recent laser flash photolysis results[5] indicate that this rate constant ($\sim 1 \times 10^6$ M^{-1} s^{-1} for the benzoyloxy radical in CCl_4) would be too slow to compete with the very fast decarboxylation rates for alkanoyloxy radicals.

Finally, the rate constant obtained for the decarboxylation of the (phenylacetyl)oxy radical **7e** (R = $PhCH_2$) obtained from **6e** seems surprisingly low. All estimations of bond dissociation enthalpies[35] and reaction rates would place this value higher than that for **7d** (R = $(CH_3)_3C$). An explanation for this observation comes from results on the rates of decarbonylation of RCO radicals. A plot[34] of the logarithm of these rates as a function of R versus calculated bond dissociation enthalpies is linear for alkyl groups, except that benzyl derivatives fall significantly below the line. However, the frequency factors for these substrates are also somewhat lower, suggesting that there is an unfavorable entropy effect in the transition state for decarbonylation. This effect is a result of the requirement that the phenyl ring assume a conformation allowing overlap with the breaking σ bond and conjugation with the developing radical center. For the case of the decarboxylation reactions where the process is more exothermic and the enthalpies of activation are undoubtably very low, the energy of the transition state may be dominated by this entropic effect. The lowering of the rate now puts **7e** slower than **7c**.

We are currently extending this approach to measure rates of decarboxylation for other cases.

Acknowledgment. We thank the NSERC of Canada for financial support and D. P. DeCosta for providing the results for **6f**. J.W.H. thanks the Sumner Foundation for financial assistance in the form of a graduate fellowship.

Photolysis of Azoalkanes. Reactions and Kinetics of the 1-Cyclopropylcyclopentane-1,3-diyl Biradical and the 1-Cyclopropylcyclopentyl Radical

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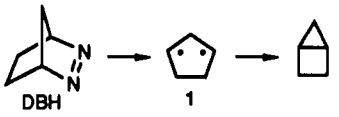
Abstract: The cyclopropylcarbinyl (CPC) rearrangement rates of 1-cyclopropylcyclopentyl (**10a**) and 1-cyclopropylcyclohexyl (**10b**) radicals to yield **34a,b** are found to be 1.45×10^7 and 1.1×10^7 s^{-1} at 24.7 °C, respectively. These values, which are based on thiophenol trapping of **10a,b**, are 6–9 times slower than that of the parent cyclopropylmethyl radical. Ring closure of homoallylic radical **34a** proceeded at a rate of 5.5×10^4 s^{-1}, which is 7 times faster than that of 3-butenyl. No 1,5-hydrogen shift was found in **34a**. The triplet 1,3-biradical **6T** analogous to **10a** was produced by triplet-sensitized photolysis of 1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**11**). Biradical **6T** rearranges to **9*E*** and **9*Z***, the latter of which undergoes rapid intramolecular disproportionation to **46*Z***. On account of its geometry, the *E* isomer cannot lead directly to a stable product; hence, it recloses to **6T** ($k_{ra} = 1.2 \times 10^5$ s^{-1}), but, interestingly, not to **6S**. If the CPC rearrangement rate of **6T** is taken to equal that of **10a**, we calculate from the product distribution that the lifetime of **6T** is 59 ns. This figure is only half the lifetime of the parent cyclopentane-1,3-diyl (**1**), showing that the perturbing effect of cyclopropyl is similar to that of methyl.

A number of photoreactions proceed via localized biradicals, intermediates that have become a recent focus of mechanistic study.[1] Because deazatation is often a clean and efficient reaction, cyclic azoalkanes[2] are an appealing source of biradicals. As illustrated by the photolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH),[3] biradicals can lead to products not easily prepared by alternate routes. Triplet-sensitized irradiation of such bicyclic azoalkanes affords triplet biradicals (designated as T) whose lifetime is a topic of current interest.[1] While a number of triplet biradicals have been observed by ESR or transient UV spectroscopy, ambient-temperature study of biradicals lacking a chromophore requires such methods as photoacoustic calorimetry,[4] oxygen trapping,[5] or CIDNP.[6]



Another approach to the study of biradicals is the free radical clock technique, wherein one or both of the radical centers is functionalized with a group capable of rapid rearrangement. From the product distribution and the rearrangement rate, which is assumed to equal that of an analogous monoradical, one can deduce the lifetime of the biradical. Several years ago, we em-

(1) (a) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240. (b) Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 6894. (c) Adam, W.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 6896. (d) Adam, W.; De Lucchi, O.; Dörr, M. *J. Am. Chem. Soc.*, **1989**, *111*, 5209. (e) Ham, S.-W.; Chang, W.; Dowd, P. *J. Am. Chem. Soc.* **1989**, *111*, 4130. (f) Burnett, M. N.; Boothe, R.; Clark, E.; Gisin, M.; Hassaneen, H. M.; Pagni, R. M.; Persy, G.; Smith, R. J.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 2527. (g) Ayscough, P. B.; Bushby, R. J.; Jarecki, C.; Sales, K. D.; Oduwole, D.; Tann, J. *Tetrahedron Lett.* **1988**, *29*, 2719. (h) Roth, W. R.; Bauer, F.; Braun, K.; Offerhaus, R. *Angew. Chem.*, Int. *Ed. Engl.* **1989**, *28*, 1056. (i) Kjell, D. P.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 4111. (j) Caldwell, R. A. In *Kinetics and Spectroscopy of Biradicals and Carbenes*; Platz, M. S., Ed.; Plenum: New York, 1990.

(2) (a) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99. (b) Adam, W.; De Lucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

(3) (a) Criegee, R.; Rimmelin, A. *Chem. Ber.* **1957**, *90*, 414. (b) Solomon, B. S.; Thomas, T. F.; Steel, C. *J. Am. Chem. Soc.* **1968**, *90*, 2249. (c) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115.

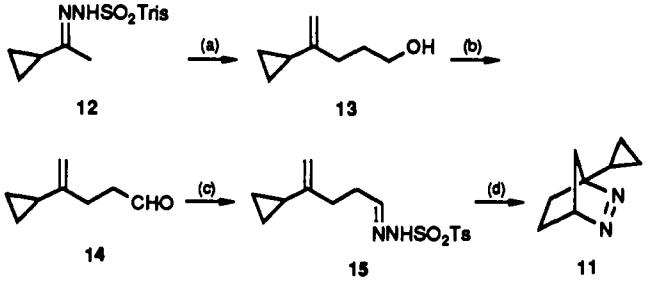
(4) Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 2681.

(5) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165.

(6) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543.

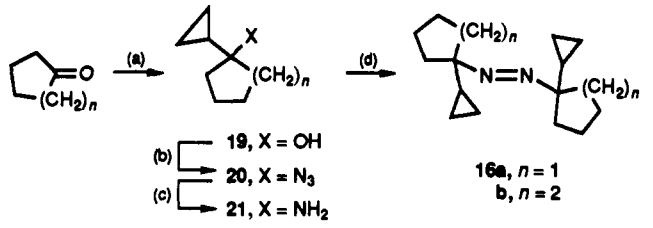
0002-7863/91/1513-2686$02.50/0

Scheme I. Synthesis of **11**[a]



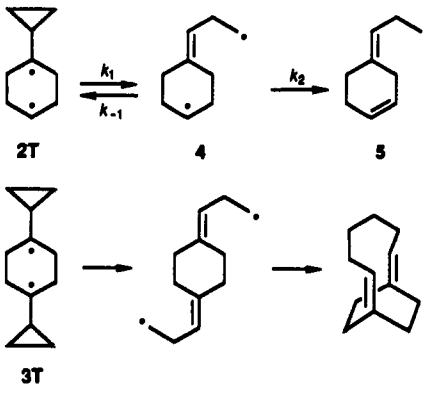
[a] Key: (a) *n*-BuLi, oxetane, 50% TMEDA/hexane; (b) PDC, CH_2Cl_2; (c) $TsNHNH_2$, MeOH; (d) $BF_3{\cdot}Et_2O$, CH_2Cl_2, −5 °C; Ts = tosyl; Tris = 2,4,6-triisopropylphenyl.

Scheme II. Synthesis of Azoalkanes **16a,b**[a]

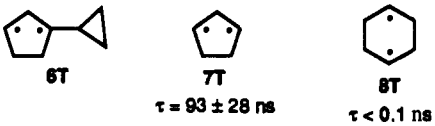


[a] Key: (a) cyclopropyllithium, Et_2O, −78 °C; (b) CF_3COOH, NaN_3, $CHCl_3$; (c) LAH, Et_2O; (d) IF_5, pyridine, CH_2Cl_2.

ployed the cyclopropylcarbinyl (CPC) rearrangement[7] to determine that the lifetimes (the reciprocal of the intersystem crossing (ISC) rate) of "spring loaded" biradicals **2T** and **3T** were 138 and 188 ns, respectively.[8,9] The stable products from **2T** and **3T**, some of which are shown here, illustrate how nature contrives to form covalent bonds from radical centers born in awkward geometries.



Because the lifetime of **2T** and **3T** was >1000-fold greater than that of the parent six-membered system of **8T**,[5] we were concerned

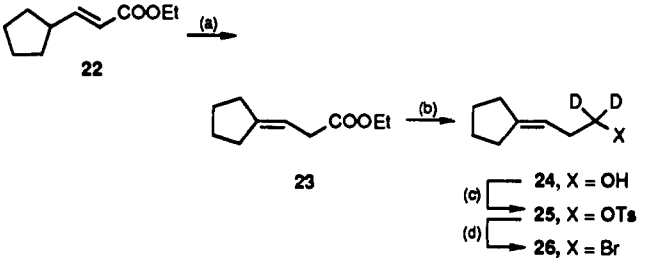


(7) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, p 227.

(8) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964.

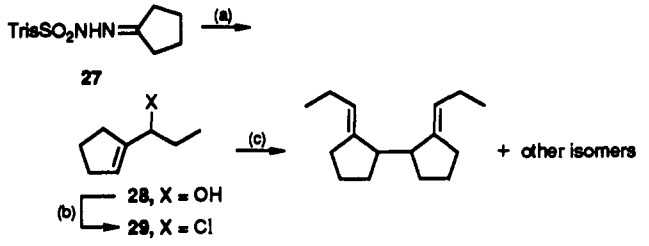
(9) The lifetimes of **2T** and **3T** have been recalculated from the product distributions[8] and new values of the CPC rearrangement rate constants determined here. We originally gave the lifetimes of **2T** and **3T** as 28 and 19 ns, respectively, including both ISC and CPC rearrangement. If only ISC had been considered, the lifetimes would have been 71 and 97 ns, values that we now know are too short.

Scheme III. Synthesis of Homoallylic Bromide **26**[a]



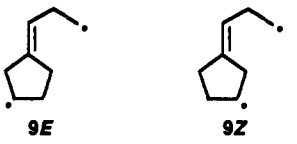
[a] Key: (a) 254 nm *hν*, pentane; (b) $LiAlD_4$; (c) TsCl, pyridine; (d) NaBr, DMF.

Scheme IV. Synthesis of Authentic Dimers[a]

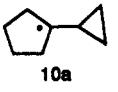


[a] Key: (a) *n*-BuLi, EtCHO, 50% TMEDA/hexane; (b) Ph_3P, CCl_4, Δ; (c) Li, ultrasound, THF; Tris = 2,4,6-triisopropylphenyl.

that the cyclopropyl group might change biradical lifetimes in general, thus undermining the free radical clock technique as a probe for such species. We have therefore examined the effect of a cyclopropyl group on the five-membered biradical **7T**, an intermediate that is much better characterized[4,5,10] and also much longer lived than **8T**. On account of its lower symmetry than **2T**, the new biradical **6T** can rearrange to an *E,Z* pair of homoallylic biradicals (**9E** and **9Z**) whose chemical fate offered an appealing subject for investigation. Understanding the reactions of each



geometrical isomer required a detailed study of **10a**, the monoradical analogous to **6**. Our general approach was to determine the CPC rearrangement rate of **10a** by competitive trapping with thiophenol and then to use this rate as a radical clock to calculate the lifetime of **6T**.



Synthesis of Compounds

The precursors used to generate **6T** and **10a** are the azoalkanes **11** and **16a**, respectively, both of which were synthesized in four steps. As seen in Scheme I, the vinyl anion from the trisylhydrazone of cyclopropyl methyl ketone reacted with oxetane to add the functionalized three-carbon unit.[11] Oxidation of **13** to the aldehyde **14**, formation of the tosyl hydrazone **15**, and Lewis acid catalyzed cyclization by the elegant method of Wilson[12] afforded the desired DBH derivative **11**. Our initial fears that

(10) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688.

(11) (a) Haynh, C.; Derguini-Boumechal, F.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, *17*, 1503. (b) Stowell, J. C. *Chem. Rev.* **1984**, *84*, 409.

Scheme V. Mechanism of Product Formation from Acyclic Azoalkanes **16a,b**

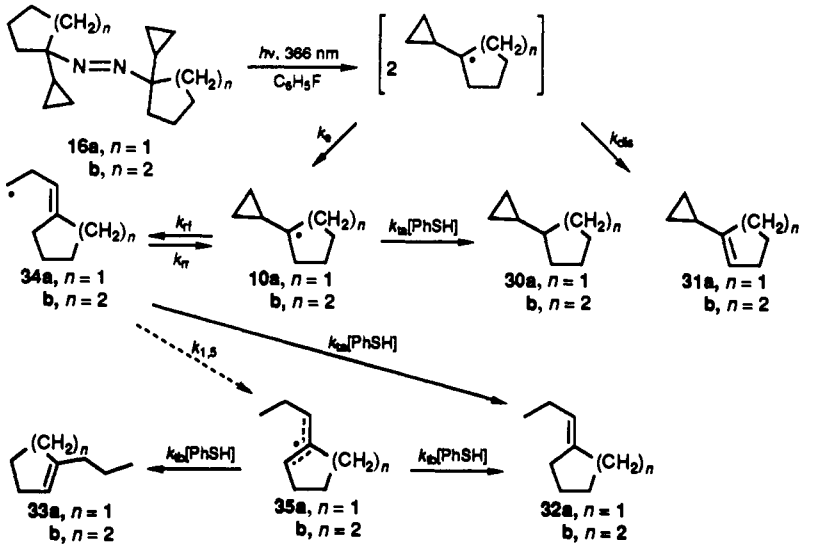


Table I. Product Yields (%)[a] from Photolysis of **16a** (0.0187 M) at 24.7 °C

$[PhSH]_i$[b,c]	$[PhSH]_{ef}$[b,d]	30a[e]	31a[f]	32a[g]	33a[h]	T/R[i]	bal[j]
0.032	0.018	39.14	23.15	37.09	0.62	0.42	87.8
0.040	0.025	40.50	19.61	39.21	0.69	0.52	89.2
0.059	0.045	46.18	22.91	30.35	0.56	0.75	89.1
0.130	0.115	55.80	19.93	23.90	0.38	1.48	89.3
0.234	0.219	62.36	19.88	17.43	0.33	2.39	88.4
0.294	0.279	65.05	20.98	13.81	0.16	3.16	89.9

[a] Errors in GC peak area measurements were propagated to obtain the standard deviation in the yields, which are given in footnotes as the average for each product at all six thiophenol concentrations. [b] Concentration in mol/L. [c] Initial. [d] Effective; see text. [e] ±0.19. [f] ±0.04. [g] ±0.09. [h] ±0.02. [i] Trapped **10a**/rearranged **10a**; see text. The first entry is ±0.02; all others are ±0.01. [j] Total yield of **30a–33a**.

Table II. Product Yields (%)[a] from Photolysis of **16a** (0.0103 M) at 58.5 °C

$[PhSH]_i$[a]	$[PhSH]_{ef}$[a]	30a[b]	31a[c]	32a[d]	33a[e]	T/R[a]	bal[a,f]
0.039	0.030	26.75	12.03	57.74	3.48	0.24 ± 0.03	78.0
0.045	0.036	29.62	14.01	52.76	3.60	0.28 ± 0.01	82.3
0.068	0.059	32.30	14.84	49.33	3.54	0.33 ± 0.04	85.4
0.144	0.135	41.94	14.35	40.94	2.78	0.63 ± 0.07	77.9
0.227	0.218	49.20	14.86	34.17	1.77	0.96 ± 0.10	82.5
0.325	0.316	55.46	12.88	29.67	1.99	1.35 ± 0.12	81.4

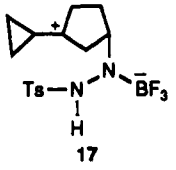
[a] See footnotes to Table I. [b] ±0.76. [c] ±0.32. [d] ±0.94. [e] ±0.26. [f] ±0.88.

Table III. Product Yields (%)[a] from Photolysis of **16b** (0.0142 M) at 25.0 °C

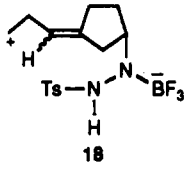
$[PhSH]_i$[a]	$[PhSH]_{ef}$[a]	30b[b]	31b[c]	32b[d]	33b[e]	T/R[a]	bal[f]
0.039	0.027	36.68	17.08	45.98	0.26	0.42 ± 0.01	85.7
0.045	0.032	41.21	17.08	41.48	0.23	0.58 ± 0.02	83.3
0.068	0.056	47.71	17.61	34.53	0.15	0.87 ± 0.02	79.2
0.118	0.106	56.76	17.73	25.41	0.09	1.53 ± 0.03	81.5
0.202	0.190	64.94	17.60	17.37	0.10	2.71 ± 0.10	83.6
0.313	0.301	69.28	17.84	12.82	0.07	3.99 ± 0.17	81.7

[a] See footnotes to Table I. [b] ±0.42. [c] ±0.11. [d] ±0.28. [e] ±0.01. [f] Total yield of **30b–33b**; ± 0.88.

the cyclization step would lead to cyclopropyl ring opening[13] (**17** → **18**) were unfounded; in fact, deliberate attempts to effect this rearrangement by heating the reaction still led to **11**.



17



18

A similar absence of CPC cation rearrangement was noted in the synthesis of **16a**, where a tertiary cyclopropylcarbinyl cation from **19a** is trapped with azide.[14] Reduction of **20** to the amine **21** followed by IF_5 coupling[15] afforded azoalkane **16a** (cf, Scheme II). Though this compound contains carbocyclic rings, we shall refer to it as "acyclic" because the azo group is not part of a ring.

A number of other compounds were synthesized in the course of this work. The first of these, the six-membered homologue (**16b**) of **16a**, was made by the same route as **16a** for the purpose of checking our earlier assumed rate constant for CPC rearrangement of **2T** and **3T**. Dideuterated homoallylic bromide **26** was required to determine the ring closure rate of the homoallylic radical to form **10a**. As shown in Scheme III, this compound was made by photochemical deconjugation[16] of α,β-unsaturated ester **22**, reduction with $LiAlD_4$, and two-step conversion of the resulting alcohol to the bromide. Allylic chloride **29**, which was required to synthesize radical dimers suspected in the decomposition of **16a**, was prepared from the corresponding alcohol **28** (cf. Scheme IV). Although **30a,b–33a,b** were known previously, authentic samples were synthesized to identify the photoproducts of **16a**.

Decomposition of 16a,b

Irradiation of **16a** and **16b** in fluorobenzene afforded **30a–32a** and **30b–32b**, respectively. The absolute yield of these hydrocarbons at various thiophenol concentrations and temperatures was determined by gas chromatography (GC) (cf., Tables I–III). The quantity T/R, which represents the ratio of trapped to rearranged products of **16a,b**, increases at higher thiophenol concentration and at lower temperature, in accord with expectation. The method used to calculate T/R and $[PhSH]_{ef}$ will be described after we consider the photolysis mechanism of **16a** (cf. Scheme V).

(12) Wilson, R. M.; Reckers, J. W.; Packard, A. B.; Elder, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 1633.

(13) Breslow, R. S. In *Molecular Rearrangements*; deMayo, P., Ed.; Wiley: New York, 1963, Part I, p 259. Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912.

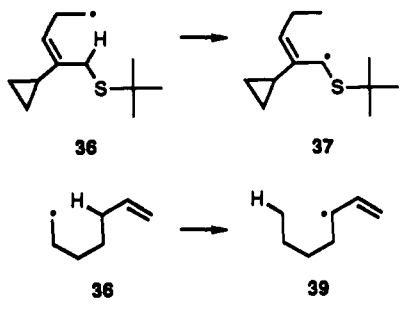
(14) (a) Balderman, D.; Kalir, A. *Synthesis* **1978**, 24. (b) Geneste, P.; Hermann, P.; Kamenka, J. M.; Pons, A. *Bull. Chim. Soc. Fr.* **1975**, 1619.

(15) (a) Stevens, T. E. *J. Org. Chem.* **1961**, *26*, 2531. (b) Nelsen, S. F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 137.

(16) (a) Kropp, P. J.; Krauss, H. J. *J. Org. Chem.* **1967**, *32*, 3222. (b) Rando, R. R.; Doering, W. von E. *J. Org. Chem.* **1968**, *33*, 1671.

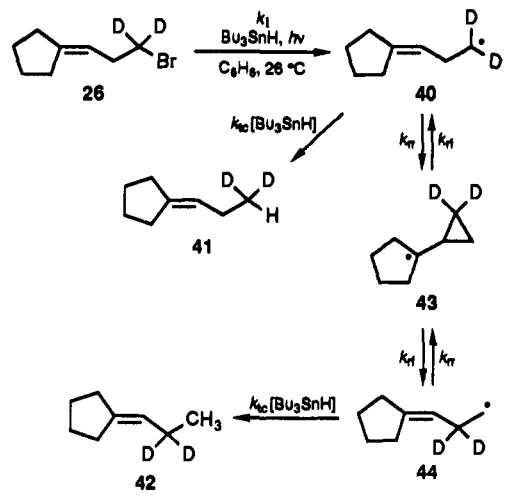
As usual for acyclic azoalkanes, deazatation produces a pair of caged radicals that either disproportionates (k_{dis}) to give **30a** and **31a** or escapes (k_e) from the solvent cage[17] to produce free **10a**. Radicals **10a** may be trapped by thiophenol to afford **30a** or they may rearrange to **34a**, which is also trapped by the thiol. CPC rearrangement within the solvent cage ($k \approx 10^7$ s^{-1}) is much slower than escape ($k \approx 10^{10}$ s^{-1}), so cage disproportionation between **10a** and **34a** is negligible. Recombination of **10a** is also neglected because (1) tertiary radicals disproportionate much more than they recombine,[18] (2) recombination dimer constituted only 2% of the product in the case of tricyclopropylmethyl radicals,[19] (3) recombination and disproportionation outside the solvent cage should be completely inhibited by thiophenol, and (4) the cage effect should be less than 60%, judging by comparison with azo-*tert*-butane.[20]

The presence of **33a** among the products cannot be accommodated by this simple scheme. We first considered the possibility that **34a** underwent a 1,5-hydrogen shift[21-23] to allylic radical **35a**, which abstracted hydrogen from thiophenol to afford **32a** and **33a**. A rate constant of 8×10^4 s^{-1} at 25 °C was reported for the similar rearrangement of **36** to **37**,[24] but the value has been revised upward to 2.7×10^6 s^{-1}.[25] Radical **38**, which has neither a substituent nor the geometric constraint[26] present in **34a**, rearranges to **39** with $k_{1,5} = 500$ s^{-1}.[27] On the basis of these analogies and on a value $k_{ta} = 1.36 \times 10^8$ M^{-1} s^{-1},[28] we estimate that between 0.004 and 17% of **34a** will undergo the 1,5-H shift at 25 °C with 0.1 M thiophenol.



A critical test of the 1,5-H shift was devised upon realizing that this process should become more important with no added thiol since **10a** would then go largely to **34a**, which would rearrange to **35a**. Like other allylic radicals, **35a** should dimerize rather than react with the solvent.[29,30] Photolysis of **16a** at 60 °C in the absence of scavenger gave almost no GC peaks in the region expected for C_{16} hydrocarbons. Because higher temperatures favor all reactions leading to **35a**, a sample of **16a** was thermolyzed in dodecane at 151 °C; however, no GC peaks were present in the C_{16} region. The absence of allylic radical dimers was demonstrated conclusively by synthesizing these compounds from allylic chloride

Scheme VI. Mechanism of Product Formation from **26**



29 (cf. Scheme IV). Capillary GC/MS showed that none of the peaks from the thermolysis of **16a** were dimers of **35a**. Since these dimers were absent under conditions that favor their formation, surely they would not be formed from photolysis of **16a** in the presence of thiophenol. If **34a** does not undergo a 1,5-H shift, then how can we explain the observed **33a** and **33b** (Tables I–III)?

The problem was resolved by a control experiment in which diphenyl disulfide was irradiated with **32a**. The observed buildup of **33a** shows that phenylthiyl radicals[31] are capable of abstracting allylic hydrogen. This result is surprising[32] because phenylthiyl radicals have been used for the geometric isomerization of olefins.[33] Although methylthiyl radicals abstract hydrogen from cyclopentene,[34] phenylthiyl radicals exhibit a rate constant less than 50 M^{-1} s^{-1} for hydrogen abstraction from cumene.[35] The observed positional isomerization, though not very efficient, is favored thermodynamically by the 3 kcal/mol lower heat of formation of an endocyclic versus exocyclic double bond in a five-membered ring.

With a reasonably secure mechanism in hand for all photolysis products, we may proceed to the calculation of T/R. It is first necessary to realize that trapping of **10a** is not the only pathway to **30a** since disproportionation creates one molecule of **30a** for every molecule of **31a**. The amount of **30a** formed by trapping of **10a** with thiophenol must be corrected by subtracting the yield of **31a**. Since **33a** is a secondary product from **32a**, these two compounds must be taken together in calculating T/R. We therefore obtain the ratio of trapped to rearranged products as T/R = [(**30a**) − (**31a**)]/[(**32a**) + (**33a**)].

The effective thiol concentration is lower than that used initially because some of it is consumed by the radicals generated. However, only a fraction of the decomposed azoalkane produces the expected free radicals on account of the cage effect (CE). The numerical value of CE is given by $k_{dis}/(k_{dis} + k_e)$ where k_{dis} and k_e are as shown in Scheme V; moreover, the value of CE can be calculated from our experimental data (Tables I–III) by CE = 2[**31a**]/[[**30a**] + [**31a**] + [**32a**] + [**33a**]]. The cage effects (42, 28, and 35%, respectively) not only are in a reasonable range but show the expected decrease at higher temperature for **16a**.[17,20] We define the effective thiol concentration as the average of its initial and final concentrations, so that $[PhSH]_{ef} = [PhSH]_i - \{[\mathbf{16a}](1 - CE)\}$.

(17) Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973, Vol. I, Chapter 4.
(18) Burshtein, A. I.; Khudyakov, I. V.; Yakobson, B. I. *Prog. React. Kinet.* **1984**, *13*, 221.
(19) Martin, J. C.; Timberlake, J., W. *J. Am. Chem. Soc.* **1970**, *92*, 978.
(20) Tanner, D. D.; Rahimi, P. M. *J. Am. Chem. Soc.* **1982**, *104*, 225.
(21) See ref. 7, p 256.
(22) Carter, W. P. L.; Tardy, D. C. *J. Phys. Chem.* **1974**, *78*, 2201.
(23) Curran, D. P.; Kim, D.; Liu, H. T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900.
(24) Campredon, M.; Kanabus-Kaminska, J. M.; Griller, D. *J. Org. Chem.* **1988**, *53*, 5393.
(25) Newcomb, M.; Glenn, A. G.; Manek, M. B. *J. Org. Chem.* **1989**, *54*, 4603.
(26) Pigou, P. E. *J. Org. Chem.* **1989**, *54*, 4943.
(27) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Chem. Commun.* **1974**, 472.
(28) Franz, J. A.; Bushaw, B. A.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 268.
(29) Korth, H.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.
(30) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 2148.
(31) Pryor, W. *Mechanisms of Sulfur Reactions*; McGraw-Hill: New York, 1962; p 89.
(32) Professor L. A. Paquette has informed us of a similar observation made in his laboratory.
(33) (a) Moussebois, C.; Dale, J. *J. Chem. Soc. C* **1966**, 260. (b) Corey, E. J.; Hamanaka, E. *J. Am. Chem. Soc.* **1967**, *89*, 2758. (c) Gollnick, K.; Schade, G. *Tetrahedron Lett.* **1968**, 689.
(34) Lunazzi, L.; Placuci, G. *J. Chem. Soc. Chem. Commun.* **1979**, 533.
(35) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1815.

CPC Rearrangement Rate of 10a,b

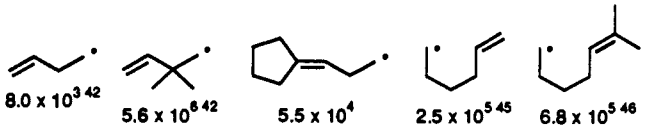
In our earlier use of the free radical clock technique to determine the lifetime of biradicals **2T** and **3T**, their CPC rearrangement rate (k_{rf}) was estimated[36] to be 2.2×10^7 s^{-1} at 25 °C on the basis of the 2.0×10^8 s^{-1} value for unsubstituted CPC radical (the parent system)[37] and the 8.9-fold decrease in the rate of cyclobutylcarbinyl rearrangement caused by α-dimethylation.[38] Since k_{rf} of the parent system has been revised to 9.4×10^7 s^{-1},[39] this approach now predicts k_{rf} for **2T** to be 1.1×10^7 s^{-1}. The present study allows us to evaluate k_{rf} more directly, thus lending greater credibility to the lifetime determination of **2T** and **3T**.

By inspection of Scheme V, it is apparent that k_{rf} is related to T/R as shown in eq 1. Plots of T/R versus $[PhSH]_{ef}$ from Tables I and II turned out to be linear ($r = 0.9986$ and 0.9995) with slopes of 10.15 and 3.86, respectively. From the thiophenol trapping

$$T/R = k_{ta}[PhSH]/k_{rf} \quad (1)$$

rate constant of 1.47×10^8 M^{-1} s^{-1},[28] the value of k_{rf} for **10a** at 24.7 °C was calculated to be 1.45×10^7 s^{-1}. Similar treatment of the data for **10b** (Table III) also gave a linear plot ($r = 0.9991$) with a slope of 13.02, corresponding to $k_{rf} = 1.13 \times 10^7$ s^{-1}. Thus, k_{rf} of **10b** agrees with our original estimate[36] of 1.1×10^7 s^{-1}, and it is close to the value of 7.4×10^6 s^{-1} measured for α,α-dimethylcyclopropylcarbinyl.[40] The CPC rearrangement of the five-membered system **10a** is 1.4 times faster than for its six-membered homologue, suggesting that conformational factors come into play.[41]

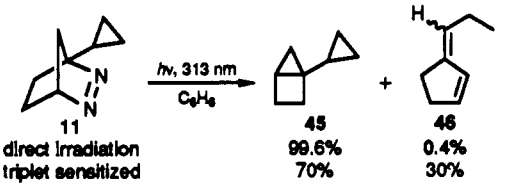
Since the CPC rearrangement rate of **10a** was 6-fold slower than that of the parent system, it seemed likely that the reverse reaction, homoallylic radical closure, might be accelerated. The value of k_{rr} is important for our biradical studies to be described in the following text; moreover, the ring closure rates of only two homoallylic radicals are known: 3-butenyl[37] and 2,2-dimethyl-3-butenyl.[42,43] Reclosure of **34a** to **10a** was investigated by use of the same technique as for the parent system, namely, reaction of dideuterio homoallylic bromide **26** with tributyltin hydride. Products **41** and **42**, which were monitored by ^{2}H NMR, were formed as shown in Scheme VI. Since isotope effects are neglected, there are only four rate constants to be considered: k_i, k_{tc}, k_{rr}, and k_{rf}. The value of k_{rr} can be determined by computer simulation with only one adjustable parameter because k_{tc} (2.4×10^6 M^{-1} s^{-1})[44] and k_{rf} (1.45×10^7 s^{-1}) are known and because the product ratio [**41**]/[**42**] is independent of k_i. Using 0.0533 M Bu_3SnH and 0.0404 M **26** in benzene, we observed [**41**]/[**42**] = 3.62. This figure could be reproduced with $k_{rr} = 5.5 \times 10^4$ s^{-1}, but a 20% uncertainty in the product ratio translates into a 50% error in k_{rr}. Our value of k_{rr} is 7 times faster than closure of the parent homoallyl radical but 100 times slower than that of the 2,2-dimethyl-3-butenyl radical, which benefits greatly from the Thorpe–Ingold effect.[42] Alkyl substitution on the vinyl terminus of the homoallyl radical accelerates closure by a larger factor than in the 5-hexenyl to cyclopentylcarbinyl radical case. Rate constants (s^{-1}, 25 °C) for these cyclizations are summarized immediately below.

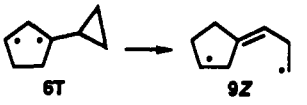


The equilibrium constant (K_e) at 25 °C for opening of **10a** to **34a** can be calculated from our data to be 1.45×10^7 s^{-1}/5.5×10^4 s^{-1} = 260. This value is 46 times smaller than that of the parent CPC radical ($K_e = 9.4 \times 10^7$ s^{-1}/8.0×10^3 s^{-1} = 1.2×10^4), most likely because the tertiary radical center in **10a** is of lower energy than the primary center in 3-butenyl. We are aware of only one other CPC rearrangement whose equilibrium constant is known.[42]

Photolysis of 11

Armed with experimental values of k_{rf} and k_{rr} for **10a**, we may now examine the more complex case of biradicals arising from bicyclic azoalkane **11**. This compound is an ideal photochemical source of triplet biradicals because its UV spectrum (λ_{max} = 346 nm) exhibits a sharp cutoff that allows selective irradiation of triplet sensitizers, because its large excited-state singlet–triplet energy gap ensures that those sensitizers will populate the azoalkane triplet state, and because the latter decomposes with high efficiency.[2a] Direct irradiation of **11** at 313 nm in pentane afforded 99.6% **45** and 0.4% **46*Z*** while triplet-sensitized decomposition (Michler's ketone, 366 nm in fluorobenzene) gave 70% **45** and 30% **46*E*,*Z***. The azoalkane excited singlet state decomposes to nitrogen and **6S** before it undergoes intersystem crossing (ISC) to triplet **11**. Triplet sensitization of **11** populates the azoalkane triplet state, which also loses nitrogen but gives only **6T**. Since closure of **6T** to **45** is spin forbidden, CPC rearrangement diverts a fraction of **6T** to homoallyl radical **9*Z***, which undergoes ISC and intramolecular disproportionation to yield **46Z**. This change in product distribution is a classic example of the spin correlation effect.[2a]





Because singlet biradicals can proceed directly to product without the need for spin inversion, it is no surprise that closure of **6S** to **45** dominates over CPC rearrangement. However, the presence of 0.4% **46*Z*** from direct irradiation of **11** suggests either that (a) **6S** was intercepted by the CPC rearrangement, (b) a small fraction of **6S** underwent ISC to **6T**, or (c) a small fraction of singlet **11** underwent ISC to triplet azoalkane before loss of nitrogen. The last possibility was favored by Buchwalter and Closs, who observed **7T** by ESR upon direct irradiation of DBH at low temperatures.[10]

The unexpected formation of **46*E*** in the sensitized photolysis of **11** was shown to be a secondary process, namely, sensitized isomerization of **46*Z***. At conversions of **11** up to 50%, NMR analysis revealed only **46*Z***. Since dienes are known to be good triplet quenchers, **46*Z*** is better able to compete with **11** for sensitizer triplets later in the reaction. The ratio of the products was found to be constant at conversions from 20 to 100% when

(36) Engel, P. S.; Keys, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 6860. Our original estimate for k_{rf} of **2T** was based on a value for the parent CPC radical that was 70% higher than the one accepted at the time.

(37) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734.

(38) Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 970.

(39) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275.

(40) Burkhard, P.; Roduner, E.; Fischer, H. *Int. J. Chem. Kinet.* **1985**, *17*, 83.

(41) (a) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc. Perkin Trans. 1* **1980**, 1473. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073.

(42) Newcomb, M.; Glenn, A. G.; Williams, W. G. *J. Org. Chem.* **1989**, *54*, 2675.

(43) Chatgilialoglu, C.; Ingold, K. U.; Tse-Sheepy, I.; Warkentin, J. *Can. J. Chem.* **1983**, *61*, 1077.

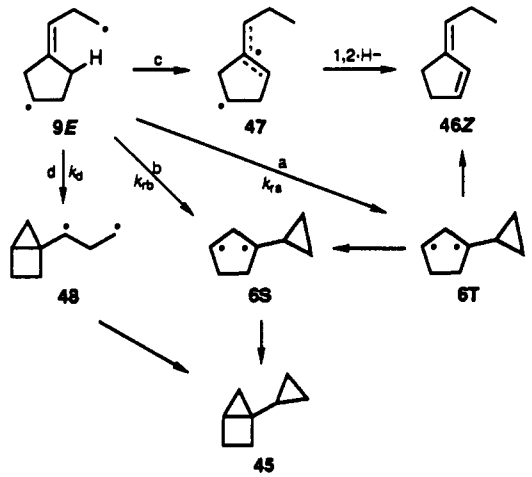
(44) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594.

(45) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739.

(46) Calculated from the relative cyclization rate of 6-methyl-5-heptenyl and 5-hexenyl at 65 °C assuming the same *A* factor for both reactions.[45,47]

(47) Beckwith, A. L. J.; Blair, I. A.; Phillipou, G. *Tetrahedron Lett.* **1974**, 2251.

Scheme VII. Hypothetical Reaction Pathways of **9E**



46Z and **46E** were considered together. Finally, the product balance was at least 94%, leaving little room for other reactions.

Thermolysis of 11

When identical solutions of **11** and DBH were thermolyzed in the same oil bath at 161.6 °C, the substituted azoalkane decomposed 2.97 times faster. This figure is somewhat smaller than the 4.27-fold rate enhancement found in the bicyclooctyl (DBO) system at 230 °C.[53] GC analysis of **11** thermolyzed at 143 °C in 1/1 C_6D_6–toluene-d_8 showed 98% **45**, 0.06% **46**, and a few minor, unidentified peaks. Since the yield of **46** was ~7 times lower than in direct photolysis (vide supra), it is unlikely that **6S** is intercepted by the CPC rearrangement because the perceptible activation energy for this process predicts *more* **46** at higher temperature. We are assuming that **6S** has the same geometry whether produced thermally or photochemically.

Mechanism of Product Formation from 6T

Since **6T** is unsymmetrical, there are two different 1,6-biradicals that might form: **9E** and **9Z**. The latter possesses a favorable geometry for intramolecular 1,5-hydrogen shift, a reaction that should be exothermic by 63 kcal/mol. The fact that **9Z** can give a conjugated diene through a six-membered transition state should accelerate this 1,5-H shift considerably relative to the analogous reaction of **4**, which proceeds with a rate constant of 2.8×10^6 s^{-1}.[8,48]

Biradical **9E** presents a much greater problem since none of its readily imagined reaction pathways (Scheme VII) afford a stable product in one step. Moreover, we observe no product for which **9E** is clearly the only precursor. It follows that either **9E** is not formed from **6T** or one or more of the pathways in Scheme VII converts **9E** to **45** or **46Z**. Path c, the 1,5-hydrogen transfer, is ruled out because it did not occur in monoradical **34a** even under optimum conditions (vide supra). We have probed the other pathways by adding a radical scavenger, 1,4-cyclohexadiene (CHD), to the triplet-sensitized decomposition of **11**. CHD was chosen because it does not interfere with triplet energy transfer from Michler's ketone to **11** and because the trapping rate constants of carbon-centered radicals with this scavenger are known.[49,50] Table IV shows the product yields and ratios obtained from **11** with increasing CHD concentration.

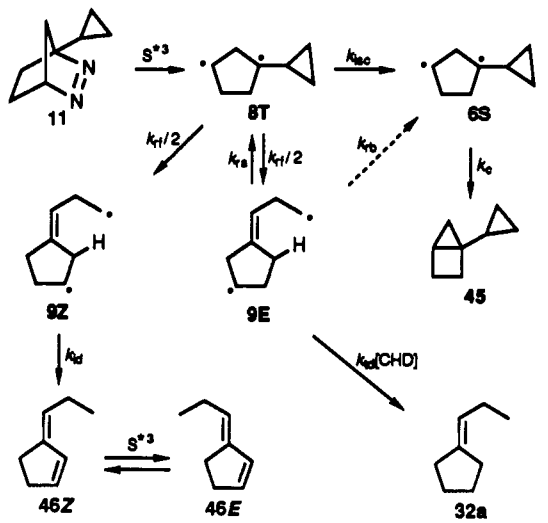
Because CHD is not a rapid hydrogen atom donor (vide infra), the new product **32a** must arise from trapping of a long-lived

Table IV. Product Yields (%) from Triplet-Sensitized Photolysis of **11** at 24.7 °C with Added CHD

[CHD][a]	1/[CHD][b]	32a[c]	45[d]	46[e]	45/46	46/32[f]	bal[g]
0.208	4.80	3.70	67.42	28.88	2.33 ± 0.02	7.82	98.2
0.411	2.43	5.66	66.06	28.28	2.34 ± 0.01	5.00	100
0.614	1.63	7.60	64.82	27.58	2.35 ± 0.06	3.63	100
0.815	1.23	8.86	63.99	27.15	2.36 ± 0.02	3.07	98.3
1.64	0.610	12.94	61.65	25.41	2.43 ± 0.01	1.96	91.8
2.81	0.356	16.22	59.24	24.54	2.41 ± 0.02	1.51	92.5

[a] Concentration in mol/L. [b] $(mol/L)^{-1}$. [c] ±0.14. [d] ±0.83. [e] ±0.33. [f] ±0.50. [g] Total yield of **32a**, **45**, **46**; ±1.0.

Scheme VIII. Triplet-Sensitized Photolysis of **11** Including CHD Trapping



biradical. If this biradical were **9Z**, the ratio **45**/**46** would increase at higher CHD concentration since **9Z** would lie on the pathway to **46** but not **45** (cf. Scheme VIII). Not only is the ratio essentially constant (cf. Table IV and this section), but intramolecular disproportionation (k_{id}) of **9Z** should proceed considerably faster than in **4** (2.8×10^6 s^{-1}, vide supra), so that trapping is most unlikely. Instead, we propose that CHD selectively traps **9E**, which is in pseudoequilibrium with **6T**. This mechanism accounts for the increase in **32a** at the expense of *both* **45** and **46** at higher CHD concentrations.

The lifetime of **9E** can be obtained from eq 2, which is readily derived from Scheme VIII. A plot of [**46**]/[**32a**] versus 1/[CHD] gave a straight line ($r = 0.9955$) with a slope of 1.42 and an intercept of 1.23. This nonzero intercept argues further against **9Z** as the precursor of both **46** and **32a** since the yield of **46** would then have to approach zero at infinite CHD concentration.

$$[\mathbf{46}]/[\mathbf{32a}] = \{(k_{ra} + k_{rb})/k_{td}[CHD]\} + 1 \qquad (2)$$

Although k_{td} has been determined as 5.8×10^4 M^{-1} s^{-1} for ethyl radicals with CHD, this value is only accurate within a factor of 3.[50] We shall instead estimate k_{td} as 1×10^5 M^{-1} s^{-1} by extrapolating the trapping rate constant of 5-hexenyl radicals in benzene at 50 °C (2.3×10^5 M^{-1} S^{-1}) to 25 °C, assuming that E_a is the same as for methyl radicals (5.5 kcal/mol).[50] Although a value of $k_{ra} + k_{rb}$ equal to 1.4×10^5 s^{-1} can now be calculated from eq 2, one more correction remains to be made.

The intercept of our plot according to eq 2 was higher than the expected 1.0, indicating that more **46** than **32a** is produced at infinite CHD concentration. Apparently, **6T** exhibits a slight preference for CPC rearrangement to **9Z** over **9E**. If Scheme VIII is modified to use different values of k_{rf} for the two pathways, we find that the slope in eq 2 equals the intercept times $(k_{ra} + k_{rb})/k_{td}$. It follows that $k_{ra} + k_{rb} = 1.15 \times 10^5$ s^{-1}, corresponding to a lifetime of 9 μs for **9E**.

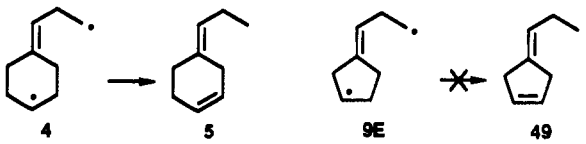
The much longer lifetime of **9E** than **4** ($\tau = 0.36$ μs) is of interest. Biradical **4** undergoes intramolecular disproportionation to **5** despite its relatively strained transition state because this reaction is faster than homoallylic ring closure, which should

(48) Recalculation of the 1,5-H shift rate of **4** with use of the original product distribution[8] and $k_{id} = 1 \times 10^5$ M^{-1} s^{-1} (cf. Scheme VIII) gives 3.0×10^6 s^{-1}. Similarly, if the second CPC rearrangement of **3T** proceeds at the same rate as **10b** (1.1×10^7 s^{-1}), the product distribution[8] leads to a 1,5-H shift rate of 1.4×10^6 s^{-1}. This discrepancy disappears if the value of k_{td} is cut in half.

(49) Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132.

(50) Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kinet.* **1985**, *17*, 1215.

proceed at similar rates in **9E**, **4**, and **34** ($k_{rr} \approx 10^4$–10^5 s^{-1}). On



4 **5** **9E** **49**

the other hand, intramolecular disproportionation of **9E** to give **49** is unfavorable. Since we observed no GC peak that could be assigned to **49**, its formation from **9E** must be at least 10 times slower than ring closure ($k_{rr} = 5.5 \times 10^4$ s^{-1}) and therefore 500 times slower than intramolecular 1,5-H shift of **4** (2.8×10^6 s^{-1}), no doubt because of the highly strained transition state required for **9E** → **49**.

Having established the trapping of **9E** but not **9Z**, we may now use the product distributions in the presence of CHD to evaluate paths a, b, and d in Scheme VII. Paths b and d represent cyclization modes of **9E** to **6S** and **48**, respectively. Since both of these 1,3-biradicals should close rapidly to **45**, k_{rb} is kinetically equivalent to k_d. Either path preceeded by CPC rearrangement of **6T** provides an alternative to the usual ISC mechanism for conversion of **6T** to **45**. Because $k_{ra} + k_{rb}$ of **9E** and k_{rr} of **34a** represent the same reaction, they ought to have the same value. These two rate constants differ by a factor of 2, but the discrepancy can be attributed to experimental error and especially to uncertainty in k_{td}.[48] In order to evaluate k_{rb} individually, we must scrutinize the kinetics of CHD trapping more closely. Equation 3, which is derived from Scheme VIII, predicts that [**45**]/[**46**]

$$[45]/[46] = 2k_{isc}/k_{rf} + k_{rb}/(k_{ra} + k_{rb} + k_{td}[CHD]) \quad (3)$$

should decrease as [CHD] increases, providing that neither k_{ra} nor k_{rb} greatly exceeds k_{td}[CHD]. From $k_{ra} + k_{rb} = 1.15 \times 10^5$ s^{-1}, $k_{td} = 1 \times 10^5$ M^{-1} s^{-1}, and the concentrations of CHD used in our trapping experiments (cf. Table IV), we conclude that $k_{ra} + k_{rb}$ cannot overwhelm k_{td}[CHD] in eq 3. The only way left for eq 3 to accommodate the observed constant ratio **45**/**46** is for k_{rb} and hence k_d to be negligibly small. It should be noted that eq 3 contains a statistical factor of 2 needed to compare **10a** with **6T**.

Although the above argument excludes paths b and d, we note that the latter was unappealing in the first place. Not only does path d involve cyclization to a housane with twice the ring strain of **6S** but it affords a 1°,2° biradical as opposed to the 2°,3° biradical arising from path b. Together, these factors make path d ~24.7 kcal/mol more endothermic than path a, whose reaction free energy is calculated from the equilibrium constant for **10a** ⇌ **34a** ($k_{rf}/k_{rr} = 260$) to be +2.9 kcal/mol. The free energy change of path d is therefore 27.6 kcal/mol, corresponding to an equilibrium constant of 5.8×10^{-21}. If the rate constant for CPC rearrangement of **48** is taken to equal that for **50** ($k_r = 2.4 \times 10^9$ s^{-1}),[51] we calculate that k_d is 1.4×10^{-11} s^{-1}. This value is very much smaller than the 1.15×10^5 s^{-1} we find for k_{ra}, thus rendering path d most unlikely.

50

There remains one pathway from **9E** to **6S** that could evade our kinetic scrutiny. A critical look at Table IV reveals that the ratio **45**/**46**, rather than being absolutely constant, actually *increases* slightly at high CHD concentration. This observation suggests that a small amount of **9Z** might be intercepted by CHD. In fact, a substantial amount of **9Z** might be trapped and yet increase in the **45**/**46** ratio only slightly if there were some other mechanism working to decrease the ratio. A kinetic leak from **9E** to **6S** is such a mechanism. Although we cannot rule out this possibility, it calls for a coincidence of rate constants, it is unnecessarily complicated, and it requires that k_{id} be unexpectedly slow.

Having ruled out paths b–d in Scheme VII, we suggest that Scheme VIII best describes the mechanism of product formation from the sensitized photolysis of **11**. The fact that **9E** arises from a triplet biradical **6T** and then recloses to **6T** but not to **6S** immediately suggests that **9E** is a triplet biradical. However, it is unlikely that **9E** would survive for 9 μs before undergoing ISC on the basis of the shorter lifetime of analogous biradicals.[52] If **9E** is an equilibrium mixture of singlet and triplet, one must say that ring closure of the triplet is greatly favored. Perhaps the fact that **6T** lies 1.6 kcal/mol below **6S** (vide infra) leads to a preference for closure of **9E** to the lower energy spin state.

Lifetime of 6T and 2T

If k_{rb} is neglected, eq 3 simplifies to eq 4, which relates k_{isc} of **6T** to the product ratio (2.34 at 24.7 °C). We assume that k_{rf} equals the rearrangement rate of **10a** (1.45×10^7 s^{-1}) and conclude that the ISC rate of **6T** is 1.7×10^7 s^{-1}, corresponding to a lifetime of 59 ns. This value is half that of **7T** but is not far from the

$$k_{isc} = k_{rf}([45]/[46])/2 \quad (4)$$

42 ns determined for 1,3-dimethyl-1,3-cyclopentanediyl by oxygen trapping.[5] It appears that the cyclopropyl group on a radical center differs little from a methyl group in its ability to shorten the lifetime of **7T**. The free-radical clock technique is therefore validated for cyclopentane-1,3-diyl (**7T**) but not necessarily for cyclohexane-1,4-diyl (**8T**). In the latter case, we can only say that the cyclopropyl group of **2T** greatly slows ISC or that the measured lifetime of **8T** is in error. Perhaps the most revealing experiment would be to determine the lifetime of **2T** or 1-methylcyclohexane-1,4-diyl[53] by the oxygen trapping method.

Since the reaction mechanism of **6T** is reasonably well represented by Scheme VIII, we must inquire whether reversibility of the CPC rearrangement affects the lifetime of the six-membered biradical **2T**. Previously, we estimated that ring opening of **2T** (see the introduction for structures and rate constants) was much faster than reclosure of **4** ($k_1 = 1.3 \times 10^4$ k_{-1}) and intramolecular disproportionation of **4** was much faster than ring closure ($k_2 = 1.6 \times 10^3$ k_{-1}).[8] The ratio of products derived from **2S** (the singlet of **2T**) to **5** is given by $(k_{isc}'/k_1)(1 + (k_{-1} + k_3)/k_2) + k_3/k_2$ where k_{isc}' is the desired ISC rate of **2T**, and k_3 is the rate of **4** → **2S** (analogous to k_{rb} in Scheme VIII). If k_3/k_2 were larger than about 0.05, corresponding to $k_3 > 1.4 \times 10^5$ s^{-1}, our value of k_{isc}' would decrease perceptibly. However, k_{rb} is surely less than 1.15×10^5 s^{-1} as we have already shown, so k_3 can be neglected. With k_3 out of the picture, all of the other quantities are known and a corrected value of k_{isc}' can be calculated from $(18\% + 21\%)/(61\%) = k_{isc}'/(1.13 \times 10^7)(1 + (5.5 \times 10^4/2.8 \times 10^6))$. It follows that $k_{isc}' = 7.09 \times 10^6$ s^{-1} and τ (**2T**) = 141 ns, which is close to the 138 ns given in the introduction. Whereas our original lifetime of **2T** was in error, the problem was the value of k_1, but reversibility of the CPC rearrangement.[9]

Activation Parameters for CPC Rearrangement of 10a and for ISC of 6T

Because the CPC rearrangement rate constant of **10a** is slower than that of the parent system, our activation parameters should differ from the E_a = 7.05 kcal/mol (log A = 13.15) found for the CPC radical itself.[39] Precise rate constants for CPC rearrangement of **10a** at two widely spaced temperatures can be calculated from the data in Tables I and II and the known values of k_{ta}.[28] These values of k_{rf} (1.45×10^7 s^{-1} at 24.7 °C and 4.84×10^7 s^{-1} at 58.5 °C) lead to E_a = 7.0 kcal/mol (log A = 12.3) for rearrangement of **10a** to **34a**.

The activation parameters for ISC of **6T** were determined by competition with the CPC rearrangement. As shown in Table V, a higher temperature during the sensitized decomposition of

(51) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 1927.

(52) Wang, J.; Doubleday, C.; Turro, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 3962.

(53) Engel, P. S.; Nalepa, C. J.; Horsey, D. W.; Keys, D. E.; Grow, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 7102.

Table V. Product Yields (%) from Triplet-Sensitized Photolysis of **11** at Various Temperatures

T, °C	$1/T \times 10^3$	**45**[a]	**46**[b]	ln ([**45**]/[**46**])	bal[c]
3.40	3.62	83.96	16.04	1.66 ± 0.03	93.1
13.70	3.49	77.88	22.12	1.26 ± 0.05	93.7
24.80	3.36	70.12	29.88	0.85 ± 0.07	92.2
41.10	3.18	59.45	40.55	0.38 ± 0.07	93.2
61.00	2.99	48.40	51.60	−0.064 ± 0.02	94.4

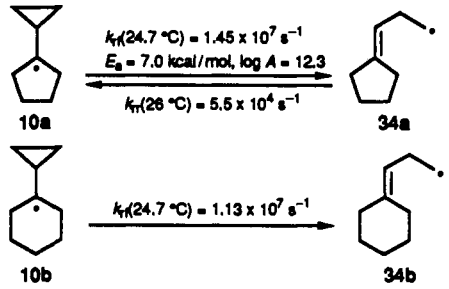
[a] ±0.87. [b] ±0.27. [c] Total yield of **45** and **46**; ±0.65.

11 enhances the formation of rearranged product **46**. Since [**45**]/[**46**] = $2k_{isc}/k_{rf}$, an Arrhenius plot of ln ([**45**]/[**46**]) versus $1/T$ should be linear, with a slope equal to the $[E_{a(rf)} - E_{a(isc)}]/R = \Delta E_a/R$. The plot of the data in Table V was indeed linear (r = 0.9980) with a slope corresponding to ΔE_a = 5.4 kcal/mol. Subtracting this value from E_a for the CPC rearrangement of **10a** (7.0 kcal/mol) gave E_a = 1.6 kcal/mol for ISC of **6T**. The y-intercept of the Arrhenius plot, −8.30, was corrected for ln 2 and log A of the CPC rearrangement, giving log A = 8.4 for ISC of **6T**.

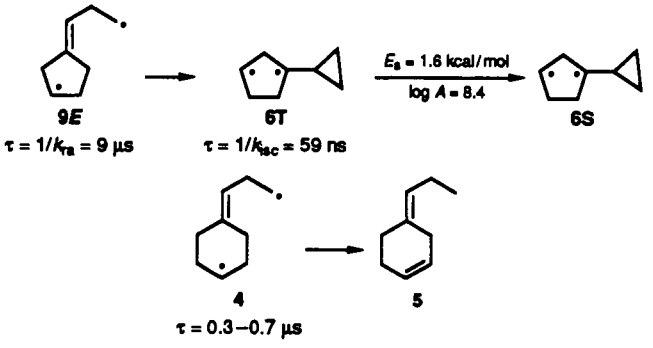
The activation energy determined for ISC of **6T** is very similar to that recently reported for **7T**[10] (1,3-diphenyl-1,3-cyclopentanediyl) and its 2,2-dimethyl substituted analogue,[54] while the low A value for ISC of **6T** is characteristic of the spin-forbidden nature of intersystem crossing.

Conclusions

The cyclopropylcarbinyl rearrangement of **10a** and **10b** has been quantified as summarized below.



The photochemistry of azoalkane **11** shows a spin correlation effect in that direct irradiation affords the housane **45** while triplet sensitization leads to **6T**, which rearranges to **9*E*** and **9*Z***. The lifetime of **6T** is governed by its rate of CPC rearrangement and ISC, while that of **9*E*** depends on its rate of ring closure to **6T**, and τ of **4** is limited by intramolecular disproportionation. Cyclopropyl substitution on a radical center shortens τ of cyclopentane-1,3-diyl by a similar factor as does methyl substitution.



Experimental Section

General Information. NMR spectra were recorded on an IBM AF-300, a Bruker AC-250, or a JEOL FX-90Q spectrometer in $CDCl_3$ or C_6D_6 solvent. Chemical shifts (δ) are referenced against $CHCl_3$ (δ 7.25) or C_6H_6 (δ 7.15). Analytical GC was carried out on an HP5890A gas chromatograph equipped with a DB-5 capillary column (0.25 mm × 30 m) and flame ionization detector. Analytical GC data were collected and manipulated on an IBM PC compatible computer. Conditions for quantitative analysis of hydrocarbon mixtures were as follows: injector temperature (inj) = 180 °C, detector temperature (det) = 250 °C, oven temperature = 35 °C, initial time = 5 min, rate = 10 °C/min. Preparative GC was performed on an Antek 300 with use of the GC columns shown in Table VI. Melting points were determined with a Mel-Temp apparatus and are uncorrected. GC/MS was performed on a Finnigan 3300 spectrometer, while high-resolution mass spectra were obtained on a CEC Du Pont 21-110B spectrometer. UV spectra were obtained on a Cary-17 or HP8452A diode array spectrometer interfaced to a PC. IR spectra were obtained on a Perkin-Elmer 1310 spectrometer.

Table VI. Preparative GC Columns[a]

designation	length, ft	material[b]
A	2	20% UCON 250-X HB (P)
B	18	20% UCON 250-X HB (P)
C	2	10% FFAP (W)
D	6	10% FFAP (W)
E	18	10% FFAP (W)

[a] All columns were 0.25-in. o.d. and contained 60/80-mesh Chromosorb. [b] Percent liquid phase. Type of Chromosorb is indicated in parentheses.

Materials. Ether and THF were distilled from Na/benzophenone, while hexane and oxetane were distilled from sodium. TMEDA was distilled from butyric anhydride and then redistilled from sodium. Trifluoroacetic acid, carbon tetrachloride, methylene chloride, chloroform, benzene, and fluorobenzene were distilled from P_2O_5. 1,4-Cyclohexadiene was passed over neutral, Brockman activity grade 1 alumina just prior to use. Decane (as internal GC standard) was distilled. Thiophenol was distilled immediately before use. Without further purification, tributyltin hydride was degassed and sealed into ampules that were stored in the dark. Pyridine was distilled from KOH, while DMF was distilled from CaH_2. Alkyllithium reagents were titrated by the method of Watson and Eastham.[55] Analytical TLC plates were visualized with a solution of 15 mL of anisaldehyde, 10 mL of concentrated H_2SO_4, 10 mL of HOAc, and 350 mL of absolute EtOH.

Photolyses. Unless otherwise noted, all samples for photolysis were degassed, sealed in 5-mm standard wall Pyrex tubes, and then completely immersed in a thermostated bath at the specified temperature. Irradiations were carried out with a 500-W Oriel high-pressure mercury lamp employing either a K_2CrO_4 (313 nm) or a 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (366-nm) filter solution.

Syntheses. Cyclopropyl Methyl Ketone (2,4,6-Triisopropylbenzenesulfonyl)hydrazone (12). Cyclopropyl methyl ketone (1.15 g, 13 mmol) was added to a stirred solution of (2,4,6-triisopropylbenzenesulfonyl)-hydrazide in 40 mL of THF. The mixture was stirred for 30 min under N_2, and the THF was removed in vacuo, giving a white, amorphous solid. The solid was dissolved in 25 mL of hot MeOH and was reprecipitated by cooling and adding water. After filtration and vacuum drying over P_2O_5, 3.3 g (66%) of **12** was obtained: mp 121–122 °C; 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.66 (m, 5 H), 1.26 (d, 18 H), 1.66 (m, 3 H), 1.86 (sept, 1 H), 4.23 (m, 2 H), 7.16 (s, 3 H). 75-MHz ^{13}C NMR δ 5.29, 6.32, 13.62, 17.91, 23.62, 24.44, 24.87, 29.87, 29.98, 30.07, 34.22, 123.75, 123.82, 124.10, 151.34, 153.18. MS (30 eV), m/e (%) 145 (65), 98 (100), 97 (100), 84 (100), 67 (100).

4-Cyclopropyl-4-penten-1-ol (13). The trisylhydrazone of cyclopropyl methyl ketone (6.4 g, 18 mmol) was dissolved in 64 mL of 50% TMEDA–hexane and cooled to −78 °C under N_2. Dropwise addition of n-butyllithium (18 mL, 40 mmol) led to an intense orange color. Stirring was continued for an additional 15 min, and then the mixture was warmed to 0 °C, resulting in gas evolution. After 15 min, no further gas was evolved and the solution turned clear yellow. Oxetane (0.94 g, 16 mmol) in 25 mL of hexane was added to the ice-cooled solution. After the solution was stirred for several hours, workup was effected by dilution with 225 mL of H_2O and extraction with 3 × 75 mL of ether. The combined ether layers were washed with 0.5 N HCl, H_2O, 0.75 M NaOH, and brine. The ether solution was dried over $MgSO_4$, filtered, and concentrated giving 1.97 g (99%) of product **13**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.39–0.46 (m, 2 H), 0.59–0.66 (m, 2 H), 1.25–1.30 (m, 1 H), 1.77 (quintet, 2 H, J = 6.5 Hz), 2.12 (t, 2 H, J = 7 Hz), 3.66 (t, 2 H, J = 6.5 Hz), 4.62 (s, 1 H), 4.64 (s, 1 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 6.24, 16.01, 31.16, 32.44, 62.85, 106.33, 150.70.

4-Cyclopropyl-4-pentenal (14). Alcohol **13** (0.63 g, 5 mmol) was added to a slurry of 4.7 g of pyridinium dichromate in 35 mL of CH_2Cl_2, and the mixture was stirred overnight. Workup was effected by dilution with ether and filtration through a Celite pad. The ether solution was

(54) Adam, W.; Reinhard, G.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1990**, *112*, 4570.

(55) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.

concentrated to a few milliliters and passed through a plug of silica gel to remove any traces of chromium species. The aldehyde was purified by distillation: yield 43%; bp 74–77 °C (3.4 mm); 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.42–0.47 (m, 2 H), 0.61–0.68 (m, 2 H), 1.23–1.27 (m, 1 H), 2.34 (t, 2 H, J = 7.5 Hz), 2.65 (t, 2 H, J = 7.8 Hz), 4.63 (s, 1 H), 4.66 (s, 1 H), 9.78 (t, 1 H, J = 1.6 Hz); 75-MHz ^{13}C NMR ($CDCl_3$) δ 6.11, 16.6, 28.40, 42.30, 107.14, 149.03, 202.39. MS (30 eV) m/e (%) 124 (5), 109 (28), 95 (30), 82 (60), 67 (100).

4-Cyclopropyl-4-pentenal Tosylhydrazone (15). Aldehyde **14** (0.13 g, 1.0 mmol) was stirred with tosylhydrazide (0.196 g, 1.06 mmol) in MeOH for several hours under nitrogen. The solvent was removed in vacuo, giving a yellow oil. The oil could be purified by chromatography on silica gel (EtOAc–hexane) but was generally used without further purification due to instability and sensitivity to air: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.28–0.62 (m, 4 H), 1.09–1.27 (m, 1 H), 1.91–2.04 (m, 4 H), 2.32 (s, 3 H), 4.61 (m, 2 H), 7.18 (m, 2 H), 7.53 (t, 1 H, J = 9.4 Hz), 7.68 (d, 1 H, J = 9.8 Hz), 7.79 (d, 1 H, J = 9.9 Hz).

1-Cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (11). The crude tosylhydrazone **15** was taken up in CH_2Cl_2 and was stirred over molecular sieves for 1 h under nitrogen. This CH_2Cl_2 solution was added dropwise to a flask containing BF_3·Et_2O (0.31 g, 2.6 mmol) cooled in an ice/salt bath. Stirring was continued, and the reaction was warmed to room temperature. Workup consisted of dilution with 1 M K_2CO_3 and extraction with CH_2Cl_2. The combined CH_2Cl_2 phases were dried over $MgSO_4$, filtered, and concentrated by careful distillation through a short Vigreux column. The crude azoalkane was purified by GC on column C: inj = 150 °C, oven = 150 °C, det = 160 °C, flow = 30 mL/min; 300-MHz ^{1}H NMR (C_6D_6) δ 0.33 (d, 1 H), 0.40–0.56 (m, 4 H), 0.58–0.83 (m, 3 H), 0.83–1.0 (m, 2 H), 1.23–1.35 (m, 1 H), 4.63 (br s, 1 H); 75-MHz ^{13}C NMR ($CDCl_3$) 2.34, 11.25, 22.44, 24.64, 42.81, 76.58; MS (30 eV), m/e (%) 107 (20), 93 (50), 91 (35), 80 (80), 79 (100), 77 (52), 67 (100); UV (hexane) λ_{max} 346 nm, ε 182.

1-Cyclopropylcyclopentanol (19a).[56] A 500-mL, three-neck, round-bottom flask equipped with a stirring bar, nitrogen inlet, and a 100-mL pressure-equalized addition funnel was charged with a solution of 7.67 g (63 mmol) of cyclopropyl bromide in 100 mL of ether. A serum stopper was inserted in the top of the addition funnel and was secured by a wire. The cyclopropyl bromide solution was cooled to −78 °C under nitrogen, and then 38 mL (62 mmol) of *tert*-butyllithium (1.6 M in pentane), which had been delivered to the addition funnel via cannula, was added dropwise to the cyclopropyl bromide solution, followed by 80 mL of ether. After the mixture had stirred for 1 h at −78 °C, cyclopentanone (84 g, 62 mmol) in 80 mL of ether was added dropwise at −78 °C. The solution was kept at −78 °C for 4 h and was then allowed to warm to room temperature over the course of 2–3 h. The reaction was quenched with 80 mL of H_2O, and the water layer was extracted once with ether. The combined ether layers were dried over $MgSO_4$, filtered, and rotary evaporated: yield 7.8 g (94%); 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.25–0.50 (m, 4 H), 0.80–1.30 (m, 1 H), 1.4–2.0 (m, 9 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 1.32, 19.95, 23.72, 38.35, 82.12; MS (30 eV) m/e (%) 126 (3), 109 (5), 98 (87), 97 (100), 84 (37), 83 (36), 70 (25), 69 (38), 55 (29).

1-Cyclopropylcyclopentylazide (20a). A 3.5-g (54-mmol) portion of NaN_3, 4 mL (53 mmol) of CF_3COOH, and 26 mL of $CHCl_3$ were placed in a 50-mL three-neck, round-bottom flask equipped with a mechanical stirrer and a 50-mL addition funnel. To the mixture, which was cooled in an ice/salt bath, was added a solution of 3.32 g (27 mmol) of 1-cyclopropylcyclopentanol in $CHCl_3$ with stirring under nitrogen. Stirring was continued for 4 h as the solution rose to ambient temperature. A 25-mL portion of concentrated NH_4OH was added, and the $CHCl_3$ layer was separated and washed twice with 20 mL of H_2O. The organic layer was dried over $MgSO_4$, filtered, and rotary evaporated to yield 3.6 g (91%) of the desired azide:[14] 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.20–0.40 (m, 4 H), 1.00–1.40 (m, 1 H), 1.40–1.90 (m, 8 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 1.32, 17.91, 23.58, 35.28; IR (CCl_4, cm^{-1}) 2090.

1-Cyclopropylcyclopentylamine (21a). The azide **20a** obtained previously was dissolved in 25 mL of ether and added dropwise to a slurry of 1.8 g (47 mmol) of LAH in 30 mL of ether under nitrogen.[57] The reaction was stirred for ~12 h and then refluxed for 1 h. Workup consisted of careful addition of H_2O to the room-temperature solution until gas evolution ceased. The ether layer was decanted, and the remaining solids were washed with 75 mL of ether. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated by rotoevaporation, giving 2.5 g (82%) of the desired amine: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.178–0.194 (d, 2 H), 0.328–0.354 (d, 2 H), 0.866–0.958 (m, 1 H), 1.18–1.91 (m, 10 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 1.04, 21.57, 24.03, 38.91, 60.10; MS (30 eV) m/e (%) 125 (28), 110 (13), 96 (100), 82 (100), 69 (41).

Azo-1-cyclopropylcyclopentane (16a). A 50-mL, three-neck, round-bottom flask equipped with a 10-mL addition funnel and a stir bar was charged with 3.0 mL (8.5 mmol) of a 2.8 M IF_5–CH_2Cl_2 solution.[15] A 1.7-g (22.1-mmol) portion of pyridine was added, and the flask was cooled in a dry ice/CCl_4 bath under nitrogen. A solution of 1.3 g (10.2 mmol) of 1-cyclopropylcyclopentylamine in CH_2Cl_2 was added dropwise to the cooled IF_5 solution. The reaction was stirred at −20 to −10 °C for 1 h and then at −10 to 0 °C for 1 h. After addition of 23 mL of H_2O, the organic layer was washed successively with 20 mL of 1 N HCl, 2 × 12 mL of 0.1 M $Na_2S_2O_3$, and 20 mL of H_2O. The organic phase was dried over $MgSO_4$, filtered, and concentrated on a rotovap. The crude product was column chromatographed on 10 g of neutral alumina with hexane elution: yield 24%; 300-MHz ^{1}H NMR (C_6D_6) δ 0.22–0.40 (m, 8 H), 1.00–1.15 (m, 2 H), 1.30–1.50 (m, 12 H), 2.15–2.25 (m, 4 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 0.818, 18.26, 24.18, 33.57, 80.28; HRMS calcd for $C_{16}H_{26}N_2$ 246.20959, found 246.21002; UV (hexane) λ_{max} 374 nm, ε 20.

1-Cyclopropylcyclohexanol (19b).[56] The compound was prepared in the same manner as **19a**, starting with 1.79 g (14.8 mmol) of cyclopropyl bromide, 8 mL (13.6 mmol) of 1.7 M *tert*-butyllithium–pentane, and 1.30 g (13.3 mmol) of cyclohexanone. A 1.09-g (59%) portion of the desired alcohol was obtained: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.30–0.33 (m, 4 H), 0.85–0.93 (m, 2 H), 1.19–1.59 (m, 10 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 0.38, 21.88, 22.05, 25.99, 37.32; MS (30 eV) m/e (%) 140 (9), 123 (5), 112 (25), 97 (100), 84 (28), 55 (35).

1-Cyclopropylcyclohexyl Azide (20b). The compound was prepared in the same manner as **20a** from 0.33 g (2.3 mmol) of **19b**, 0.38 g (5.8 mmol) of NaN_3, and 0.4 mL of CF_3COOH:[14] yield 91%; 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.38–0.53 (d, 4 H), 0.70–2.60 (m, 11 H); IR (CCl_4, cm^{-1}) 2900, 2480, 2065.

1-Cyclopropylcyclohexylamine (21b). The compound was prepared in the same manner as **21a** from 0.26 g (1.6 mmol) of **20b** and 0.22 g (5.8 mmol) of LAH:[57] 250-MHz ^{1}H NMR ($CDCl_3$) δ 0.24–0.28 (m, 4 H), 0.79–0.90 (m, 3 H), 1.19–1.54 (m, 10 H); 65-MHz ^{13}C NMR ($CDCl_3$) δ −0.45, 21.92, 22.45, 26.07, 38.05, 48.90; MS (30 eV) m/e (%) 139 (17), 124 (12), 110 (15), 95 (100), 83 (33), 68 (12).

Azo-1-cyclopropylcyclohexane (16b). The compound was prepared in the same manner as **16a** from 2.88 g (20.4 mmol) of **21b**, 1 mL (16.9 mmol) of IF_5, and 3.51 g (44.4 mmol) of pyridine.[15] The crude product was column chromatographed on 30 g of neutral alumina with hexane elution to give 0.27 g of solid product that was recrystallized from methanol: mp 46–48 °C; yield 11%; 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.22–0.34 (m, 8 H); 0.92–0.97 (m 2 H); 1.25–1.43 (m, 12 H); 1.48–1.54 (m, 4 H); 1.90–1.95 (m, 4 H); 75-MHz ^{13}C NMR ($CDCl_3$) δ 0.039, 20.04, 22.25, 26.14, 33.23, 68.48; HRMS calcd for $C_{18}H_{30}N_2$ 274.24089, found 274.24111; UV (hexane) λ_{max} 384 nm, ε 25.

Ethyl 3-Cyclopentylidenepropanoate (23).[58] The nonconjugated ester was prepared by 254-nm irradiation of ethyl 3-cyclopentylpropenoate (**22**)[59] (0.95 g, 5.7 mmol) in 47 mL of dry pentane in a 2.3-cm-diameter quartz tube under nitrogen. The reaction was followed by capillary GC under the conditions used for hydrocarbon analysis described in General Information. Approximately 20 h of irradiation time was required to complete the photoisomerization: 250-MHz ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 6.8 Hz), 1.56–1.68 (m, 4 H), 2.17 (br t, 2 H), 2.25 (br t, 2 H), 2.98 (dd, 2 H, J = 6.0 Hz, J = 1.0 Hz), 4.11 (q, 2 H, J = 7.2 Hz), 5.4 (br s, 1 H); 63-MHz ^{13}C NMR ($CDCl_3$) δ 14.30, 26.30, 26.50, 29.0, 33.70, 35.30, 60.50, 111.5, 147.4, 172.6; MS (30 eV) m/e (%) 168 (88), 140 (68), 123 (100), 122 (51), 95 (69), 94 (100), 93 (67).

3-Cyclopentylidene[1,1-^{2}H]-1-propanol (24). The dideuterated alcohol was prepared by reduction of **23** (0.93 g, 5.5 mmol) with excess $LiAlD_4$ in ether. The product was isolated by careful dilution with H_2O, filtration, and concentration. The alcohol was distilled at 1 mm in a molecular still, giving 0.41 g (58%) of the desired product: 300-MHz ^{1}H NMR (C_6D_6) δ 1.44–1.65 (m, 5 H), 2.08–2.21 (m, 6 H), 5.09–5.15 (m, 1 H); 46-MHz ^{2}H NMR (C_6D_6) δ 3.40 (br s); 75-MHz ^{13}C (C_6D_6) δ 26.36, 26.42, 28.93, 33.02, 33.78, 115.4, 147.2; MS (30 eV) m/e (%) 125 (35), 95 (100), 93 (61), 67 (40).

3-Cyclopentylidene[1,1-^{2}H]-1-propanol, Tosyl Ester (25). A (0.42 g, 3.2 mmol) portion of alcohol **24** was added to an ice/salt cooled solution of tosyl chloride (0.84 g, 4.4 mmol) in 4 mL of pyridine. A white precipitate formed after 30 min, but stirring was continued until TLC showed the reaction to be complete (~2 h). Workup was effected by

(56) Traas, P. C.; Boelens, H.; Takken, H. J. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 57.

(57) Procedure adapted from: Timberlake, J. W.; Alender, J.; Garner, A.; Hodges, M. L.; Ozmeral, H.; Szilagyi, S. *J. Org. Chem.* **1981**, *46*, 2082.

(58) Gerkin, R. M.; Rickborn, B. *J. Am. Chem. Soc.* **1967**, *89*, 5850.

(59) Prepared by the method used for the six-membered homolog according to: Wadsworth, W. S.; Emmons, W. D. *Organic Syntheses*; Wiley: New York, Collect. Vol. V, p 547.

addition of 40 mL of H_2O and extraction with CH_2Cl_2. The CH_2Cl_2 layers were combined and extracted with 2 N HCl until the washings were acidic and then dried over K_2CO_3, filtered, and concentrated on a rotovap to give 0.64 g (71%) of the desired tosylate: 300-MHz ^1H NMR ($CDCl_3$) δ 1.50–1.66 (m, 4 H), 2.05–2.28 (m, 6 H), 2.43 (s, 3 H), 5.02–5.09 (m, 1 H), 7.31 (d, 2 H, J = 8.1 Hz), 7.83 (d, 2 H, J = 8.2 Hz); 75-MHz ^{13}C ($CDCl_3$) 21.71, 26.28, 26.37, 28.79, 29.23, 33.71, 113.2, 128.0, 133.4, 144.7, 147.6; MS (30 eV) m/e (%) 155 (23), 109 (100), 95 (49), 93 (58), 91 (84).

1-Bromo-3-cyclopentylidene-1,1-dideuteriopropane (26). Tosylate **25** (0.63 g, 2.2 mmol) was stirred with NaBr (0.33 g, 3.2 mmol) in 7 mL of DMF for 2 days, at which time TLC (SiO_2, 20% EtOAc/hexane) showed complete reaction. The mixture was worked up by addition of 100 mL of H_2O and extraction with ether. The ether solution was washed with H_2O, dried over $MgSO_4$, filtered, and concentrated on a rotovap. The crude bromide was chromatographed on 12 g of silica gel with hexane eluent to afford 0.43 g (100%) of the bromide **26**; 300-MHz ^1H NMR (C_6D_6) 1.35–1.53 (m, 4 H), 1.93 (br t, 2 H, J = 6.7 Hz), 2.11 (br t, 2 H, J = 5.5 Hz), 2.26 (d, 2 H, J = 7 Hz), 5.06–5.11 (m, 1 H); 46-MHz ^2H NMR (C_6H_6) 2.93 (br s); 75-MHz ^{13}C (C_6D_6) δ 26.47, 26.55, 28.83, 33.27, 33.81, 116.97, 146.26; MS (30 eV) m/e (%) 192 (100), 190 (100), 111 (38), 81 (58), 67 (38).

Cyclopentanone (2,4,6-Triisopropylbenzenesulfonyl)hydrazone (27).[60] To a solution of 1.90 g (23 mmol) of distilled cyclopentanone in 50 mL of dry THF was added 6.9 g (23 mmol) of solid 2,4,6-triisopropylbenzenesulfonyl)hydrazide. The mixture was stirred at room temperature for 30 min. The THF was removed under vacuum, and the residual solid was recrystallized by dissolution in warm methanol, cooling in ice, and addition of water. The pure product (5.8 g, 70%) was collected by suction and dried under vacuum: mp 125–130 °C dec (lit.[60] mp 133–134 °C dec); 90-MHz ^1H NMR ($CDCl_3$) δ 1.25 (d, 18 H), 1.80 (br s, 4 H), 2.00–2.50 (m, 4 H), 2.95 (sept, 1 H), 4.30 (sept, 2 H), 7.10 (s, 3 H, NH and arom H's).

1-Cyclopentenyl-1-propanol (28).[61] A solution of 2.7 g (7.4 mmol) of **27** in 27 mL of dry 50% TMEDA–hexane solution was cooled to −78 °C under nitrogen, and 6.5 mL of 2.2 M *n*-BuLi–hexane was added dropwise. The resulting dark orange solution was stirred for 15 min, and then the cooling bath was replaced with an ice bath. As the solution warmed, gas was evolved and the solution became less cloudy. Gas evolution was complete after 15 min, and the solution was recooled to −78 °C. Freshly distilled propionaldehyde (0.77 g, 13 mmol) was added in 6 mL of dry hexane. The mixture was stirred for 30 min at −78 °C and warmed to 0 °C for 15 min and then to room temperature for 30 min. Workup was accomplished by addition of 75 mL of water and extraction with ether. The combined ether layers were washed with 1 N HCl and three times with water. The organic layer was dried over $MgSO_4$, filtered, and rotary evaporated to afford **28** (0.72 g, 77%). A portion of the product was purified by preparative GC (column C, inj = 185 °C, oven = 125 °C, det = 165 °C): 300-MHz ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.4 Hz), 1.60 (m, 3 H), 2.27 (quint, 2 H, J = 7.4), 2.34 (br m, 4 H), 4.18 (t, 1 H, J = 6.3 Hz), 5.58 (br d, 1 H, J = 1.1 Hz); 75-MHz ^{13}C NMR ($CDCl_3$) δ 9.89, 23.46, 28.46, 31.09, 32.23, 72.83, 125.65, 146.96; MS (30 eV) m/e (%) 126 (58), 97 (100), 79 (61, 69 (56), 67 (62), 57 (17), 55 (18); HRMS calcd for $C_8H_{14}O$ 126.10446, found 126.10475.

1-Cyclopentenyl-1-chloropropane (29). A solution of 1.17 g (4.5 mmol) of triphenylphosphine, 0.44 g (3.5 mmol) of **28**, and 0.25 mL of nonane as an internal standard in 5 mL of dry CCl_4 was heated under nitrogen in a 75 °C oil bath. According to GC, the reaction required ~15 h. The CCl_4 was removed under vacuum, the remaining solids were rinsed from the reaction flask with hexane, and the heterogeneous mixture was filtered through a Celite pad. The filtrate was extracted with water, and the organic layer was dried over $MgSO_4$, filtered, and concentrated to give 0.31 g (62%) of **29**. A small sample was collected by preparative GC (column C, inj = 185 °C, oven = 100 °C, det = 155 °C): 300-MHz ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 7.3), 1.88 (m, 4 H), 2.35 (br m, 4 H), 4.50 (t, 1 H, J = 6.3), 5.69 (d, 1 H, J = 1.9); 75-MHz ^{13}C NMR ($CDCl_3$) δ 11.65, 23.30, 30.34, 30.94, 32.35, 63.37, 128.67, (4° carbon not visible); MS (30 eV) m/e (%) 146 (3), 144 (10), 109 (59), 108 (65), 93 (100), 91 (57), 79 (70), 77 (65), 67 (72); HRMS calcd for $C_8H_{13}Cl$ 144.07058, found 144.07024.

Synthesis of Authentic Allylic Radical Dimers. A 94-mg portion of lithium dispersion with 1% Na (30% in mineral oil) under an argon atmosphere was washed twice with 5-mL portions of dry THF. A solution of 0.46 g (3.2 mmol) of **29** in 5 mL of dry THF was added to the lithium, and the mixture was immersed up to the solvent line in a laboratory ultrasonic cleaner. After 1 h of sonication and mechanical stirring under argon, the initially gray suspension had become orange. Capillary GC analysis after 2 h showed complete disappearance of the starting allylic chloride. The reaction was worked up by careful dilution with water, and addition of a small amount of saturated aqueous NH_4Cl. The mixture was extracted three times with hexane and dried over $MgSO_4$. The resulting solution was concentrated to 5 mL by short-path distillation. GC/MS analysis showed the presence of *n*-propylcyclopentene, propylidenecyclopentane, and numerous dimers from the resulting allylic radicals. A typical fragmentation pattern for these dimers was m/e (%) 218 (6), 189 (13), 109 (93), 108 (100), 93 (58), 67 (65).

PhSH Trapping Studies of Radicals 10a,b. 16a. Six solutions of 0.0187 M azoalkane, 0.0214 M decane (internal standard), and PhSH in C_6H_5F were prepared for photolysis at 366 nm. The concentrations of PhSH were 0.0322, 0.0397, 0.0585, 0.1299, 0.2342, and 0.2938 M. Irradiation was carried out for 35 min at 24.7 °C. Capillary GC analysis of the hydrocarbon product mixtures gave the results listed in Table I. A similar experiment at 58.5 °C employed azoalkane and decane concentrations of 0.0103 and 2.61 × 10^{-3} M, respectively. The thiol concentrations were 0.0388, 0.0451, 0.0681, 0.1443, 0.2269, and 0.3251 M. Results are given in Table II.

16b. An experiment similar to that with **16a** was carried out at 25.0 °C. The concentrations of azoalkane and decane were 0.0142 and 3.40 × 10^{-3} M, respectively, while the PhSH was 0.0388, 0.0451, 0.0681, 0.1181, 0.2017, and 0.3126 M. Results are given in Table III.

Deuterium Scrambling Experiments on 3-Cyclopentylidene[1,1-^2H]-1-bromopropane. A solution of 0.0404 M bromide **26**, 0.0139 M C_6D_6, and 0.0533 M Bu_3SnH was prepared in C_6H_6, degassed, and sealed in a 5-mm NMR tube. The solution was irradiated with a sun lamp at 26 °C and was followed by ^2H NMR. The bromide signal at 2.9 ppm disappeared as two new signals at 0.93 and 1.9 ppm grew in. The new signals represent propylidenecyclopentane deuterated at either the homoallylic (**41**) or allylic (**42**) position, respectively. The ratio of signals upon complete reaction of the bromide was 3.65/1.

Identification of Products from the Triplet-Sensitized Photolysis of 1-Cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene. Approximately 100 mg of **11** isolated by preparative GC (column E) and 5.4 mg of xanthone in 0.5 mL of pentane were photolyzed at 366 nm until complete disappearance of the azoalkane was observed by GC (column E, inj = 130 °C, oven = 177 °C, det = 173 °C). The photoproducts were separated and collected by preparative GC (column B, inj = 191 °C, oven = 177 °C, det = 171 °C, flow = 46 mL/min).

1-Cyclopropylbicyclo[2.1.0]pentane: 300-MHz ^1H NMR ($CDCl_3$) δ −0.17 to −0.14 (m, 1 H), 0.11–0.16 (m, 1 H), 0.27–0.50 (m, 3 H), 0.51–0.53 (m, 1 H), 0.99–1.05 (m, 1 H), 1.22–1.35 (m, 1 H), 1.35–1.45 (m, 1 H), 1.45–1.58 (m, 1 H), 1.93 (d, 2 H, J = 1.7 Hz); 75-MHz ^{13}C ($CDCl_3$) δ 2.56, 3.24, 12.61, 16.64, 19.91, 21.41, 26.07, quaternary carbon not visible; MS (30 eV) m/e (%) 93 (45), 91 (48), 80 (46), 79 (100), 77 (42), 67 (13).

(*Z*)**-3-Propylidenecyclopentene**: 300-MHz ^1H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 6.6 Hz), 2.05–2.25 (m, 2 H), 2.50 (br s, 4 H), 5.14 (t, 1 H, J = 7.2 Hz), 6.08 (br s, 1 H), 6.38 (d, 1 H, J = 2.7 Hz); 75-MHz ^{13}C ($CDCl_3$) δ 14.61, 22.26, 28.90, 31.04, 119.6, 129.7, 137.5, 4 °C not visible; MS (30 eV) m/e (%) 108 (10), 93 (100), 91 (40).

(*E*)**-3-Propylidenecyclopentene**: 300-MHz ^1H NMR ($CDCl_3$) δ 0.98 (t, 3 H, J = 5.4 Hz), 2.05 (br s, 2 H), 2.50 (br s, 4 H), 5.30 (t, 1 H, J = 7.2 Hz), 5.98 (t, 1 H, J = 2.5 Hz), 6.12 (d, 1 H, J = 5.5 Hz); 75-MHz ^{13}C ($CDCl_3$) δ 14.10, 22.86, 25.68, 31.92, 121.2, 134.5, 135.88, quaternary C not visible; MS (30 eV) m/e (%) 108 (10), 93 (100), 91 (40).

Direct Irradiation of 11. A sample of 0.0175 M **11** in pentane at 23 °C was irradiated at 313 nm for 20 min. Capillary GC analysis showed the products to be 99.6% 1-cyclopropylbicyclo[2.1.0]pentane (**45**) and 0.4% 3-propylidenecyclopentene (**46**).

Triplet-Sensitized Photolysis of 11. A solution of 0.05515 M **11**, 0.0539 M decane (internal standard), and 2.325 × 10^{-3} M Michler's ketone (triplet sensitizer) in fluorobenzene was prepared. Seven aliquots of this solution were irradiated at 366 nm and 43.8–44.0 °C for varying periods of time to ensure that product ratios did not vary with the duration of photolysis. The results are given in Table VII.

Table VII. Product Ratios in the Triplet Sensitized Photolysis of **11**

time, min	% conversion[a]	[45]/[46][b]	bal[c]
1	20.3	1.38	95.1
2	33.3	1.36	93.5
5	74.0	1.36	96.1
16	80.0	1.36	95.5
30	98.0	1.35	93.6
55	100	1.36	93.9

[a] Percent azoalkane reacted. [b] ±0.02. [c] Total yield of **45** and **46**.

(60) Baba, T.; Avasthi, K.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1571.

(61) Gocmen, M.; Soussan, G.; Freon, P. *Bull. Soc. Chim. Fr.* **1973**, 1310.

The remaining samples were irradiated at 366 nm for a period of 1 h at various temperatures. The product mixtures were analyzed by capillary GC, and the results are given in Table V.

Thermolysis of 11. Degassed, sealed NMR samples of DBH and **11** in toluene-d_8 were thermolyzed simultaneously at 161.6 °C. The disappearance of azoalkane bridgehead hydrogen(s) was followed by NMR with the solvent aromatic protons as a standard. Plots of ln of the corrected peak area versus time were linear with slopes of -1.59×10^{-4} s^{-1} ($r = -0.9982$) for DBH and -4.72×10^{-4} s^{-1} ($r = -0.9988$) for **11**.

A degassed, sealed NMR sample of **11** was thermolyzed in a 1/1 mixture of toluene-d_8 and benzene-d_6 at 143 °C. Product analyses under the standard conditions showed 98% **45** and 0.06% **46**.

Biradical Trapping with CHD. Six solutions of 0.0542 M azoalkane **11**, 0.0392 M decane, 4.57×10^{-3} M Michler's ketone, and 1,4-cyclohexadiene in C_6H_5F were prepared. The concentrations of CHD were 0.2082, 0.4116, 0.6140, 0.8048, 1.604, and 2.806 M. The solutions were irradiated at 366 nm and 24.7 °C for 1 h. The products were analyzed by capillary GC, giving the results in Table IV.

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Supplementary Material Available: Synthesis and spectral properties of authentic hydrocarbons **30a-33a** and **30b-33b** (5 pages). Ordering information is given on any current masthead page.

Cooxidation Reaction in the Singlet Oxygenation of Cyclic and Benzylic Sulfides: *S*-Hydroperoxysulfonium Ylide Intermediate As a New Epoxidizing Species

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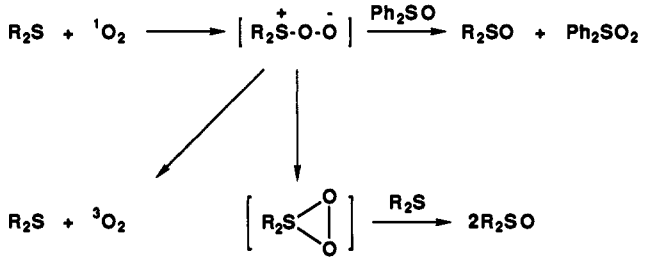
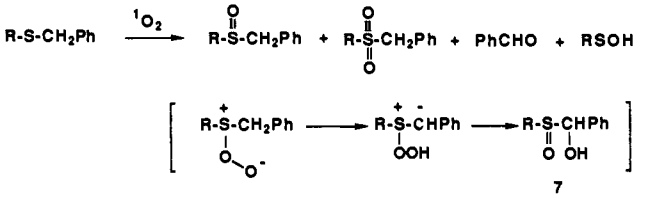
Abstract: The reaction of singlet oxygen with a series of 3-benzoyl-4-(methoxycarbonyl)thiazolidine derivatives and alkyl benzyl sulfides in methylene chloride in the presence of olefins has been investigated. The reaction of singlet oxygen with the sulfides caused cooxidation of olefins to the corresponding epoxides in substantial yields. The epoxidation of olefins by the active oxidizing species generated in photosensitized oxygenation of the sulfides is provided, suggesting that the new epoxidizing species is probably the *S*-hydroperoxysulfonium ylide intermediate derived from a persulfoxide intermediate by intramolecular α-proton abstraction.

The photooxidation of sulfides continues to yield fascinating results. In the past more than two decades, the reactions of singlet oxygen ($^1O_2$) with a wide variety of sulfur-containing compounds including sulfides[1-9] and disulfides[10] have been reported. Since some of the naturally occurring sulfur compounds isolated so far have sulfur-oxygen bonds, these S-oxidation products can play important roles in biochemical reactions.[11] For instance, me-

Scheme I



Scheme II



(1) For reviews, see: Ando, W.; Takata, T. In *Singlet O_2*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 3, Chapter 1, p 1 and references cited therein.

(2) (a) Schenck, G. O.; Krausch, C. H. *Angew. Chem.* **1962**, *74*, 510. (b) Schenck, G. O.; Krausch, C. H. *Chem. Ber.* **1963**, *96*, 517. (c) Krausch, C. H.; Hess, D.; Schenck, G. O. Unpublished results quoted by Gollnick (Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1).

(3) (a) Foote, C. S.; Denny, R. W.; Weaver, L.; Chang, Y.; Peters, J. W. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 139. (b) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (c) Foote, C. S.; Peters, J. W. *IUPAC Congr., 23rd, Spec. Lect.* **1971**, *4*, 129. (d) Kacher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *26*, 765. (e) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 5949. (f) Gu, C.-L.; Foote, C. S. *Ibid.* **1982**, *104*, 6060. (g) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *Ibid.* **1983**, *105*, 4717. (h) Jensen, F.; Foote, C. S. *Ibid.* **1987**, *109*, 1478. (i) Foote, C. S.; Jensen, F. *Ibid.* **1988**, *110*, 2368.

(4) (a) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191. (b) Ando, W.; Kabe, Y.; Kobayashi, S.; Takyu, C.; Yamagishi, A.; Inaba, H. *J. Am. Chem. Soc.* **1980**, *102*, 4526. (c) Ando, W.; Miyazaki, H.; Akasaka, T. *Tetrahedron Lett.* **1982**, *23*, 2655. (d) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203. (e) Takata, T.; Tamura, Y.; Ando, W. *Tetrahedron* **1985**, *41*, 2133. (f) Akasaka, T.; Ando, W. *Tetrahedron Lett.* **1985**, *26*, 5049. (g) Ando, W.; Sonobe, H.; Akasaka, T. *Ibid.* **1986**, *27*, 4473. (h) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085. (i) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *Ibid.* **1988**, *110*, 494.

(5) (a) Skold, C. N.; Schlessinger, R. H. *Tetrahedron Lett.* **1970**, 791. (b) Wasserman, H. H.; Strehlow, W. *Ibid.* **1970**, 795. (c) Murray, R. W.; Jindal, S. L. *Photochem. Photobiol.* **1972**, *16*, 147. (d) Casagrande, M.; Gennari, G.; Cauzzo, G. *Gazz. Chim. Ital.* **1974**, *104*, 1251. (e) Stary, F. E.; Jindal, S. L.; Murray, R. W. *J. Org. Chem.* **1975**, *40*, 58. (f) Cauzzo, G.; Gennari, G.; Da Re, F.; Curci, R. *Gazz. Chim. Ital.* **1979**, *109*, 541. (g) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761.

(6) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947.

(7) (a) Sinnreich, D.; Lind, H.; Batzer, H. *Tetrahedron Lett.* **1976**, 3541. (b) Tezuka, T.; Miyazaki, H.; Suzuki, H. *Ibid.* **1978**, 1959.

(8) Correa, P. E.; Riley, D. P. *J. Org. Chem.* **1985**, *50*, 1787.

(9) (a) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787. (b) Clennan, E. L.; Chen, X. *Ibid.* **1989**, *111*, 8212. (c) Clennan, E. L.; Yang, K. *Ibid.* **1990**, *112*, 4043.

(10) (a) Murray, R. W.; Jindal, S. L. *J. Org. Chem.* **1972**, *37*, 3516. (b) Stary, F. E.; Jindal, S. L.; Murray, R. W. *Ibid.* **1975**, *40*, 58.

0002-7863/91/1513-2696$02.50/0