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UV Laser Photochemistry: Triplet Biradical Trapping Efficiencies and Lifetimes

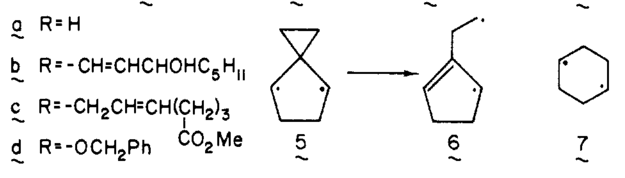
Waldemar Adam,*[†] Klaus Hannemann,[†] and R. Marshall Wilson*[‡]

Contribution from the Institut für Organische Chemie der Universität Würzburg, D-8700 Würzburg/Am Hubland, West Germany, and the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. *Received July 18, 1985*

Abstract: The trapping of triplet 1,3-cyclopentadiyl (**1a**) and the triplet 1,4-biradical 2-[2-ethyl]cyclopent-2-enyl (**6**) with molecular oxygen has been studied quantitatively. The lifetime of **1a** has been found to range between 720 and 900 ns and that of **6** between 53 and 94 ns depending on the solvent. The biradical **1a** was found to be trapped in essentially quantitative yield with no indication of oxygen-catalyzed intersystem crossing. In contrast, **6** was found to be trapped in 54–79% yield with the residual biradical quenching being due to oxygen-catalyzed intersystem crossing. These and other biradical trapping data have been correlated with 1,3-biradical geometries and found to be in accord with Salem's rules for spin-orbit coupling in triplet biradicals.

During the past several decades significant advances have been made in the direct observation and study of the behavior of biradicals. In spite of these strides very little progress has been made toward the observation of simple parent biradical systems. Since these parent systems do not contain appended chromophores, they do not absorb in the region of the spectrum accessible to modern laser spectroscopy techniques. For those chromophorically enhanced biradicals that have been studied by laser spectroscopy,[1] there is no standard against which to gauge the degree to which the appended chromophores alter the behavior of the biradical. The single exception is 1,3-cyclopentadiyl (**1a**) that has been studied by ESR spectroscopy in low-temperature matrices and found to have a triplet ground state.[2] Consequently, there is a significant need for the development of techniques applicable to the study of localized simple biradicals in solution. Oxygen trapping of biradicals has been applied to simple triplet biradicals in qualitative studies of their behavior under ambient conditions.[1,3] In this report we describe a quantitative application of the oxygen-trapping method to the study of triplet biradicals in solutions.

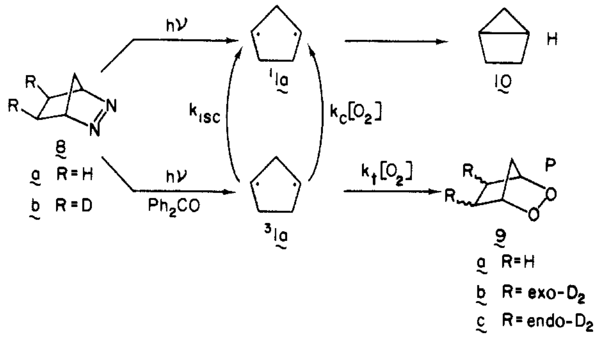
To date we have applied benzophenone-sensitized decomposition of azoalkanes under oxygen pressures of up to about 15 atm in trapping studies of the triplet biradicals **1a–d**, **2–4**, **6**, and **7**. From this rather limited but expanding sampling of biradical systems, it is becoming apparent that the success of this biradical-trapping technique is highly variable. For instance, the simple 1,3-biradicals **1a–d** and **4** are all trapped with high efficiency.[4] The spiro-1,3-biradical **5** undergoes a rapid ring cleavage to the 1,4-biradical **6** which in turn is trapped with moderate efficiency.[5] The simple 1,4-biradical **7** is trapped with very low efficiency,[6] and the bicyclic 1,3-biradicals **2** and **3** as well as related bicyclic biradicals are untrappable under the conditions employed to date.[7] On the basis of these qualitative studies, we have selected biradicals **1a** and **6** for further more quantitative studies of their trapping behavior with oxygen.



General Considerations

The various processes thought to be involved in the oxygen trapping of triplet biradicals are outlined in Scheme I with azoalkane **8a** as an example. Biradical generation from **8a** can be realized through either the direct irradiation of the azo chromophore in which case the single biradical ^{1}**1a** results or through the benzophenone-sensitized photodecomposition of **8a** in which case the triplet biradical ^{3}**1a** results. In the absence of oxygen, ^{3}**1a** will undergo spontaneous ISC (k_{ISC}) to ^{1}**1a** which in turn will collapse to the hydrocarbon **10**. In the presence of oxygen, two additional pathways for the disppearance of ^{3}**1a** must be considered. These are oxygen-catalyzed ISC ($k_c[O_2]$) to ^{1}**1a** and oxygen trapping to form the peroxide **9a** ($k_t[O_2]$) shown in Scheme I. In principle it should be possible to determine the efficiency of either the hydrocarbon **10** or peroxide **9a** formation as a function of oxygen pressure and to estimate k_{ISC}, k_c, and k_t from these data. For the successful implementation of this analysis it is essential that the biradicals be generated initially in their triplet

Scheme I



[†] Institut für Organische Chemie der Universität Würzburg.

[‡] University of Cincinnati.

(1) Wilson, R. M. "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, New York, 1985; Vol. 7, Chapter 5.

(2) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857.

(3) (a) Wilson, R. M.; Wunderly, S. W.; Walsh, T. F.; Musser, A. K.; Outcalt, R.; Geiser, F.; Gee, S. K.; Brabender, W.; Yerino, L., Jr.; Conrad, T. T.; Tharp, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 4429 and references therein. (b) Wilson, R. M.; Geiser, F. *Ibid.* **1978**, *100*, 2225. (c) Wilson, R. M.; Rekers, J. W. *Ibid.* **1981**, *103*, 206. (d) Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1978**, *100*, 4512. (e) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1976**, *59*, 2273. (f) Pagni, R. M.; Burnett, M. N.; Hassaneen, H. M. *Tetrahedron* **1982**, *38*, 843. (g) Roth, W. R.; Scholz, B. P.; Breuckmann, R.; Jelich, K.; Lennartz, H.-W. *Chem. Ber.* **1982**, *115*, 1934 and references therein. (h) Ito, Y.; Matsuura, T. *J. Am. Chem. Soc.* **1983**, *105*, 5237 and references therein.

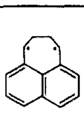
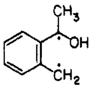
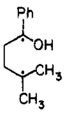
(4) Biradical **1a**: ref 3b. Biradical **1b**: Wilson, R. M.; Moats, D.; Ranganathan, R.; Conrad, T. T.; Merwin, R. K.; Schnapp, K. A., submitted for publication. Biradical **1c**: Wilson, R. M.; Schnapp, K., unpublished results. Biradical **1d**: Adam, W.; Hössel, P., unpublished results. Biradical **4**: ref 3c.

(5) Adam, W.; Hannemann, K.; Hössel, P. *Tetrahedron Lett.* **1984**, *25*, 181.

(6) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1984**, *106*, 7646.

(7) Adam, W.; Hannemann, K.; Wilson, R. M. *Angew. Chem.* **1985**, *97*, 1072.

Table I. Rate Constants for Biradical Quenching by Oxygen

	$k_{O_2}(M^{-1}\ s^{-1})^a$	$k_{O_2}(M^{-1}\ s^{-1})^b$
	Experimental Values	
	2.4×10^9 (MeOH, 30 °C)[c,d]	9.6×10^8 (CCl_4, 8 °C) 1.4×10^9 (PhH, 7 °C)
	1.3×10^9 (cyclohexane, 30 °C)[c,e]	8.4×10^8 (CCl_4, 8 °C) 1.2×10^9 (PhH, 7 °C)
	4.6×10^9 (MeOH, 30 °C)[f,g]	2.1×10^9 (CCl_4, 8 °C) 3.0×10^9 (PhH, 7 °C)
	6.2×10^9 (MeOH, 30 °C)[f,h]	2.8×10^9 (CCl_4, 8 °C) 4.0×10^9 (PhH, 7 °C)
	Theoretical values	
$k_{O_2} = k_t + k_c = (^4/_9)2 \times 10^5(^T/_\eta)$		2.1×10^9 (CCl_4, 8 °C) 3.1×10^9 (PhH, 7 °C)

[a] Experimentally determined values. [b] k_{O_2} adjusted to standard solvent viscosity and temperature conditions used in trapping studies. [c] Direct observation. [d] See ref 9. [e] See ref 10. [f] Observation of paraquat radical cation formation. [g] See ref 11. [h] See ref 12.

states and that the formation of singlet biradicals through direct absorption be excluded. Therefore, in this work the benzophenone-sensitization method has been employed by using the 363.7-nm line of an argon ion laser as the excitation source. Figure 1 shows the relative optical densities of **8a** and benzophenone in the spectral region of interest. With a 2:1 molar ratio of benzophenone to azoalkane, only about 0.05% of the 363.7-nm laser line is absorbed directly by the azoalkane **8a**. Thus in the absence of oxygen this method provides the triplet biradical ^{3}**1a** to the virtual exclusion of the singlet biradical ^{1}**1a**. However, in the presence of oxygen, the azoalkane **8a** will compete with oxygen for the triplet benzophenone, and as the oxygen pressure is increased the formation of ^{3}**1a** will be suppressed to the extent that the formation of ^{1}**1a** eventually will predominate. Fortunately the direct absorption of light by the azoalkane **8a** is so small under the laser irradiation conditions that much less than 1% of the biradicals generated are formed in their singlet states even under the highest oxygen pressures used in the work described below. The same situation exists for the generation of biradical **6** and in neither case was it necessary to make corrections for the trace amounts of singlet biradicals that might have been formed.

Given this single condition that all biradicals are born in their triplet states, eq 1, which is based on the pathways outlined in Scheme I, can be applied. Here H refers to the mole fraction

$$1/P = \frac{1}{1-H} = \frac{1}{T_f} + \frac{1}{k_t\tau[O_2]} \qquad (1)$$

of hydrocarbons and other products derived from biradicals that were not trapped and P refers to the mole fraction of peroxides and other products derived from the peroxide trapping products. The trapping factor, $T_f = k_t/(k_t + k_c)$, is a measure of the relative amounts of oxygen trapping vs. oxygen-catalyzed ISC. Thus a T_f of 1.0 indicates 100% trapping at infinite oxygen pressure. Whereas, trapping factors less than 1.0 are indicative of some degree of oxygen-catalyzed ISC ($k_c \neq 0$) of the triplet to the singlet biradical. Finally $\tau = k_{ISC}^{-1}$ and is equal to the lifetime of the triplet biradical in the absence of oxygen.[8]

In order to apply eq 1 in the determination of triplet biradical lifetimes, it is necessary to have some direct measure of the rate constant for the reaction of triplet biradicals with oxygen, $k_{O_2} = k_t + k_c$. A number of values for rate constants of this type have been determined,[1] and those for several of the more thoroughly studied systems are listed in Table I. For purposes of comparison, these rate constants have been adjusted for solvent viscosity and temperature to the standard sets of conditions used in this work.

Since these reactions involve the interaction between two triplet species, they might well be influenced by the spin statistics thought to be associated with processes of this type. Frequently it is assumed that when two triplet species collide only $^4/_9$ of the collisions, the singlet and triplet collision complexes, can give rise to some form of net chemical change.[13] The remaining $^5/_9$ of the collisions, the quintet collision complexes, do not seem to lead to bond formation between the collision partners and are thought to be chemically unproductive. Consequently, the final entries in Table I are theoretical estimates of the diffusion-controlled rate

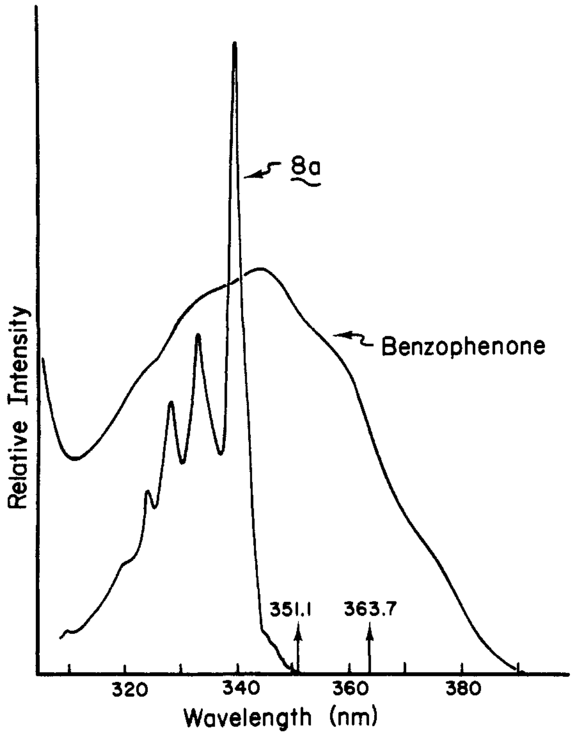


Figure 1. Relative absorption intensities of alkane **8a** and benzophenone. The two argon ion laser lines that may be used to excite the benzophenone selectively are shown on the wavelength axis. In this work only the 363.7-nm line was used.

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(8) A much more complex version of this relationship has been developed on a quantum yield basis by Scaiano and Small, ref 3d.

(9) Wirz, J, personal communication.

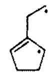
(10) Findlay, D. M.; Tchir, M. F. *J. Chem. Soc., Faraday Trans. 1* **1976**, 1096.

(11) Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 7713.

(12) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *48*, 354. Small, R. D., Jr.; Scaiano, J. C. *Ibid.* **1977**, *50*, 431. Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126.

(13) (a) Caldwell, R. A.; Creed, D. *J. Am. Chem. Soc.* **1977**, *99*, 8360. (b) Caldwell, R. A.; Creed, D. *J. Phys. Chem.* **1978**, *82*, 2644. (c) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216. (d) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819.

Table II. Biradical Lifetimes (τ) and Trapping Factors (T_f) with Oxygen

biradical	solvent	T_f^{-1} (intercept)	$(k_t\tau)^{-1}$ (slope, M)	r (corr coef)	T_f	$k_t\tau$ (M^{-1})	τ (ns)
 **^{3}1a**	CCl_4[a]	1.02	5.40×10^{-4}	0.996	0.977 ± 0.004	1.85×10^3	900 ± 40[c]
	PhH[b]	1.01	4.49×10^{-4}	0.991	0.991 ± 0.01	2.23×10^3	720 ± 40[d]
 **^{3}6**	CCl_4[a]	1.84	9.37×10^{-3}	0.994	0.54 ± 0.06	107	94 ± 12[c]
	PhH[b]	1.26	7.70×10^{-3}	0.992	0.79 ± 0.09	130	53 ± 20[d]

[a] At 8 °C. [b] At 7 °C. [c] $k_t + k_c = 2.1 \times 10^9\ s^{-1}$. [d] $k_t + k_c = 3.1 \times 10^9\ s^{-1}$.

constants which have been adjusted for the spin statistics of reactions between two triplet species.[14] The agreement between these theoretical values and the experimental values listed in Table I seems quite good. Therefore, rather than setting k_{O_2} used in this work to be equal to one of the experimental values listed in Table I, we have elected to set k_{O_2} equal to the appropriate intermediate theoretical value listed at the bottom of Table I.

Determination of Oxygen Concentrations

The oxygen concentrations used in this work have been determined by means of a simple and general volumetric method described in the Experimental Section. They have been found to be directly proportional to oxygen pressure to at least 10 atm. The proportionality constants for several sets of standard biradical trapping conditions were determined to be the following: for benzene at 7 °C, 8.21×10^{-3} M atm^{-1}, $r = 0.999$; for CCl_4 at 8 °C, 1.27×10^{-2} M atm^{-1}, $r = 0.997$; for $CFCl_3$ at −20 °C, 1.96×10^{-2} M atm^{-1}, $r = 0.999$. Literature values are available for the benzene and CCl_4 solubility constants[15] and are in close agreement with the values determined by this method.

Determination of the Lifetime of ^{3}1a

In the oxygen trapping of ^{3}**1a** the strained and quite unstable peroxide **9a** is the principal product. Since this substance decomposes under the reaction conditions, it was necessary to use the hydrocarbon **10** to evaluate the extent of oxygen trapping. It was shown that **10** is formed with a quantum yield of 1.0 in the absence of oxygen[16] and is inert under the trapping conditions. Furthermore, for short irradiation times the mass balance **9a** + **10** (P + H as defined for eq 1) approaches unity. In a further control experiment the photochemistry of the exo,exo-D_2 azoalkane **8b**[17] (Figure 2) was examined under the trapping conditions and found to afford a 1.0:1.0 mixture of the exo, exo-D_2 and endo,-endo-D_2 peroxides **9b** and **9c**, respectively. This result clearly indicates that at the time of oxygen trapping the nitrogen unit has been lost. Thus, the species undergoing trapping is the 1,3-cyclopentadiyl triplet ^{3}**1a** rather than a precursor diazenyl biradical. In addition this observation shows that ^{3}**1a** must be a time-averaged planar species.

The results of the quantitative trapping experiments in CCl_4 are shown in Figure 3, and the parameters derived from these data as well as those in benzene are listed in Table II. Each data point in Figure 3 is the result of at least three determinations. The primary source of error in these data arises from the difficulty in maintaining oxygen concentrations at their equilibrium values throughout the course of a determination. This problem is particularly severe at low oxygen pressures where the oxygen concentration is more readily depleted. The following steps were taken in order to minimize this type of error: all solutions were equilibrated for at least 0.5 h before irradiation, vigorous magnetic stirring was maintained throughout the equilibration and irradiation periods, the laser beam was diverged, and the irradiation was conducted in intervals of 10 s followed by 10-s dark periods. With this procedure both the trapping factor (T_f) and the lifetime (τ) of ^{3}**1a** can be estimated with a precision of better than 10% (Table II). Thus, the largest source of error probably is associated with the uncertainty of the k_{O_2} ($k_t + k_c$) values used to calculate τ (vide supra).

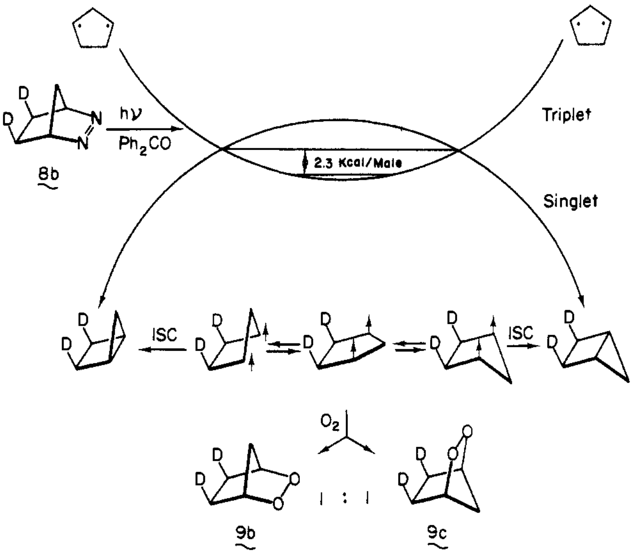


Figure 2. Singlet- and triplet-energy surfaces of 1,3-cyclopentadiyl (**1a**) and the trapping of its deuterated time-averaged planar derivative with oxygen.

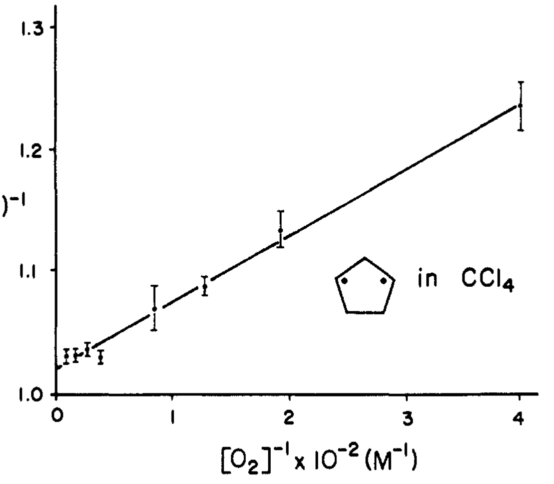


Figure 3. Double reciprocal plot of the trapping efficiency of triplet 1,3-cyclopentadiyl (**1a**) as a function of oxygen concentration in carbon tetrachloride: H = mol fraction of **10** formed.

The trapping factor (T_f) can be determined with much greater certainty and in both the CCl_4 and benzene systems was found to be very close to unity. These trapping factors not only indicate that ^{3}**1a** is undergoing very little if any oxygen-catalyzed ISC but also support the contention offered earlier that there is very little direct absorption of light by the azoalkane **8a**. If **8a** were ab-

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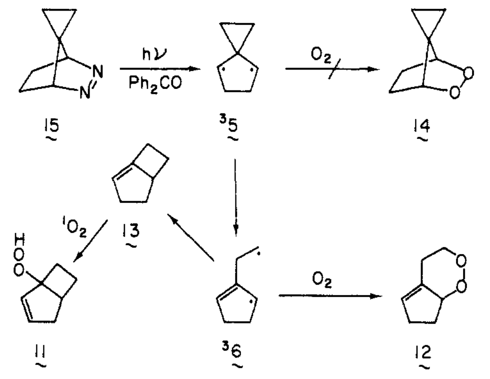
(14) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1979; p 314. Riddick, J. A.; Bunger, W. B. "Organic Solvents"; Wiley: New York, 1970.

(15) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

(16) Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* **1971**, *93*, 6347.

(17) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1.

Scheme II



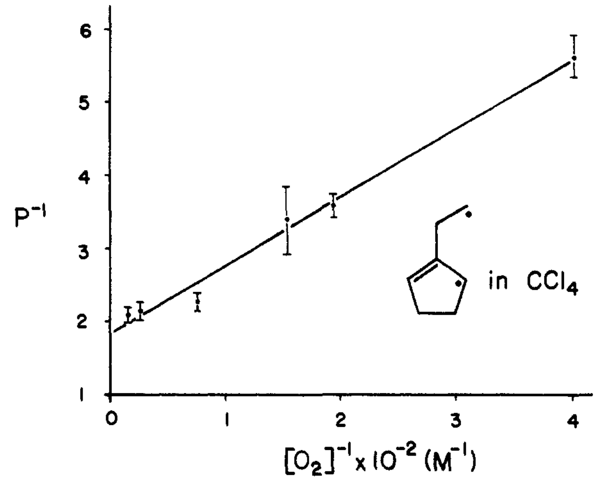
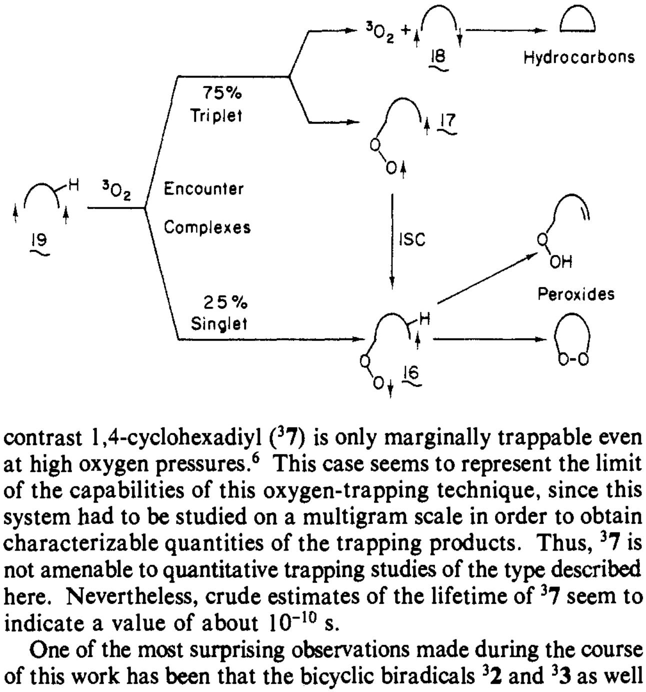


Figure 4. Double reciprocal plot of the trapping efficiency of triplet **6** as a function of oxygen concentration in carbon tetrachloride: P = mole fraction of **12** formed.

Scheme III



sorbing significant quantities of light, the data would be expected to show substantial deviation from linearity at high oxygen pressures.

The most striking result obtained in this study is the surprisingly long lifetime (τ) found for ^{3}**1a**. This lifetime is in accord with the earlier qualitative observation of Clark and Steel, who reported a lifetime for ^{3}**1a** of at least 10^{-7} s.[16] Little significance is associated with the minor variation in the lifetime of ^{3}**1a** in the two solvents.

Determination of the Lifetime of ^{3}6

The oxygen trapping of ^{3}**6** (Scheme II) has been studied qualitatively[5] and found to afford the peroxides **11** and **12** as well as the hydrocarbon **13**. The peroxide **14** could not be detected even in trace amounts, and arguments have been presented which indicate that ^{3}**5** undergoes rapid cyclopropane cleavage to form ^{3}**6** before trapping by oxygen can occur.[5] Thus, in the present study the freely rotating biradical ^{3}**6** in which the cyclopropane ring has been cleaved is the species being probed by oxygen.

The considerations involved in the study of ^{3}**1a** apply equally well to this study of ^{3}**6** with one exception. In this system the hydrocarbon **13** is oxidized further to the hydroperoxide **11** by singlet oxygen generated under the trapping conditions. Furthermore since **11** is quite labile, the H-product branch (eq 1) cannot be used to evaluate the trapping characteistics of ^{3}**6**. Instead the P-branch, **12**, must be determined quantitatively in order to characterize ^{3}**6**. Fortunately **12** is an unusually stable peroxide which is not affected by the GLC analysis procedure. Nevertheless this reliance upon the quantitative determination of a peroxide product and the possibility that minor amounts of less stable peroxide trapping products may have escaped detection indicate that the parameters estimated for this system have significantly greater uncertainty then those found for ^{3}**1a**. Therefore, this study is best considered only semiquantitative.

A typical plot of eq 1 for ^{3}**6** in CCl_4 is shown in Figure 4, and the parameters derived from these data and with benzene as the solvent are listed in Table II. It can be seen that the precision of these data is substantially less than that for ^{3}**1a**. In spite of these potential problems associated with the quanitative analysis of peroxide products, it can be seen from Figure 4 that a reasonable degree of precision can be obtained with this P-branch approach. Finally it should be noted that even if the method of analysis systematically underestimated the extent of peroxide-trapping product formation by 20–30%, the lifetime of ^{3}**6** should not deviate beyond the experimental limits indicated in Table II.

Consequently it seems safe to conclude that oxygen-catalyzed ISC does occur to a significant extent with ^{3}**6** and that the lifetime of ^{3}**6** is about an order of magnitude shorter than that of ^{3}**1a**. Finally, biradical lifetimes in the range of 50–100 ns estimated for ^{3}**6** seem to be typical for freely rotating biradicals.[1]

Trapping of Related Triplet Biradicals

Qualitative oxygen-trapping studies have been conducted with a variety of other triplet biradicals. In general substituted 1,3-cyclopentadiyls ^{3}**1b–d**[4] undergo efficient trapping by oxygen with little or no hydrocarbon formation at high oxygen pressures. Thus these systems all seem to parallel closely the behavior of ^{3}**1a**. In contrast 1,4-cyclohexadiyl (^{3}**7**) is only marginally trappable even at high oxygen pressures.[6] This case seems to represent the limit of the capabilities of this oxygen-trapping technique, since this system had to be studied on a multigram scale in order to obtain characterizable quantities of the trapping products. Thus, ^{3}**7** is not amenable to quantitative trapping studies of the type described here. Nevertheless, crude estimates of the lifetime of ^{3}**7** seem to indicate a value of about 10^{-10} s.

One of the most surprising observations made during the course of this work has been that the bicyclic biradicals ^{3}**2** and ^{3}**3** as well as other related bicyclic biradical species are untrappable. Thus even at high oxygen pressures (10–15 atm) these bicyclic biradicals afford only the conventional photoproducts. Credibility is lent to these observations by the similar observations of Turro and co-workers, who were unable to observe trapping of azo-derived bicyclic biradicals at oxygen pressures as high as 100 atm.[18] Furthermore our previous success in characterizing the oxygen-trapping products of ^{3}**7**,[6] even though they are formed in only about 5% yield, would seem to exclude the possibility that the lack of trapping observed with ^{3}**2** and ^{3}**3** is due to some limitation of this trapping technique. Finally, this complete failure to find any evidence for oxygen trapping is most surprising in the case of ^{3}**2** which is nothing more than a distorted 1,3-cyclopentadiyl analogue, the undistorted parent ^{3}**1a** of which is trapped with high efficiency.

Discussion

The results presented here are best discussed within the framework provided in Scheme III. Since these trapping reactions all involve collisions between two triplet species, the triplet biradical

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[18] Turro, N. J.; Cherry, W. R.; Mirbach, M. J.; Mirbach, M. F.; Ramamurthy, V. *Mol. Photochem.* **1978–1979**, *9*, 111.

and triplet oxygen, the spin statistics of these encounter complexes must be considered in any discussion of these reaction mechanisms. As mentioned earlier, both theoretical considerations and the observed rate constants for the quenching of several types of triplet biradicals with oxygen indicate that about $^5/_9$ of the encounter complexes have a quintet multiplicity and are chemically unproductive. This leaves the singlet ($^1/_9$) and triplet ($^3/_9$) encounter complexes as the possible sources of oxygen-trapping and spin-catalyzed ISC as shown in Scheme III. In principle, oxygen trapping could take place through either a singlet or a triplet encounter complex. The primary difference between these two pathways is that singlet trapping might proceed in a concerted fashion, whereas triplet trapping would have to proceed in a stepwise fashion and thus would seem to require an intermediate peroxybiradical (**17** in Scheme III). In contrast, oxygen-catalyzed ISC via biradical **18** would be expected to proceed only through the triplet encounter complex.

There have been relatively few studies which have endeavored to evaluate the relative contributions of these singlet and triplet encounter complexes in the chemistry of triplet biradicals. Scaiano and Small[3d] have examined the reaction of oxygen with triplet Norrish type II biradicals. They have observed both trapping with oxygen to form hydroperoxide products and oxygen-enhanced ISC. In these systems the catalyzed ISC results in an increase in the quantum yields for the Norrish type II fragmentation products. Caldwell and Creed[13b] have examined the effect of oxygen on the [2 + 2] addition of dimethyl fumarate to phenanthrene. They have reported only trace amounts of undefined oxygen-trapping products but did observe small enhancements of cyclobutane formation in the presence of oxygen. This effect was ascribed to oxygen-catalyzed ISC. They also reported that oxygen has virtually no effect upon the formation of oxetane products which also occur in these systems. One of us has observed a significant oxygen enhancement in oxetane yields with *p*-benzoquinone and styrene.[3a] This reaction is also accompanied by substantial amounts of oxygen trapping to form trioxanes. The results of Scaiano and Small[3d] are particularly interesting since they indicate that the relative amounts of trapping to catalyzed ISC is about 25:75. These results suggest that trapping by oxygen might proceed only through singlet encounter complexes and oxygen spin catalysis only through triplet encounter complexes. Finally, it should be mentioned that with the exception of the benzoquinone work, these studies have all been conducted over a rather narrow range of oxygen pressures ($\leq$1 atm).

In the present work trapping factors (T_f in eq 1) of much higher than 0.25 have been observed. In fact in the case of ^{3}**1a** trapping takes place to the virtual exclusion of oxygen-catalyzed ISC. Thus, it seems clear that trapping can occur through triplet as well as singlet encounter complexes. At this juncture nothing is known about the factors which influence the partitioning of the triplet encounter complexes between stepwise trapping via **17** and spin catalysis via **18** in Scheme III.

Since trapping can occur to the virtual exclusion of catalyzed ISC, one might then ask if in some biradical systems catalyzed ISC can occur to the exclusion of trapping. It must be noted that if this extreme case can occur, then the relationship defined by eq 1 becomes indeterminant and a failure to observe trapping might be erroneously interpreted to mean that the triplet biradical has a lifetime of $<10^{-10}$ s. This question of exclusive catalysis of ISC vs. short triplet biradical lifetimes is much more difficult to evaluate. At high oxygen pressure (up to about 15 atm) there are three known triplet biradical systems that exhibit no detectable oxygen-trapping products. These are the following: (1) the preoxetane biradical derived from *p*-benzoquinone and *trans*-1,2-di-*tert*-butylethylene,[19] (2) the preoxetene biradicals derived from *p*-benzoquinone and a variety of acetylenes,[3a,19] and (3) the bicyclic biradicals such as **2** and **3** reported here. At low oxygen pressures (up to about 1 atm) only the phenanthrene and dimethyl fumarate derived 1,4-biradical seems to undergo catalyzed ISC to the virtual exclusion of trapping.[13b] However, this result should be confirmed at high oxygen pressures and with analytical procedures suitable for detecting unstable, high molecular weight peroxide-trapping products.

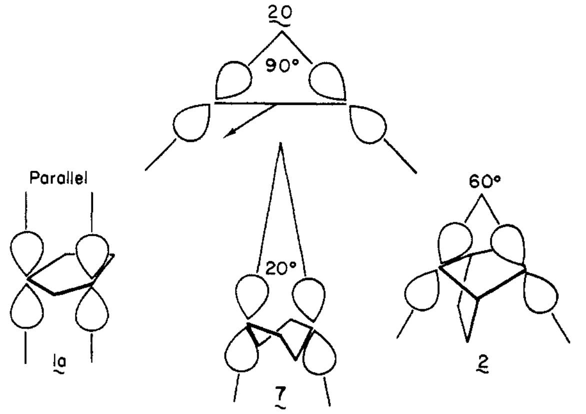

Figure 5. The average angles between biradical orbital axes for the conformationally constrained biradicals **1a**, **2**, and **7** as compared to an optimum biradical geometry for triplet–singlet ISC **20**. The arrow in **20** indicates the requisite orientation of the magnetic moment of the triplet sublevel.

The results reported here strongly indicate that trapping can occur through both singlet- and triplet-encounter complexes, whereas spin-catalyzed ISC should occur only through the triplet-encounter complex (Scheme III). Spin catalysis might completely suppress trapping in the triplet-encounter complexes, but there would appear to be no general mechanism through which trapping can be completely avoided in the singlet-encounter complexes of the simple, unhindered parent biradicals under discussion here. The failure of the *p*-benzoquinone-*trans*-1,2-di-*tert*-butylethylene preoxetane biradical to undergo trapping may be due to severe steric hindrance to oxygen attack. Schemes involving reversible oxygen trapping in which, for example, the peroxy biradicals **16** or **17** (Scheme III) undergo loss of oxygen to form either the singlet or triplet biradicals **18** or **19** might be considered but would seem to be unfavorable energetically especially when **18** and **19** are localized biradicals.[20] Thus, in the cases of the unhindered, localized biradicals **2** and **3**, steric hindrance to oxygen trapping or reversible-oxygen trapping would not seem to provide an adequate explanation for the complete failure of these biradicals to undergo oxygen trapping.

On the other hand, triplet biradical lifetimes (τ in eq 1) would be expected to play an important role in determining the trapping efficiency of a given biradical. The lifetimes of the untrappable bicyclic biradicals **2** and **3** under consideration here and the acetylene derived preoxetene biradical described earlier might be particularly significant in this regard. Salem and Rowland[21] have proposed a set of conditions that should favor spontaneous ISC from triplet to singlet biradicals and, hence, attenuate triplet biradical lifetimes. According to this model, one important factor in determining the rate of spontaneous ISC in biradicals is the geometry of the spin-bearing orbitals with respect to each other. If the axes of the spin-bearing biradical orbitals are 90° to each other and mutually orthogonal to the magnetic moment of the triplet sublevel, then spontaneous ISC can occur with conservation of spin through the transfer of an unpaired electron from one spin-bearing orbital to the other. These geometric requirements are satisfied by several orbital configurations, but the geometry of **20** shown in Figure 5 would seem to be the most relevant for the azo-derived biradicals under consideration here. Comparison of this ideal geometry of **20** with the time-averaged geometries of biradical **1a**, **7**, and **2** is quite intriguing. The parallel orbital configuration of 1,3-cyclopentadiyl (**1a**) would seem to be least

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(19) Wilson, R. M.; Wunderly, S. W., unpublished results.

(20) The dissociation of hydroperoxy radicals is known, but only when the resulting carbon radical is stabilized by conjugation. Chan, H. W.-S.; Levett, G.; Matthew, J. A. *J. Chem. Soc., Chem. Commun.* **1978**, *756*. Porter, N. A.; Weber, B. A.; Weenen, H.; Khan, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5597.

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

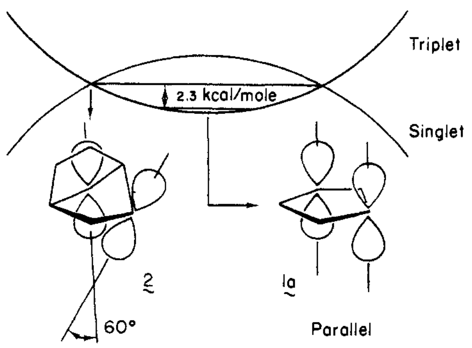

Figure 6. Relationship between spin-bearing orbital axes and triplet-singlet splitting energies for 1,3-cyclopentadiyl (**1a**) and its conformationally distorted analogue **2**.

suitable for spontaneous ISC according to this criterion. The twist-boat geometry for 1,4-cyclohexadiyl (**7**) would be somewhat more suitable for spontaneous ISC, and the rigid geometries of the bicyclic biradicals **2** and **3** would be more suitable for spontaneous ISC. Thus, this orbital geometry correlation proposed by Salem and Rowland would predict that k_{ISC} for **2** and **3** > **7** > **1a** and, hence, τ for **1a** > **7** > **2** and **3**. This ordering is in complete accord with the trapping efficiencies observed in this work. Furthermore, **1a**, **2**, and **7** is the first series of conformationally constrained, localized biradicals to be studied in this regard. As such, these results are much less subject to the usual uncertainties associated with the effects of conformational populations and substituents upon the lifetimes of the triplet biradicals. Finally, it should be mentioned that in biradicals bearing a vinyl-radical terminus similar orbital-geometry factors may play an important role in attenuating triplet lifetimes.[1] The untrappable acetylene-derived preoxetene biradicals mentioned earlier are members of this class.

In addition to the possible orbital geometry correlation outlined above, there may well be a correlation between biradical singlet-triplet splittings and lifetimes. Again this correlation is best discussed in terms of **1a** and **2**. It should be noted that **2** is a sterically rigid analogue of **1a** in which the 1,3-cyclopentadiyl unit has been distorted and fixed in nonplanar geometry. If this is the only effect of the ethylene bridge in **2**, then the singlet-triplet splitting of **2** might be approximated from the well-known energy profiles of **1a**. The singlet-triplet splitting of the planar conformation of **1a** is thought to be about 2-3 kcal/mol (Figure 6) with the triplet being the ground state.[22] According to the calculations of Doubleday and Dougherty,[23] any distortion of a trimethylene biradical from a geometry similar to that of **1a** (parallel orbital axes) to a geometry similar to that of **2** (angle between orbital axes = 60°) moves the system from a well-defined triplet ground state into a singlet-triplet crossing region (Figure 6). Consequently ISC should be endothermic in the case of **1a** and thermoneutral in the case of **2**. Therefore, **2** seems to be a system in which ISC is particularly favorable on the basis of both thermodynamic and spin-orbital considerations. While these correlations may be fortuitous, they do indicate an ordering of biradical lifetimes of τ for **1a** > **7** > **2** and **3**, and this ordering is consistent with the observed oxygen-trapping efficiencies. In addition, the lifetime of the freely-rotating triplet biradical **6** is consistent with those of other freely-rotating biradicals[1] and would be expected to fall in between the two extremes represented by the lifetimes of **1a** and **2** on the basis of orbital geometry considerations. The quantitative oxygen-trapping results reported here would seem to restrict further the triplet biradical lifetime of **6** to a time domain between those of **1a** and **7**.

One final point requires further discussion. For this we must return to the most difficult question of the relative importance of oxygen-catalyzed ISC vs. trapping. It has been hypothesized that spin-catalyzed ISC might occur indiscriminately from all triplet biradical geometries or at least have a different conformational dependence than spontaneous ISC.[13b] From the results reported here it appears that **1** is in some way protected against catalyzed ISC. It seems reasonable to assume that both spontaneous and catalyzed ISC occur more efficiently from biradical geometries that correspond to regions of singlet-triplet crossings. However, these singlet-triplet crossing regions need not necessarily correspond to the orbital geometries that are most favorable for spin-orbital coupling.[23] Spontaneous ISC should be favored by geometries that are both in singlet-triplet crossing regions and approximate the 90° orbital configuration most suitable for spin-orbital coupling. In contrast oxygen-catalyzed ISC should also be favored in singlet-triplet crossing regions but should not be as dependent on orbital geometries favorable to spin-orbital coupling. If this working hypothesis is correct, then spin-catalyzed ISC should occur over a much greater range of conformations than the spontaneous process. Accordingly, the two processes should display somewhat different conformational dependences, but dependences which are related in that those geometries most suitable for spontaneous ISC should also be favorable for catalyzed ISC. On this basis it might be argued that the triplet biradical **2** should be a system favorably disposed to both types of ISC and may undergo catalyzed ISC to the exclusion of trapping. However, if this is the case, there must be some mechanism by which the singlet encounter complexes can be rendered totally ineffective in producing trapping products. It is not at all obvious what this mechanism might be especially since these simple localized bicyclic biradicals are so closely related to 1,3-cyclopentadiyl (**1a**) which itself undergoes very efficient trapping with oxygen. Thus, for the present at least, it is felt that the most straightforward explanation for the complete failure of bicyclic biradicals such as **2** and **3** to undergo any detectable trapping with oxygen is that these biradicals have extremely short triplet lifetimes. Thus, this work provides the least ambiguous test to date of the orbital geometry requirements that were originally proposed by Rowland and Salem for spin-orbital coupling in biradicals and indicates that these geometric factors do indeed play an important role in determining biradical lifetimes.

Summary

A technique for the quantitative study of "spectroscopically invisible", localized triplet biradicals has been developed. A monochromatic laser light source is used to generate triplet biradicals to the exclusion of the singlet species. The trapping of these triplet species with oxygen has been studied quantitatively over a wide range of oxygen pressures. From these data estimates can be obtained not only for the relative efficiencies of oxygen-catalyzed ISC and trapping but also for the triplet biradical lifetimes. The trapping efficiencies determined by this method clearly demonstrate that nearly quantitative trapping of triplet 1,3-biradicals such as 1,3-cyclopentadiyl (**1a**) can be realized. Furthermore the triplet biradical lifetimes estimated by this method show a surprisingly wide variation from slightly less than 10^{-6} s for 1,3-cyclopentadiyl (**1a**) to $<10^{-10}$ s for its bicyclic analogue **2**. The dependence of these lifetimes on biradical geometries seems to correlate quite well with the geometry requirements proposed by Rowland and Salem for spin-orbital coupling in biradicals.

Experimental Section

General. Routine ^{1}H NMR spectra were recorded with a Hitachi Perkin-Elmer R-24B spectrometer, and ^{2}H NMR spectra were recorded with a Bruker WM-400 spectrometer. Absorption spectra were recorded with a Cary 17 spectrophotometer. A Coherent Supergraphite CR 18 argon ion laser fitted with a selected UV tube was used as the irradiation source. The UV laser lines were separated by means of an external quartz prism and the 363.7-nm line was used in all irradiations. All irradiations were conducted as previously described[3a] in Griffin-Worden tubes inside of which had been sealed magnetic stirring bars and with the tubes mounted in an aluminum cooling jacket. The desired air or oxygen pressures were achieved by means of a calibrated pressure regulator.

Product analyses were conducted with a Carlo Erbo Fractovap 2900 capillary gas chromatograph operated with 0.3 mm i.d. glass capillary

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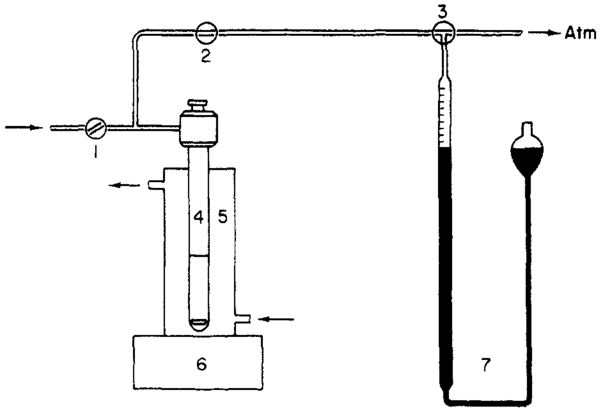

Figure 7. An extremely simple apparatus for measuring gas solubilities in solvents: 1–3, valves; 4, Griffin–Worden tube; 5, thermostated aluminum jacket; 6, magnetic stirring motor; 7, gas buret.

columns and a splitter ratio of 1:50. For the analysis of bicyclo[2.1.0]pentane (**10**) an 86-m PPG column was used with injector, column, and detector temperatures of 125, 20, and 150 °C, respectively (N_2: 0.5 kg/cm^2), and 2-methylbutadiene was used as the internal standard. Diazabicyclo[2.2.1]heptene (**8a**) was analyzed with a 40-m OV 101 column with injector, column, and detector temperatures of 125, 40, and 150 °C, respectively (N_2: 0.4 kg/cm^2), and *n*-nonane used as the internal standard. The spirodiazabicyclo[2.2.1]heptene (**15**) and the dioxabicyclo[4.3.0]nonene (**12**) were analyzed with a 50-m Carbowax 20 M column with injector, column, and detector temperatures of 150, 70, and 175 °C, respectively (N_2: 1.1 kg/cm^2), and the diazabicyclo[2.2.1]heptene (**8a**) was used as an internal standard. All response factors of standards vs. products were determined in calibration runs.

Chemicals. Benzophenone was recrystallized twice from ethanol. The azoalkanes were prepared and purified according to the published procedures: precursor azoalkane for biradicals **1a**,[24] **6**,[25] and **2**.[26] The purity of the azoalkanes was verified by GLC in all cases. The hydrocarbons **10**, **13**, and that derived from the biradical **2** were prepared photochemically from the corresponding azoalkanes[24,25b,27] and purified by preparative GLC on a Varian 920 instrument. The peroxide trapping products **9a** and **12** were prepared as described[3b,5] and purified by low-temperature column chromatography on silica gel. Peroxide formation was monitored routinely by TLC on silica gel followed by visualization with a ferrous thiocyanate spray.[28]

Determination of Oxygen Solubility. In a Griffin–Worden tube (see Figure 7) was placed 10 mL of solvent under 2–10 atm of oxygen and the same experimental conditions that were used in the lifetime determinations. The solvent was shaken vigorously for several minutes and stirred magnetically for 30 min (Figure 7, valve 1 open, valve 2 closed). The pressure was then carefully released so that no bubbles formed in the solvent (Figure 7, valve 1 closed, valves 2 and 3 open to atmosphere). Upon release of the pressure the Griffin–Worden tube was connected to a gas buret (Figure 7, valve 1 closed, valves 2 and 3 open to buret), and the dissolved oxygen was liberated by agitating the Griffin–Worden tube. The volume of oxygen released was determined after 30 min and was corrected for solvent vapor pressure and normalized to standard conditions. Data obtained by this extremely simple procedure were highly reproducible, in good agreement with literature data where available, and displayed a linear relationship between oxygen pressure and solubility over the entire pressure range for all solvents examined. The solubility constants obtained in this manner are given in the text for benzene, CCl_4, and Freon-11 ($CFCl_3$).

Procedure for Biradical Lifetime Determinations. A stock solution of 0.05–0.1 M azoalkane and 0.2 M benzophenone was prepared. A measured volume (3 mL) of this stock solution was introduced into a Griffin–Worden tube in which a magnetic stirring bar had been sealed. The solution was stirred at the desired air or oxygen pressure at constant temperature for 30 min to ensure equilibration. In order to obtain reproducible results, vigorous stirring is required throughout the equilibration and irradiation period. Then the sample was irradiated with the 363.7-nm line of an argon ion laser (UV output 0.7 W all lines). The laser beam was expanded by means of a quartz lens ($f = 40$ mm) to an approximate diameter of 1 cm. The total irradiation time was usually about 3.5 min, the time required for ca. 40–60% conversion of the azoalkane. To further ensure oxygen equilibrium conditions and enhance the reproducibility of the data, the samples were irradiated for 10-s periods interspersed with 10-s dark periods. Aliquots (100 μL) of the reaction mixture were withdrawn, combined with an equal volume of a solution of the internal standard, and analyzed with a capillary GLC as described in the General Section. At least three independent runs were conducted at each oxygen pressure.

General Procedure for Preparative Oxygen-Trapping Reactions. A solution (5–30 mL) of the azoalkane (0.07–0.10 M) and benzophenone (0.10–0.13 M) in $CFCl_3$ was cooled to −20 °C in a Griffin–Worden tube which was pressurized to 5–10 atm with oxygen. The solution was allowed to equilibrate for 1 h prior to irradiation with the 363.7-nm line of an argon ion laser (UV output 2.5–3.0 W all lines). The irradiation times varied from 30 min to 8 h depending upon the structure of the azoalkane. Optimum yields were obtained when irradiation was stopped at ca. 60% conversion of the azoalkane. Isolation of the peroxide products was achieved by removal of the solvent under vaccuum at 0 °C followed by −20 °C column chromatography on silica gel with CH_2Cl_2 as the eluent.

Photolysis of [5,6-*exo*-D_2]-2,3-Diazabicyclo[2.2.1]hept-2-ene (8b). Following the general procedure outlined above, 297 mg (3.03 mmol) of **8b** and 540 mg (2.97 mmol) of benzophenone in 30 mL of $CFCl_3$ were irradiated for 2.5 h under 8 atm of oxygen. Low-temperature chromatography on silica gel afforded 148 mg of unreacted **8b** and 53 mg (34%) of the dideuterated endoperoxides **9b** and **9c** the mixture of which had ^{2}H NMR ($CFCl_3/CDCl_3$, 400 MHz) δ 1.63 (s, D_{endo}) and 1.89 (s, D_{exo}). Integration of these two peaks provided a ratio for **9c**:**9b** of 1.0:1.0.

Photolysis of Tricyclic Azoalkanes. The tricyclic azoalkane precursors to biradicals **2** and **3** were photolyzed according to the general procedure. These photolyses were examined under a wide variety of conditions including oxygen pressures of up to 10 atm, irradiation times as long as 22 h, and conversions of the azoalkanes of up to 100%. The reactions were monitored by NMR, TLC, and GLC. In no instance was the formation of peroxide products observed. Only the usual hydrocarbon products were formed.

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Registry No. 1a, 56564-28-4; **6**, 99808-46-5; **8a**, 2721-32-6; **8b**, 60400-43-3; **9b**, 70109-86-3; **9c**, 99268-07-2; **15**, 19446-70-9.

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