Finally, our earlier results[3] for aromatic ketones indicated that biradical lifetimes are usually in the 30–100-ns range, while in the case of aliphatic ketones in the gas phase O'Neal et al. reported a value of $\sim 10\ \mu s$.[5] The results reported in this communication strongly suggest that this difference is real and should be largely attributed to the difference in molecular structure. While it is clear that the lifetimes of simple aliphatic biradicals are substantially longer than those of aromatic ones, the reasons for this difference are as yet unclear. In the case of aromatic biradicals we have proposed that the lifetimes were controlled by intersystem crossing;[3] whether this conclusion can be generalized remains to be seen, and it seems certain that the detailed study of a large number of biradical processes will be required before the intricacies of their behavior can be unveiled.

References and Notes

(1) P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 287 (1972); P. J. Wagner, P. A. Keslo, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *ibid.*, **94**, 7506 (1972); P. J. Wagner and K.-C. Liu, *ibid.*, **96**, 5952 (1974).
(2) M. Hamity and J. C. Scaiano, *J. Photochem.*, **4**, 229 (1975); R. D. Small, Jr., and J. C. Scaiano, *Ibid.*, **6**, 453 (1976/77); J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1977); R. D. Small, Jr., and J. C. Scaiano, *ibid.*, **100**, 4512 (1978); J. Grotewold, C. M. Previtali, D. Soria, and J. C. Scaiano, *J. Chem. Soc., Chem. Commun.*, 207 (1973); R. D. Small, Jr., and J. C. Scaiano, *Macromolecules*, **11**, 840 (1978); R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977).
(3) R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828, 2126 (1977); *J. Am. Chem. Soc.*, **99**, 7713 (1977); *Chem. Phys. Lett.*, **48**, 354 (1977).
(4) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971); J. C. Scaiano, M. V. Encina, and E. A. Lissi, *Rev. Chem. Interm.*, in press.
(5) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Am. Chem. Soc.*, **96**, 3351 (1974).
(6) Y. Kusokawa and M. Anpo, *J. Phys. Chem.*, **79**, 2225 (1975).
(7) J. C. Dalton, M. W. Geiger, and J. J. Snyder, *J. Am. Chem. Soc.*, **98**, 398 (1976).
(8) 4-Carboxy-1-methylpyridynium is among the series of substrates which also trap the biradicals from aromatic ketones, e.g., γ-methylvalerophenone, though they are considerably slower than paraquat dications.[9]
(9) R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, in press.
(10) All kinetic measurements were carried out at 400 nm where the reduced forms of both **1** and **2** show strong absorptions. A detailed spectroscopic study from 360 to 680 nm showed that the spectra of the reduced species agreed well with those previously reported.[11]
(11) J. A. Farrington, M. Ebert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta*, **314**, 372 (1973); L. K. Patterson, R. D. Small, Jr., and J. C. Scaiano, *Radiat. Res.*, **72**, 218 (1977); P. Neta and L. K. Patterson, *J. Phys. Chem.*, **78**, 2211 (1974).
(12) M. V. Encina and E. A. Lissi, unpublished results.
(13) J. D. Coyle, *J. Chem. Soc. B*, 2254 (1971).
(14) Based on $k_q = 1 \times 10^{10}\ M^{-1}\ s^{-1}$.
(15) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1888 from the Notre Dame Radiation Laboratory.

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Stereochemistry of the Indene Phototransposition Reaction and the Mechanistic Implications Theoreof[1]

Sir:

There has recently been considerable interest in phototransposition reactions which have the net effect of interchanging atoms which are 1,3 related within a five-membered ring, i.e. eq 1. Examples have been reported for various heterocycles,[2] for [$^{13}C_2$]cyclopentadiene,[3] and for several alkyl-substituted indenes.[4] Two mechanisms will readily accommodate these interconversions—a multistep process involving initial [$\pi^2 + \pi^2$] intramolecular cycloaddition and a "conju-
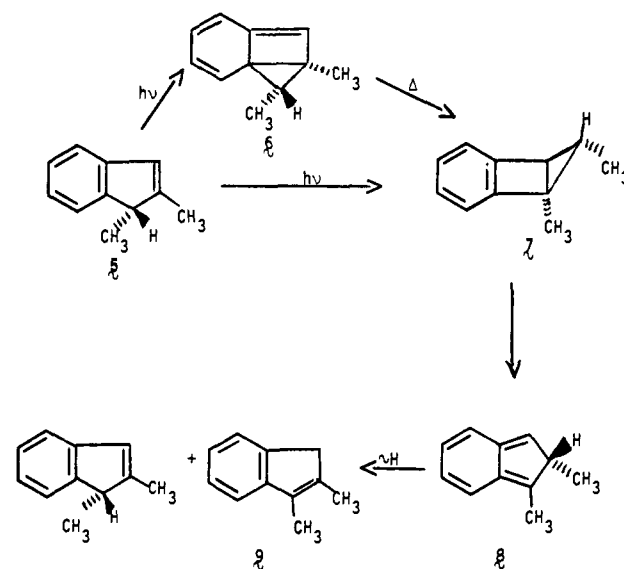

(1)
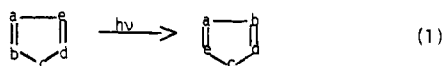
Scheme I. Initial [$\pi^2 + \pi^2$]
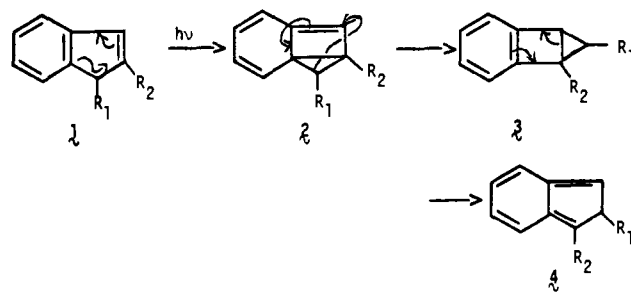
Scheme II. "Conjugated Di-π-methane"
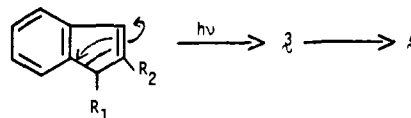
Scheme III

gated di-π-methane" rearrangement. These are shown in Schemes I and II as exemplified by the indene rearrangement (the ultimate products from which are a pair of isomeric indenes resulting from 1,5 hydrogen shifts in the isoindene **4**). In both of the above schemes, migration of the central atom is the critical step, and we herein report that, within the indene series, *this migration proceeds with remarkable stereospecificity to give clean inversion at the migrating center.*

Our observation, presented in terms of the two mechanistic options, is shown in Scheme III.[5] The molecule studied (**5**) gives rise to a partially degenerate rearrangement with *virtually equal formation of 2,3-dimethylindene* (**9**) *and the starting material.* This ratio was determined by photolyzing 1-methyl-2-trideuteriomethylindene. The amount of **9**-d_3 formed was determined by VPC, and the amount of 1-trideuteriomethyl-2-methylindene (**10**) was determined by NMR analysis of a VPC-purified mixture of the 1,2-dimethylindene (d_3) isomers. The ratio of **10** to **9**-d_3 was 0.93.

Photolysis of 0.01 M hexane solutions of optically active (S)-(+)-**5**[6] to as much as 28% formation of **9** (and therefore $\sim$54% rearrangement) led to only a 1% average change in the specific rotations of **5**, measured at nine different wavelengths with a Cary Model 60 spectropolarimeter. Lower conversion runs gave even smaller amounts of racemization; for example, 9.6% formation of **9** is accompanied by 0.06% diminution in rotation of **5**! If one assumes that the 1,5 hydrogen shift converting **8** to **5** is suprafacial (the allowed path for this six-

:lectron ground-state process), the complete retention of optical activity in **5** requires that **7** has been formed with complete inversion at the migrating carbon, as depicted in Scheme III.

This result is consistent with either of the two routes shown, i.e., a four-electron, ground-state, 1,3 sigmatropic shift of **6** to **7**, or a concerted, six-electron, excited-state di-π-methane isomerization of **5** to **7**.[9] It is inconsistent with a photochemical conversion of **6** to **7**, such as has been suggested for the cyclopentadiene phototransposition.[3] Since thermal 1,3 sigmatropic shifts in bicyclopentenes have likewise been ruled out,[10] the "conjugated di-π-methane" option for cyclopentadiene seems most attractive.[11] In fact, we now favor this alternative for the indene series as well, since all attempts to obtain NMR or UV spectral evidence for **6** have been without success. This is the case even upon photolysis at -90 °C, at which temperature rearrangement still occurs (albeit with reduced efficiency). More telling is the fact that the total photorearrangement of **5** has a $\phi \simeq 0.25$.[12] If one assumes that the inefficiency is solely due to competitive first-order reversion of **6** to **5** (vs. the 1,3 shift of **6** to **7**), than the E_{act} for the 1,3 shift is *at most* ~ 0.7 kcal/mol higher than that for reversion. A comparison of the bond and strain energies involved in the two steps makes clear that this small difference is unrealistically low.[13]

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References and Notes

(1) Organic Photochemistry. 42. Part 41: T. Nylund and H. Morrison, *J. Am. Chem. Soc.*, in the press.
(2) Some examples include (a) P. Beak and W. Messer, *Tetrahedron*, **25**, 3287 (1969); (b) M. Kojima and M. Maeda, *Tetrahedron Lett.*, 2379 (1969); (c) W. M. Williams and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **94**, 3955 (1972); (d) M. Maeda and M. Kojima, *J. Chem. Soc., Chem. Commun.*, 439 (1973); (e) J. A. Barltrop, A. C. Day, and R. W. Ward, *ibid.*, 131 (1978).
(3) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **99**, 4851 (1977).
(4) F. J. Palensky and H. Morrison, *J. Am. Chem. Soc.*, **99**, 3507 (1977); A. Padwa, R. Loza, and D. Getman, *Tetrahedron Lett.*, 2847 (1977).
(5) The scheme is drawn using one diastereomeric representation of **6** and **7**; though these structures would be sterically favored, the significance of the observation is independent of whether the cyclopropane ring is up or down.
(6) Prepared from optically active 3-phenylbutanoic acid[7] using the method of Meurling.[8] The substrate so prepared has $[\alpha]^{27}_D +109°$ (c 1.7, benzene) (lit.[8] $[\alpha]^{25}_D +115°$ (c 2.0, benzene)).
(7) A.-M. Wieder and G. Bergson, *Acta Chem. Scand.*, **18**, 1484 (1964).
(8) L. Meurling, *Acta Chem. Scand., Ser. B*, **28**, 399 (1974).
(9) Clean inversion of the methane carbon in di-π-methane rearrangements has been demonstrated; cf. H. E. Zimmerman, T. P. Gannett, and G. E. Keck, *J. Am. Chem. Soc.*, **100**, 323 (1978); H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *ibid.*, **96**, 4630 (1974).
(10) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **99**, 4853 (1977), and references therein.
(11) Reference 10, footnote 11.
(12) Determined by monitoring **9** and using the 0.93 ratio determined from the deuteriomethyl series.
(13) There is evidence for the 1,3 shift mechanism in certain heterocycle photorearrangements; cf. ref 2c and 2e.

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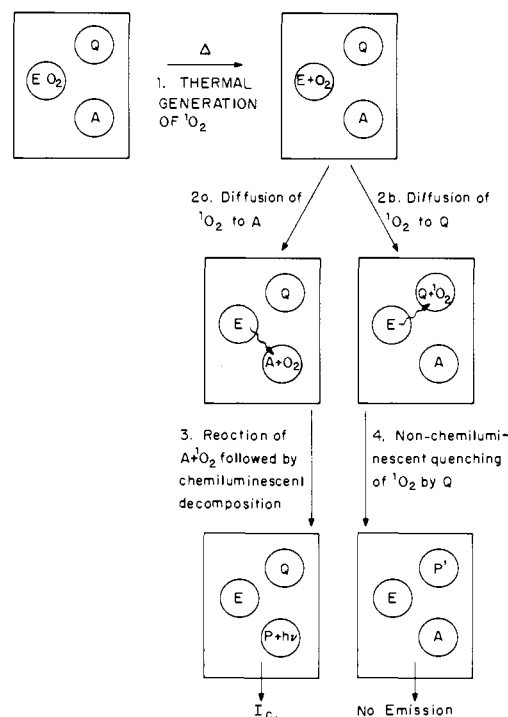*West Lafayette, Indiana 47907*
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Figure 1. Schematic representation of the chemiluminescent system designed to measure $^1O_2$ diffusivity and reactivity in polymers. Step 1 is thermal decomposition of a naphthalene endoperoxide (EO_2) to generate $^1O_2$ at a polymer site distinct from that of $^1O_2$ acceptor (A) and $^1O_2$ quencher (Q). Step 2 involves either diffusion to the site of A (step 2a) or to the site of Q (step 2b). Step 3 is the reaction of $^1O_2$ with A to yield detectable chemiluminescence. Step 4 is the nonchemiluminescent quenching of $^1O_2$ which is competitive with step 3 and therefore is competitive with chemiluminescence.

chemical pathways leading to polymer disintegration are known with certainty. We report a simple, nonphotochemical method for generation and quantitative investigation of the physical and chemical properties of $^1O_2$ in polymer films. Conceptually, our method (Figure 1) employs (1) an endoperoxide (EO_2) which may be solubilized in polymer films and which is capable of generating $^1O_2$ thermally at convenient temperatures; (2) a singlet oxygen acceptor, A, which forms an adduct AO_2 upon reaction with $^1O_2$; (3) selection of adducts (AO_2) which are capable of decomposing in the polymer with the production of a chemiluminescent product P. Quantitative measurement of the chemiluminescence intensity I_{CL} as a function of the concentration of A, C_A, at constant temperature provides information concerning physical properties (diffusivity) of $^1O_2$ in the polymer film. Measurement of I_{CL} as a function of the addition of singlet oxygen quenchers (Q) at fixed C_A and temperature provides information concerning the chemical properties (reactivity) of $^1O_2$ toward these quenchers in the polymer systems.[2]

The compounds employed in this study are given in Chart I. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) films were used as test matrices to explore the feasibility of the

Generation, Diffusivity, and Reactivity of Singlet Oxygen in Polymer Matrices. A Convenient and Sensitive Chemiluminescent Technique

Sir:

Singlet oxygen $^1O_2$ has been suggested as an important contributor to thermal and photochemical degradation of polymers.[1] In spite of a vast and ever expanding literature, neither the method of generation of $^1O_2$ nor the details of the

Chart I

EO_2 A AO_2 P

1 R = H
2 R = CH_3

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