleophiles was of special interest. To explore this point, **10** was exposed to boron trichloride (2.4 equiv) at −78 °C (1 h) in methylene chloride and then allowed to warm to 0 °C over 15 min and kept there for 40 min. Addition of methanol then led to a 70:30 mixture of the methyl ester **11** and tetralone in quantitative yield. On the other hand, a 75% yield of tetralone is obtained if the reaction is stirred at room temperature for 17 h before quenching (eq 10).



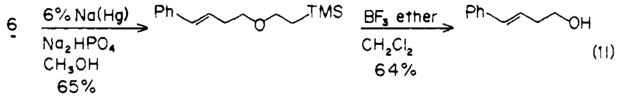
15

The use of 2–4 equiv of titanium tetrachloride, initially at −78 °C and then at −10 to 0 °C, led to 5-, 6-, and 7-membered rings from **15**–**17**. While quantitative data do not exist, the ease of cyclization appears to follow the order 6 > 5 > 7. Thus, for example, use of the boron catalyst with **16** led to the indanone in only 14% yield in contrast to the 75% yield of eq 10. Furthermore, cyclization of **15** produced the peri-bridged six-membered ring in great predominance (68% yield) over the angularly fused five-membered ring (1% isolated yield). Cyclization times for **16** and **17** were approximately 3.5 and 18 h, respectively. The high regioselectivity of this cyclization reaction is noteworthy.[12]



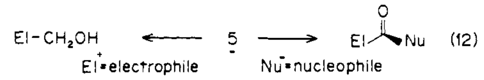
16 n=1 62%
17 n=3 51%

One additional application of these new nucleophiles is their ability to undergo desulfonylation[13] so that they serve as a synthon for a hydroxymethyl anion[14] as shown in eq 11. It is conceivable



to also employ a monosulfonylalkoxymethane[15] in a similar sequence with simple electrophiles; however, the carbanions derived from such a monosulfonyl species fail to serve as a nucleophile in palladium- catalyzed reactions.

It does appear that **5** has the functional equivalence of a carbonyl 1,1-dipole as well as a hydroxymethyl carbanion so that the transformations summarized in eq 12 are possible. While the



details of the unmasking have yet to be elucidated, it would seem likely that acyl sulfones are indeed intermediates although it cannot be ascertained whether they are the actual species undergoing the final acylation.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, National Cancer Institute, for their generous support of our programs. P.O. gratefully acknowledges a NATO postdoctoral fellowship administered through SERC of the United Kingdom.

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(12) Cf.: Johnson, W. S. *Org. React.* **1944**, *2*, 114. Sethna, S. *Friedel-Crafts Relat.* **1964**, *pt. 2, 3*, 911.

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(14) Seebach, D.; Meyer, N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 438. Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290. Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900. Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1983**, *24*, 3163, 3165.

(15) Cf.: Schank, K.; Schroeder, F.; Weber. *Liebigs Ann. Chem.* **1979**, 547 and earlier references therein. Gokel, G.; Gerdes, H. M.; Miles, D. E.; Hufnal, J. M.; Zerby, G. A. *Tetrahedron Lett.* **1979**, 3375. Tanaka, K.; Matsui, S.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3619.

Direct Observation and Chemistry of Triplet 1,6-Biradicals in the Norrish I Reaction

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The familiar Norrish I (α-cleavage) photoreaction of cycloalkanones occurs dominantly from the triplet state of the ketone and follows the mechanism depicted in Scheme I.[1] The transients in this reaction, particularly the biradicals, have not hitherto been observed. We now report the observation and the lifetime of two such biradicals. Deuterium isotope effects for one are consistent with the familiar triplet biradical → singlet biradical → product mechanism.

The photochemistry of **1a** has already been reported;[2] the aldehyde **3a** is the only significant product, requiring $k_A >> k_K$. The multiplicity is largely or exclusively triplet.[2b] For **1b**, we observe (in methanol solvent) only aldehyde **3b** accompanied by three small GC peaks totalling ≤2% of the area for **3b**. There is no detectable methyl ester peak in the NMR as would have been expected from methanolysis of any ketene formed via k_K. Clearly, $k_A >> k_K$ for **2b** also.

Irradiation with either a mode-locked or a Q-switched Nd-YAG laser at ca. 10 mJ/pulse (10-ns fwhm, 266-nm fourth harmonic) affords a moderately strong transient for **1a**, λ_{max} ≤310 nm, and a very strong transient for **1b**, λ_{max} 330 nm in heptane and 335 nm in methanol (Figure 1). The transient lifetimes (nanoseconds) in heptane (methanol) are, for **2a**, 49 (50) ± 5%, for **2b**, 56.2 (66.7) ± 2%, and for **2c**, 57.1 (67.6) ± 2%. Mass spectrometric analysis of **2c** showed d_0 < 1%, d_1 = 10%, d_2 = 79%, and d_3 = 10%; NMR showed 0.1 H at δ 2.59 (H-3) and 1.8 H at δ 2.51 (H-6).

Three assignments are possible for the transient according to Scheme I: S_1 of the ketone, T_1 of the ketone, or the triplet biradical. Since the fluorescence of **1b** (3.3 ± 0.3 ns) is much faster than decay of the transient absorption, the transient from **1b** at least is not the ketone singlet. The transients are affected

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† On leave from the Department of Chemistry, University of Tsukuba, Japan.

(1) Weiss, D. S. In "Organic Photochemistry", Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, pp 347ff. Provides a good recent review.

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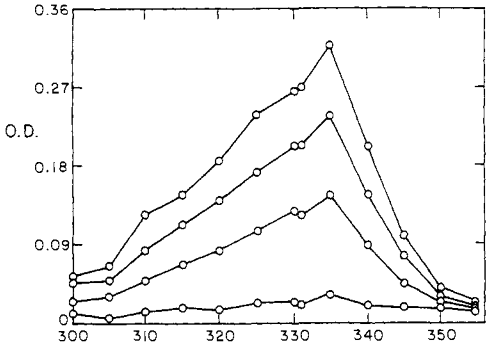
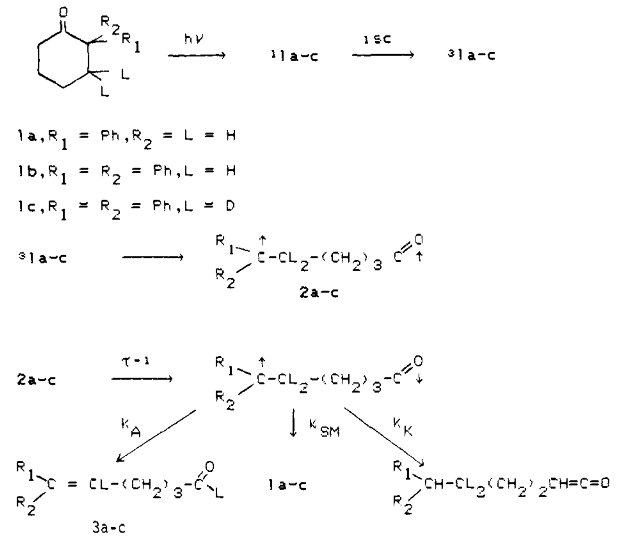


Figure 1. Spectrum of biradical **2b** integrated over a ca. 30-ns window centered 32, 64, 103, and 335 ns after the peak of the laser pulse.

Scheme **I**



in intensity but not significantly in lifetime by isoprene up to concentrations of 0.3 M ($k_Q \leq 10^7$ M^{-1} s^{-1}). Since ^{3}**1a–c** would be expected to be quenched at or near the diffusion-controlled rate by isoprene, the low k_Q militates against triplets as the correct assignment.[3] We conclude that the transients are indeed the biradicals **2a–c**. The λ_{max} of **2b** is in good agreement with that for benzhydryl radical[4] and that for other biradicals with the benzhydryl terminus.[5]

Isotope effects suggest that there is an intermediate subsequent to the observed biradical. We have prepared the dideuterio compound **1c** by the known route[6] and have studied isotope effects on the biradical lifetime and on the quantum yield of unsaturated aldehyde. Replacement of the hydrogen that is transferred produces a negligible effect on the lifetime: $\tau_H^{-1}/\tau_D^{-1} = 1.01_5 \pm 0.03$ in both solvents. The effect on quantum yield of **3** is, however, significant: $\phi(\mathbf{3b})/\phi(\mathbf{3c}) = 0.26_7/0.19_3 = 1.36$ (±6% estimated).

Since the yields of **2b** and **2c** are identical (±5%) as measured by their maximum absorbance, all or nearly all of the effect on quantum yield must be ascribed to an intermediate subsequent to the observed biradical. From Scheme I the obvious interpretation is that the observed species is the triplet biradical, and the subsequent intermediate is the singlet biradical. Intersystem crossing from triplet to singlet biradical is the lifetime-determining process, as for Norrish II biradicals.[7] Assuming that **2** is formed with 100% efficiency, $\phi(\mathbf{3}) = k_A/(k_{SM} + k_A)$; assuming further that k_{SM} is independent of deuteration affords $k_A{}^H/k_A{}^D = 1.52$ (±8% estimated), undoubtedly nearly all due to the primary isotope effect on transfer of the hydrogen. To the extent that fluorescence causes inefficiency in formation of **2** the actual isotope effect will be slightly higher.

Since there is no analogue to the OH group of Norrish II biradicals which causes a substantial increase of lifetime in H-bond accepting solvents,[8] these Norrish I biradicals show similar lifetimes in hydrocarbon and alcohol solvents. The lifetimes are in the range of those for twisted olefin triplets[9] (1,2-biradicals), Norrish II 1,4-biradicals,[7] and other 1,4-biradicals.[10] Kossanyi et al. estimated a much longer lifetime for the Norrish I biradical derived from 2-ethyl-4,4-dimethylcyclohexanone,[11] but a Norrish I 1,8-biradical is only some 3-fold longer lived than **2**.[12]

It is expected that the lifetime of biradicals will be affected by two opposing factors as the number of carbons between the termini is varied.[13] Spin–orbit coupling will decrease with increasing distance between the termini, tending to increase the lifetime. However, the larger distance leads to closer degeneracy on the average of singlet and triplet biradicals, which will facilitate intersystem crossing and diminish the lifetime. Although a proper comparison requires identical termini,[14] the results available suggest rough cancellation of these factors in common biradicals.

The independence of biradical lifetime on deuteration shows the absence of involvement of the reaction coordinate in the intersystem crossing process. Shaik and Epiotis[17] have suggested that certain nuclear motions that couple well with a change in orbital angular momentum may participate in the intersystem crossing mechanism. In the present case, transfer of H(D) in a linear or nearly linear geometry for the critical atoms is a reasonable model for the transition state. This is not a motion that couples with a change in orbital angular momentum and consequently should occur subsequent to, not simultaneously with, intersystem crossing.

Disproportionation of Norrish II biradicals is a 1,5-hydrogen transfer process like k_A. Given the precedents from studies of that reaction,[18,19] our value of $k_H{}^A/k_D{}^A$ is unexceptional.[20]

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(3) The triplet lifetime of **1a** was previously reported as 3 ns: Wagner, P. J.; Spoerke, R. *J. Am. Chem. Soc.* **1969**, *91*, 4437. See ref 2b for evidence that two conformationally distinct triplets, both short-lived, are involved.

(4) Norman, I.; Porter, G. *Proc. R. Soc. London, Ser. A* **1955**, *230*, 399. Favaro, G. *Spectrochim. Acta, Part A* **1970**, *26A*, 2327.

(5) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.

(6) Fortin, E. J.; Forest, M.; Gravel, D.; Rousseau, Y. *Can. J. Chem.* **1973**, *51*, 3445.

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(8) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1978**, *59*, 246.

(9) (a) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174. (b) Bonneau, R. *J. Photochem.* **1979**, *10*, 439. (c) Gorner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835. (d) Gorner, H. *Ibid.* **1982**, *86*, 2028. (e) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1981**, *103*, 4553. (f) Caldwell, R. A.; Singh, M. *Ibid.* **1982**, *104*, 6121; (g) *Ibid.* **1983**, *105*, 5139.

(10) Caldwell, R. A.; Creed, D. *J. Phys. Chem.* **1978**, *82*, 2644; *J. Am. Chem. Soc.* **1977**, *99*, 8360.

(11) By an assumption that its rate constant for reaction with butanethiol was 10^6 M^{-1} s^{-1}: Guiard, B.; Furth, B.; Kossanyi, J. *Bull. Soc. Chim. Fr.* **1974**, 3021. In reality, rate constants are probably higher, which would lead to calculated lifetimes more nearly in accord with the direct observation data. For kinetics of reactions of biradicals with thiols, see: Encinas, M. V.; Wagner, P. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 1357.

(12) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586.

(13) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(14) The present acyl–akyl biradical is obviously electronically rather different from the more common alkyl–alkyl biradicals of (e.g.) the Norrish II type. The only comparison that could be made from previous data suggests that such a structural change might not cause a gross change in lifetime: compare the biradical derived from photolysis of *o*-phthalaldehyde (1.6 μs)[15] with that derived from photolysis of 2,4,6-triisopropylbenzophenone (3.1 μs).[16]

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(19) Coulson, D. R.; Yang, N. C. *J. Am. Chem. Soc.* **1966**, *88*, 4511. A quantitative isotope effect was not given but the quantum yields reported for the Norrish II reaction of 2-hexanone-5,5-d_2 are consistent with an effect roughly of the magnitude we observe.

Acknowledgment. We thank Dr. Jean Kossanyi for helpful discussions. The National Science Foundation (Grants CHE 7915228 and CHE 8213637) provided financial support. H.S. thanks the Japan/U.S. Cooperative Photosynthesis and Photoconversion Research Program for financial support. Transient experiments were performed at the Center for Fast Kinetics Research at the University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas. Mass spectral and NMR analyses of **1b** and **1c** were performed respectively on a Hitachi RMU-6MG mass spectrometer at The University of Tsukuba and a Nicolet NT 360 NMR spectrometer at the Research Institute for Polymers and Textiles, Tsukuba.

Registry No. 1a, 1444-65-1; **1b**, 22612-62-0; deuterium, 7782-39-0.

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(20) Wagner and Chiu (Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134) have, however, observed a substantially larger isotope effect in one case.

Automerization Mechanism and Structure of the $C_{11}H_{11}$ Armilenyl Cation

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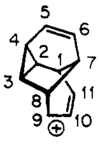
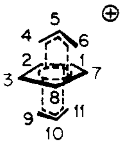
The facile nuclear permutations of the "[3.5.3]armilenyl" cation (**1**)—(1,2,3,8,7)(4,6.9,11)(5,10)—have hitherto obscured any umambiguous structural assignment. The options have been (i) the classical 9-tetracyclo[5.4.0.0^{2,4}.0^{3,8}]undeca-5,10-dienyl cation (**1a**), (ii) an entirely organic sandwich whose cyclopentadienide ring is spanned in C_2 symmetry by two mutually perpendicular 1,3-dehydroallyl ligands (**1b**), or else (iii) the C_s variant of **1b**, achieved by a mere 9° internal rotation.[1a] The permutations have been analyzed by Longuet-Higgins group theory,[2] and the static structure by EHT[3a] and CNDO calculations.[3b] **1** was the first reported $(CH)_{11}$ cation, and it might yet be the most stable of all;[4] both the cation[1] and its 9-hydroxyl derivative[5] have since been obtained from alcohol, chloride, and ketone precursors that represent as many as five structurally isomeric carbon skeletons.

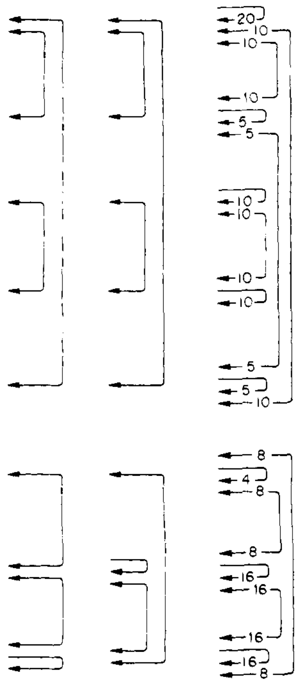


1a



1b

Table I. ^{13}C NMR Assignments of **1a** and Alternative Exchange Diagrams for Its Automerization

			exchange diagrams of alternative mechanisms[c]		
NMR signal	δ_C[a]	assignment[b]	allylic alkylation 1-jump	Wagner–Meerwein 3-jump	sandwich random
a	214.66	9, 11			
b	144.34	6			
c	139.65	5[d]			
d	137.22	10[d]			
e	71.61	4			
f	57.32	7			
g	56.24	1, 8			
h	43.73	2, 3			

[a] 75.47 MHz, −164.1 °C, $FSO_3H/SO_2ClF/SO_2F_2/CHFCl_2/CHF_2Cl$ solution of *anti*-bicyclo[4.3.2]undeca-2,4,6,10-tetraen-9-ol.[1b] [b] Reference 6a. [c] Reference 6b. [d] Alternative c/d assignments are possible but mechanistically irrelevant.

We now report the experimentally required resolution, both of this structural problem and of the mechanistic problem that the correct structure reveals.

Contemporary ^{13}C NMR techniques resolve the previously reported[1a] three lines into eight (Table I). Their number excludes **1b**, and their dispersion excludes its C_s variant. Only **1a** remains.

Figure 1 revives **1b**, albeit now as a potential transient in the automerization of **1a**. Rapid rotation of its cyclopentadienyl ring should randomly generate any of the 20 **1a** label isomers by the radial "sandwich" mechanism. The perimeter of this figure illustrates the originally proposed alternative: the rare allylic alkylation of a cyclopropane ring with inversion of configuration.[7]

The third and final alternative appears in Figure 2. Its exchange diagram (Table I) requires the C1,8 signal to broaden with temperature half as rapidly as the C2,3 signal. The sandwich mechanism requires an equal rate for both signals, whereas the alkylation mechanism requires the first of these signals to broaden twice as rapidly as the second. Figure 3 leaves no doubt but that the last of these mechanisms is most consistent with the data. The associated activation parameters (−160 → −80 °C) are $\Delta H^{\ddagger} = 5.2(1)$ kcal/mol and $\Delta S^{\ddagger} = 0(1)$ cal/(mol deg).

The allylic alkylation mechanism is not merely sufficient to accomodate these data, it is also necessary—at least in the sense

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[†] Procter and Gamble Co. Fellow, 1981–1982. Taken in part from the Ph.D. Thesis of J.P.D., Cornell University, 1984. Current address: Department of Chemistry, University of Rochester.

(1) (a) Goldstein, M. J.; Kline, S. A. *J. Am. Chem. Soc.*, **1973**, *95*, 935; **1981**, *103*, 2910. (b) Goldstein, M. J.; Tomoda, S.; Pressman, E. J.; Dodd, J. A. *Ibid.* **1981**, *103*, 6530. (c) Fujise, Y.; Yashima, H.; Sato, T.; Itô, S. *Tetrahedron Lett.* **1981**, 1047.

(2) (a) Trindle, C.; Bouman, T. D. *Jerusalem Symp. Quantum Chem. Biochem.* **1973**, *6*, 51. (b) Trindle, C.; Bouman, T. D. *Int. J. Quantum. Chem. Symp.* **1975**, *No. 9*, 255. (c) Trindle, C.: Bouman, T.; Datta, S.; Duncan, C. *Comput. Chem. Res. Educ. Proc. Int. Conf.* **1977**, 261.

(3) (a) Hoffmann, R.; Rossi, A., private communication. (b) Trindle, C.; Hwang, J.-T.; Hough, D. *Tetrahedron* **1974**, *30*, 1393.

(4) The monocyclic isomer has not yet been reported.

(5) (a) Groves, J. T.; Ma, K. W. *Tetrahedron Lett.* **1973**, 5225; (b) *Ibid.* **1975**, 1411. (c) Aumann, R. *Chem. Ber.* **1977**, *110*, 1432.

(6) (a) Carbon assignments derive from peak areas, from the high-temperature δ_C averages (161.33, 138.59, 51.23 ppm), and by analogy with those of the structurally unambiguous *exo*-6-tricyclo[3.3.1.0^{2,4}]non-7-enyl cation; Cf. Supplementary Material. (b) The succinct exchange diagram notation of Oth et al. (Oth, J. F. M.; Müller, K.; Gilles, J.-M.; Schröder, G. *Helv. Chim. Acta* **1974**, *5*, 1415) is only trivially extended to accommodate the random process.

(7) Inversion is reported for the electrophilic bromination of cyclopropane (Lambert, J. B.; Schulz, W. J., Jr.; Mueller, P. H.; Kobayashi, K. *J. Am. Chem. Soc.* **1984**, *106*, 793) and for automerizations of the cyclopropylcarbinyl cation (Olah, G. A.; Kelly, D. P.; Jeuel, C. L.; Porter, R. D. *Ibid.* **1970**, *92*, 2544. Majerski, Z.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 665. Wiberg, K. B.; Szeimies, G. *Ibid.* **1970**, *92*, 571) and *exo*-deltacyclyl cation (Freeman, P. K.; Balls, D. M.; Blazevich, J. N. *Ibid* **1970**, *92*, 2051).

(8) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

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