success of many-step pulsed chain transfer will depend critically on the relative reactivity of the cyclic monomer and the chain-transfer agent and will be limited by impurities in the feed, by eventual slow decomposition of intermediates, and by incomplete chain transfer.

Concluding Remarks

Several features of these well-defined Mo and W alkylidene catalyst systems should be emphasized in closing. First, all five-coordinate metallacyclobutane intermediates are likely to be distorted significantly from ideal TBP or SP forms, both because of the bulky nature of the ligands and because of the strong electronic perturbations caused by the different ligands, especially by the imido ligand. A given distorted five-coordinate species should be able to rearrange relatively easily to another distorted species. Therefore a variety of readily interconvertible intermediate metallacyclobutane complexes should be accessible on the time scale of a polymerization reaction. Second, steric interactions in the coordination sphere well away from the metal center in four- or five-coordinate complexes probably can be as important as interactions near the metal in the primary coordination sphere. They apparently slow down ring-opening polymerization overall and, in the process, discriminate effectively between various reaction pathways. The fact that 5,6-disubstituted norbornenes and 2,3-disubstituted norbornadienes form relatively stable metallacyclobutane intermediates could be ascribed to a slowing down of the core rearrangement that is required prior to formation of the next alkylidene ligand. Third, all ligands except reactants and products are covalently bound to the metal. Therefore steric and electronic effects of the ligands that control reactivity and stereochemistry are maintained throughout the catalytic cycle, a circumstance that should be more successful relative to one in which catalysts contain labile donor ligands.

Living polymerizations that are as controlled as the ring-opening polymerizations discussed here are extremely rare. The fact that many functionalities can be tolerated by molybdenum catalysts, a wide variety of norbornenes and norbornadienes are readily available by Diels–Alder reactions, and acetylenes have some potential as comonomers in such systems creates the potential for applying this technology in a variety of interesting ways. Related catalysts based on rhenium[34] have been developed[35] that may be even more tolerant of functionalities and allow even more control over ring-opening reactions of highly strained monomers. Discovering the nature and controlling the reactivity of ROMP catalysts that contain later transition metals such as ruthenium[4a,36] remains a challenging goal, but one that now appears to be within reach.

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Localized Cyclic Triplet Diradicals. Lifetime Determination by Trapping with Oxygen

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Diradicals play a crucial role in photochemistry in that they constitute the link between covalent bonds, i.e., maximum electronic interaction, and "double radicals", i.e., no interaction of the odd electrons.[1] The lifetimes and chemical reactivity of triplet diradicals generally are governed by the relatively slow triplet–singlet intersystem crossing (ISC) to the singlet states, which in turn usually undergo rapid collapse to products. However, given sufficiently long lifetimes, both triplet and singlet diradicals will undergo chemical trapping. The quantitative study of the trapping of

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diradicals with oxygen provides valuable insights into the factors that affect diradical lifetimes and, hence, their chemical reactivity in solution and is the subject of this Account.

Methods for Diradical Detection

The method of choice for the direct detection of triplet diradicals is ESR spectroscopy, which provides information about the distance between the two unpaired electrons, the symmetry of the molecule, and the multiplicity of the molecule.[2] However, this technique requires that the diradical be isolated in a matrix. The direct detection of diradicals with π-delocalized spins also can be achieved by UV/vis spectroscopy in solution or matrices.[1e,f,3] In fact, most of the triplet diradical lifetimes available to date have been determined by time-resolved UV spectroscopy.[4] In addition, matrix isolation also allows direct detection of diradicals by IR spectroscopy.[5]

Useful indirect methods for the spectroscopic detection of diradicals that are frequently "invisible" to absorption spectroscopy are time-resolved photoacoustic calorimetry[6] and chemically induced dynamic nuclear polarization (CIDNP).[7]

Another indirect method for the chemical detection of diradicals consists of electron transfer trapping with dipyridinium salts.[8] Electron transfer from the diradical to the dipyridinium salt generates the radical cation of the salt, which is easy to observe spectroscopically. An alternative chemical method is based upon the rearrangement of cyclopropylcarbinyl radicals.[9] Despite the intensive synthetic work required to prepare the requisite cyclopropyl derivatives, this "free radical clock" method is being employed increasingly in the estimation of diradical lifetimes.

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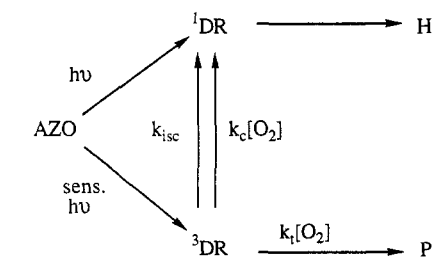
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Table I
Some Selected Examples of Diradical Trapping Reactions with Molecular Oxygen

starting material	diradical	oxygen trapping product	ref
			10b
			10b, 12a
			11, 12b
			12c
			12d
			3c
			12e
			12f
			12g
			12h
			12i

Scheme I

P   Peroxides.

H   Hydrocarbons.

k_{isc} Rate constant for intersystem crossing.

k_c Rate constant for oxygen-catalyzed intersystem crossing.

k_t Rate constant for oxygen trapping.

However, the most widely applied method for the chemical detection of spectroscopically "invisible" di-

radicals is their trapping with oxygen.[10-12] A sampling of these oxygen trapping reactions and the associated peroxide products is given in Table I.

Trapping of Diradicals with Oxygen

In general, oxygen trapping reactions are limited to triplet diradicals,[10b] since with few exceptions[11] singlet diradicals are too short-lived for bimolecular trapping. The lifetimes of triplet diradicals ($^3\tau$) are usually,[3a,13] but not always,[13a,14] determined by ISC and are equal to the reciprocal of the rate constant for ISC (k_{isc}) (eq 1).

$$^3\tau = 1/k_{isc} \tag{1}$$

The oxygen trapping method for the determination of triplet diradical lifetimes entails a quantitative study of peroxide formation as a function of oxygen concentration.[15] Triplet diradicals are generated by benzophenone-sensitized laser photolyses of azoalkanes (Scheme I). In the absence of oxygen, the triplet diradical ^3DR will undergo spontaneous ISC (k_{isc}) to ^1DR, which will cyclize and/or fragment to hydrocarbon products (H). In the presence of oxygen, two additional pathways for the annihilation of ^3DR must be considered. These are the trapping ($k_t[O_2]$) of ^3DR to form peroxides (P) and the oxygen-catalyzed ISC ($k_c[O_2]$) to give ^1DR and hydrocarbon (H). The efficiency of either hydrocarbon or peroxide formation as a function of oxygen concentration can be determined and, from these data, k_{isc}, k_c, and k_t estimated.

The successful implementation of this analysis requires that ^3DR be generated through photosensitization with the rigorous exclusion of ^1DR formation from

Figure 1. Double reciprocal plot of the trapping efficiency of triplet 1-phenyl-1,4-cyclohexanediyl as a function of oxygen concentration in benzene (20 °C).

Table II
Rate Constants [$k(O_2)$] for the Reaction of Triplet Diradicals with Molecular Oxygen

diradical	$k(O_2)$,[a] M^{-1} s^{-1} × 10^{-10}	solvent[b]	ref
	~0.1	benzene	4a
	0.24	methanol	11
	0.5	benzene/ methanol (1:4)	4f
	0.65	methanol	17a
	1.5 / 3.9	methanol / acetonitrile	17b
	1.4 / 4.2	methanol / acetonitrile	17b
	0.46	methanol	17c
	0.9	benzene	4b, 17d
	2.1	acetonitrile	4b, 17d
	1.5 ± 0.3 / 1.5 ± 0.3	acetonitrile / benzene	15g
	0.75 ± 1.0 / 0.43 ± 0.8	acetonitrile / benzene	15g
	2.2 ± 0.2 / 1.6 ± 0.1 / 1.2 ± 0.3	acetonitrile / benzene / n-heptane	15f
	1.8 ± 0.2 / 1.3 ± 0.1	acetonitrile / benzene	15g

[a] Determined by time-resolved laser flash spectroscopy. [b] At ambient temperature (20–30 °C).

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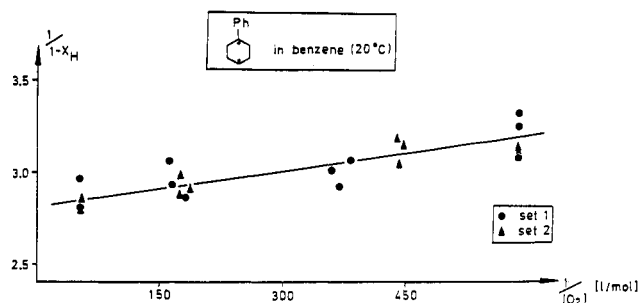
direct absorption by the azoalkane. The argon ion laser serves as an ideal light source for the exclusive excitation of the sensitizer, benzophenone. Thus, for example, the 364-nm argon laser line will only excite the benzophenone, and the direct photolysis of 2,3-diazabicyclo-[2.2.1]hept-2-ene derivatives (λ_{max} = ca. 340 nm) can be completely avoided. For 2,3-diazabicyclo[2.2.2]oct-2-ene derivatives (λ_{max} = 380 nm), the argon laser lines in the 333-nm region must be used.
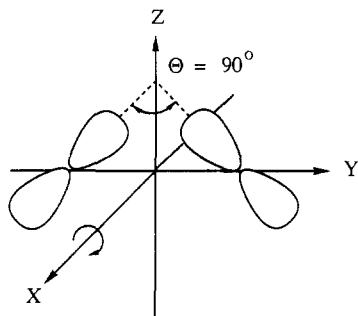
Figure 2. Orbital orientation for optimal spin–orbital coupling.

Given this essential condition that all diradicals be born in their triplet states, an expression (eq 2) for peroxide and hydrocarbon formation based on the pathways outlined in Scheme I can be derived.[15d] In

$$1/X_P = 1/(1 - X_H) = 1/T_f + 1/k_t(^3\tau)[O_2] \quad (2)$$

this equation, X_H refers to the mole fraction of hydrocarbon products derived from untrapped diradicals and X_P refers to the mole fraction of peroxides and associated decomposition products formed via oxygen trapping. The trapping factor, $T_f = k_t/(k_t + k_c)$, is a measure of the relative amounts of oxygen trapping versus oxygen-catalyzed ISC. Thus, when $T_f = 1.0$, 100% of the diradicals are trapped at infinite oxygen concentration, whereas when $T_f < 1.0$, oxygen-catalyzed ISC from ^{3}DR to ^{1}DR without the formation of peroxides is occurring to the extent of $1 - T_f$. The $^3\tau$ term is the lifetime of ^{3}DR in the absence of oxygen (eq 1). A typical reciprocal plot of the trapping efficiency as a function of oxygen concentration is shown in Figure 1. From the slope $(1/k_t(^3\tau))$ and the intercept $(1/T_f = (k_t + k_c)/k_t)$, the lifetime of ^{3}DR ($^3\tau$) can in principle be calculated from eq 2, provided that the rate constant for the reaction of ^{3}DR with oxygen $(k(O_2) = (k_t + k_c))$ is known.

To date only a few $k(O_2)$ values are known (Table II), so that calculated values must often be used (eq 3).[15e] It is currently thought that when two triplets such as ^{3}DR and $^3O_2$ collide, only the one singlet and three triplet collision complexes lead to products, whereas the five quintet collision complexes are chemically unproductive.[16] Consequently, triplet–triplet reactions should have a maximum rate constant of 4/9, the diffusion-controlled rate constant for singlet–singlet reactions (k_{diff} in eq 3). The validity of this spin statistical factor has never been rigorously demonstrated

$$k(O_2) = k_t + k_c = (4/9)k_{diff} \quad (3)$$

tistical factor has never been rigorously demonstrated for the reaction between ^{3}DR and $^3O_2$. However, the ^{3}DR lifetimes calculated by using this 4/9 factor are frequently in excellent agreement with the lifetimes determined by transient spectroscopy.[15e–g]

A convenient method for estimating k_{diff} is to employ the Smoluchowski–Einstein–Stokes relationship (eq 4). Initial attempts to determine the triplet lifetimes of the 1,3-cyclopentanediyl in a variety of solvents using this relationship met with failure.[15e] However, when the

original Smoluchowski diffusion equation was used (eq 5), reasonable agreement was achieved.[15e] Thus, diffusion control (k_{diff}) obtains for the trapping of ^{3}DR with $^3O_2$, but k_{diff} and $k(O_2)$ must be estimated by using eq 5 and eq 3, respectively.

$$k_{diff} = (2 \times 10^5)T/\eta \quad (4)$$

$$T = \text{temperature (kelvin)}$$

$$\eta = \text{solvent viscosity (poise)}$$

$$k_{diff} = (10^{-3})4\pi N_L[D(O_2) + D(A)][r(O_2) + r(A)] \quad (5)$$

$$N_L = \text{Avogadro number}$$

$$D = \text{diffusion constant}$$

$$r = \text{diffusion radius}$$

Triplet lifetimes of diradicals in the $0.1 \leq {}^3\tau \leq 1000$ ns range can be determined with this oxygen trapping technique. At the upper limit ($^3\tau \leq 1000$ ns), ISC is so slow that essentially complete diradical trapping always occurs. At the lower limit ($^3\tau \geq 0.1$ ns), negligible diradical trapping is observed, since ISC is significantly faster than the diffusion-controlled reaction with oxygen. Unfortunately, one cannot be sure whether failure to observe trapping is due to a short diradical lifetime or to the complete dominance of oxygen-catalyzed ISC. In the diradical systems analyzed quantitatively to date (Table III), a substantial trapping component (>36%) has always been observed. Therefore, at this point, we tend to assume that failure to observe trapping is the result of a short diradical lifetime rather than highly efficient oxygen-catalyzed ISC.

The extensive oxygen trapping results listed in Table III indicate that trapping with oxygen is a valuable technique for assessing lifetimes of localized triplet diradicals that are "invisible" to absorption spectroscopy. The advantage of being able to study such localized diradicals without perturbing chromophores, such as phenyl groups, is that subtle factors affecting the ISC process are not masked by much more powerful substituent effects.[15g] Furthermore, the isolation and thorough characterization of the peroxide trapping products tends to confirm the structure of the transient species being studied.

Intersystem Crossing Rules

Since excellent reviews on ISC in diradicals have been published,[1e,f,18] this topic will be reviewed only briefly here. Two different mechanisms might give rise to the crucial ISC step, namely, electron–nuclear hyperfine coupling (HFC) and spin–orbit coupling (SOC). SOC has recently been identified as the dominant ISC mechanism in diradicals.[4d,7b,13c,19]

In the first theoretical treatment of SOC specifically applied to diradicals, Salem and Rowland[1d] identified three main factors that should influence ISC via SOC: (1) the ionic character of the singlet wave function, (2) the orbital orientation, and (3) the distance between the diradical termini. Since SOC is proportional to the zwitterionic character of the singlet state, increasing ionic character in the diradical should facilitate ISC

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(rule 1). If the axes of the spin-bearing orbitals in the diradical are oriented 90° to each other and are mutually orthogonal to the resultant magnetic moment of the triplet sublevel (Figure 2), then spontaneous ISC can occur with conservation of the total angular momentum of the system (rule 2). Finally, increasing the distance between the radical termini should make ISC slower as a result of reduced orbital overlap (rule 3). On the other hand, strong overlap due to the close approach of the radical termini increases the energy gap between the singlet and triplet diradical states. The larger this singlet–triplet energy gap (ΔE_{ST}), the slower ISC will be. Furthermore, when either the "through space" or "through bond"[20] interaction of the radical orbitals dominates, a singlet ground state is expected, but when these interactions are of comparable magnitude, a triplet ground state is feasible.[1d]

In an extension of the static Salem–Rowland model for ISC, Shaik and Epiotis[21] have focused on the dynamic aspects of ISC by considering nuclear motions as well. They found that internal rotation and pyramidalization of the spin-bearing atoms promote coupling of the singlet and triplet states and, thus, may induce ISC.

The 1,3-Cyclopentanediyl Family

The geometric requirements for ISC (rule 2) would indicate that the parallel orbital orientation of triplet 1,3-cyclopentanediyl (1) should not be conducive to effective SOC. The time-averaged planarity of 1 was confirmed by ESR[22a] and by deuterium labeling in oxygen trapping experiments.[15d] In this diradical, the "through bond" and "through space" interactions[20] of the radical orbitals are balanced[22b] such that the ground state is a triplet lying 3.8 kJ/mol[22c] below the singlet state. Indeed, the observed long lifetime of ^{3}1 ($^3\tau$ ca. 100 ns, Table III)[15e] is consistent with this model.

$$\Theta \sim 0° \qquad \Theta \sim 45° \qquad \Theta \sim 60°$$

$$\mathbf{1} \qquad\qquad \mathbf{3} \qquad\qquad \mathbf{10}$$
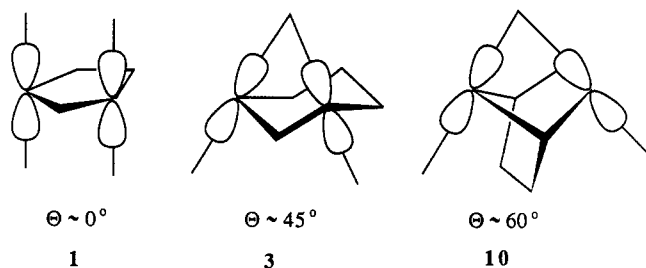
Molecular mechanics calculations[23] suggest that in the lowest energy conformations the interorbital angles for 1, 3, and 10 are 0°, 45°, and 60°, respectively. Therefore, the orientation of the radical orbitals in 1,3-cyclohexanediyl (3) is more suitable for SOC, and in fact 3 does exhibit a shorter triplet lifetime ($^3\tau$ = 10–20 ns)[15c] than the planar 1 ($^3\tau$ = 93–115 ns). It is interesting to note that methyl substitution on the spin-bearing carbons of these diradicals has only a minor affect on $^3\tau$.[24]

(20) Hoffmann, R. *Acc. Chem. Res.* 1971, 4, 1.
(21) (a) Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* 1978, 100, 18. (b) Shaik, S. S. *J. Am. Chem. Soc.* 1979, 101, 2736, 3184.
(22) (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* 1979, 101, 4688. (b) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* 1983, 105, 284. (c) Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F., III *J. Am. Chem. Soc.* 1979, 101, 2245. (d) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* 1982, 104, 6533.
(23) An MMPMI program, kindly provided by K. E. Gilbert and J. J. Gajewski, Serena Software, Bloomington, IN, was used for this work. This program has been parameterized for radical centers with the odd electron in a 2p atomic orbital for planar systems extending to sp³-hybridized atomic orbitals for puckered systems.

Since the trapping factors (T_f) for 1 and 3 are unity within the experimental error, oxygen-catalyzed ISC is negligible in these systems. Thus, the lower oxygen trapping efficiency of 3 relative to that of 1 must be due to the shorter triplet lifetime of 3, rather than to oxygen-catalyzed ISC. Furthermore, theoretical work on trimethylene[22b,d] predicts that distortion of the planar geometry of 1 toward the puckered geometry of 3 should cause a decrease in ΔE_{ST} and, thus, faster ISC.

The geometry of the bicyclic 1,3-diradical 10 ($\Theta \sim$ 60°) is even more favorable for spontaneous ISC. A similar geometry is also found in the other conformationally constrained bicyclic triplet diradicals 11–14. Indeed, attempted oxygen trapping of these diradicals even at 10 atm of oxygen failed,[15d] suggesting that the lifetimes of these diradicals are all shorter than the diffusion limit ($^3\tau \leq 0.1$ ns). Thus, it would seem that conformationally governed ISC provides the simplest rationalization for the variations in the lifetimes of these rather similar 1,3-diradicals, and that these oxygen trapping results constitute significant experimental support for the Salem–Rowland orbital orientation arguments (rule 2).

The short lifetime ($^3\tau \leq 0.1$ ns) of ^{3}6 was explained in terms of facile spirocyclopropane ring opening to the allyl-stabilized triplet 1,4-diradical 15.[15a] However, the ca. 100-fold reduction in the triplet lifetimes of the *gem*-dimethyl-substituted 1,3-diradicals 7–9 is puzzling.[11f] Since no spirocyclopropane ring opening was observed for the 1,3-cyclopentanediyl 8, one must ascribe the failure to observe oxygen trapping of diradical 8 to a short triplet lifetime ($^3\tau \leq 0.1$ ns). Thus, the alternative explanation of steric hindrance to oxygen approach by the *gem*-dimethyl group does not seem to be the reason for the failure of oxygen to trap diradicals 6–8. Furthermore, since planar structures are predicted for these diradicals by MMPMI calculations,[23] conformational factors do not seem to be the source of this triplet lifetime attenuation.

Perhaps *gem*-dimethyl substitution perturbs the balance between the "through space" and "through bond" interactions in 1. The buttressing effect (Thorpe–Ingold) of *gem*-dimethyl substitution in 7–9 could reduce the endocyclic angle between the radical sites, increase their overlap, and strengthen the "through space" interaction to favor a singlet ground state. Alternatively, weakened "through bond" coupling as a result of *gem*-dimethyl substitution also might promote a singlet ground state.[22b] Even allylic stabilization in the 1,3-diyl 9 does not seem to offset this trend. Preliminary results indicate that monoalkyl substitution between the radical centers also drastically shortens triplet lifetimes.[15l] Thus, perturbation of the "through bond" coupling appears to be responsible for the more effective ISC in these substituted systems.

The 1,4-Cyclohexanediyl Family

Conformational influence on the lifetimes of triplet 1,4-diradicals is subject to controversy.[4h] Theoretical work on tetramethylene[25] suggests that this parent 1,4-diradical lies on a broad, flat potential energy surface, characterized by a profusion of thermally accessible singlet–triplet intersections. Since ISC occurs only

(24) Bushby, R. J. *J. Chem. Soc., Perkin Trans. 2* 1985, 1211.
(25) Doubleday, C.; McIver, J.; Page, M. *J. Am. Chem. Soc.* 1985, 107, 7904.

Table III
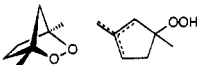### Triplet Diradical Lifetimes Determined by Trapping with Molecular Oxygen
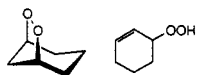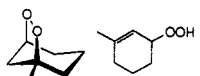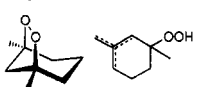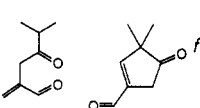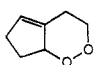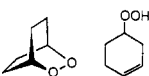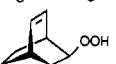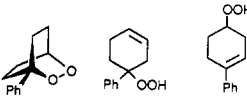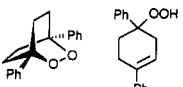
|	diradical[a]	solvent/temp, °C	trapping product	trapping factor[b]	lifetime,[c] $^3\tau$, ns	ref
1		n-heptane/8		1.02 ± 0.02	93 ± 11	15e
		benzene/8			115 ± 20	
		isopropyl alcohol/8			93 ± 28	
2		n-heptane/8		1.06 ± 0.05	42 ± 7	15e
3		n-dodecane/8		0.95 ± 0.30	10–20	15h
					$(56 ± 18)^d$	15e
4		n-dodecane/8		0.87 ± 0.30	10–20	15h
					$(52 ± 21)^d$	15e
5		n-dodecane/8		1.05 ± 0.50	10–20 $(40 ± 20)^d$	15h,e
		CCl₄/8		0.76 ± 0.10	$(94 ± 15)^d$	15h
6		CFCl₃/−20	see entry for 15	–	<0.1	9e
7		CFCl₃/−20	none	–	<0.1	9e
8		CFCl₃/−15	none[e]	–	<0.1	9e
9		CFCl₃/−15		–	>1	9e
10		CFCl₃/−20	none	–	<0.1	15c
11		CFCl₃/−20	none	–	<0.1	15d
12		CFCl₃/−20	none	–	<0.1	15i
13		CFCl₃/−20	none	–	<0.1	15i
14		CFCl₃/−20	none	–	<0.1	15i
15		benzene/7		0.80 ± 0.10	$(52 ± 20)^d$	15a,9e
		CCl₄/8		0.52 ± 0.10	$(97 ± 25)^d$	15i
16		CFCl₃/−20		–	≈0.1[g]	15b,d
17		CFCl₃/−20		–	≈1[g]	15f,j
18		benzene/25	none	–	0.3 > $^3\tau$ > 3.3[j]	9f
19		benzene/20		0.36 ± 0.01	280 ± 40[h]	15f,g
		benzene/25		–	275 ± 15[i]	15f,g
		acetonitrile/25		–	248 ± 15[i]	15f,g
		n-heptane/25		–	260 ± 60[i]	15f,g
20		CFCl₃/−10		–	≈390[g]	15g
		benzene/25		–	365 ± 20[i]	15g
		acetonitrile/25		–	310 ± 20[i]	15g
21		benzene/25		–	390 ± 50[i]	15g
		acetonitrile/25		–	380 ± 30[i]	15g

Table III (Continued)

diradical[a]	solvent/temp, °C	trapping product	trapping factor[b]	lifetime,[c] $^3\tau$, ns	ref
22	benzene/25		–	30 000 ± 4000[i]	15g
	acetonitrile/25		–	27 000 ± 2000[i]	15g

[a] Generated by means of benzophenone-sensitized laser photolysis of the corresponding azoalkane. [b] $T_f = k_t/(k_t + k_c)$. [c] Determined by using $k(O_2)$ from eqs 3 and 5, unless otherwise stated. [d] Determined by using $k(O_2)$ from eqs 3 and 4. [e] No cyclopropane ring-opened products detected. [f] Presumably derived from the decomposition of oxygen trapping products. [g] Estimated by preparative oxygen trapping. [h] Determined by quantitative oxygen trapping using $k(O_2)$ from time-resolved laser flash spectroscopy. [i] Determined by means of time-resolved laser flash spectroscopy. [j] Determined by the cyclopropylcarbinyl rearrangement.

in the vicinity of these singlet–triplet crossing points, it may be significant that singlet–triplet degeneracy is easy to achieve in tetramethylene.

Triplet 1,4-cyclohexanediyl (**16**) may be generated from 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO).[15b] Even if short-lived diazenyl diradicals[26] intervene, deuterium labeling studies[27] provide evidence that ^{3}**16** is born in the boat or twist-boat conformations. The boat conformation, **16a**, should be a geometry of high ISC efficiency according to the orbital orientation hypothesis (rule 2) and should be repeatedly accessed in the equilibrium between twist-boat conformations. Indeed, ^{3}**16** seems to be about 1000-fold shorter lived ($^3\tau$ ca. 0.1 ns)[15b] than the planar ^{3}**1**.

16a

The cyclohexanediyl **17** is the first bicyclic, localized triplet diradical observed to be trapped with oxygen,[15f] and the oxygen trapping technique indicates that it has a triplet lifetime of ca. 1 ns. MMPMI calculations[23] for **17** suggest an interorbital angle Θ of about 50° with sufficient flexibility to reach the triplet–singlet intersections, thus accounting for its short triplet lifetime.

The allyl-stabilized triplet 1,4-diradical **15** is about 10-fold shorter lived ($^3\tau$ ca. 10 ns)[9f] than ^{3}**1**. Again, conformational flexibility of **15** due to the free rotation of the exocyclic radical terminus might account for its relatively short lifetime. However, the allyl stabilization of the endocyclic radical center must counteract this mobility effect to some degree as this system is a relatively long-lived 1,4-diradical.

The triplet 1,4-cycloheptanediyl **18** possesses a higher degree of conformational flexibility than ^{3}**16**. MMPMI calculations for **18** suggest that boat and twist-boat conformations are favored and should be conformations of high ISC efficiency. Thus, it is not surprising that ^{3}**18** has a short lifetime ($0.3 < \tau < 3.3$ ns).[9g]

Phenyl-Substituted Diradicals

The introduction of phenyl groups at the radical sites can have a substantial stabilizing effect and significantly

extend the diradical lifetimes. This pronounced substitution effect can obscure more subtle effects influencing the triplet lifetimes of the diradicals. This phenomenon is nicely illustrated by the remarkable trends in the triplet lifetimes of phenyl-substituted 1,4-cyclohexanediyls, **19** and **20**, and 1,3-cyclopentanediyls, **21** and **22**.[15g]

While the introduction of a single phenyl group to **16** dramatically increases the triplet lifetime ($^3\tau$ 19:16 ca. 3000), the effect of phenyl substitution is only moderate in **1** ($^3\tau$ 21:1 ca. 4). The opposite trend is found upon introduction of the second phenyl group; a marginal lifetime increase is observed for the 1,4-cyclohexanediyl system ($^3\tau$ 20:19 ca. 1.3), while a pronounced enhancement is observed for the 1,3-cyclopentanediyl system ($^3\tau$ 22:21 ca. 75). Furthermore, **22** is also unusual in its significantly smaller rate constant for oxygen trapping as compared to its monophenyl analogue **21** as well as **19** and **20**, which all react at essentially the diffusion limit (Table II).

It is tempting to attribute the increase in the triplet lifetimes of the 1,4-cyclohexanediyls caused by phenyl substitution to relaxation to a chair conformation **16b**. Diradicals **19** and **20** both should readily access a relaxed chair conformation within their rather long lifetimes. The expected triplet ground state[15f] and the parallel orientation of the radical orbitals of **16b** should favor slow ISC and, thus, are consistent with the long lifetimes of **19** and **20**. Furthermore, on the basis of this chair conformation, **16b**, one would expect only β-scission to the corresponding dienes with no cyclization to the bicyclo[2.2.0]hexanes, as confirmed experimentally.[15f,28]
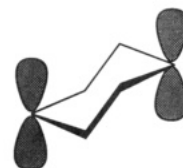
16b

Nevertheless, these conformational arguments should be regarded with some reservation. Other factors also might contribute to the increase in the lifetimes of these diradicals upon phenyl substitution: (1) delocalization at the radical center(s) might diminish the spin densities at the benzylic sites and thereby reduce the overlap necessary for effective SOC; (2) conjugation should introduce some rigidity, which would inhibit pyramidalization of the benzylic sites; and (3) stabilization of the diradical thermodynamically relative to product formation should impart kinetic persistence.[15g]

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Presumably all of these factors contribute to the unusually long triplet lifetime of **22**, which is as persistent as typical "non-Kekulé" diradicals.[1g,h]

Summary and Conclusions

While this oxygen trapping method holds great promise, some shortcomings and precautions should be emphasized. In particular, the lack of rate constants for the reaction of specific diradicals with oxygen, $k(O_2)$, constitutes a severe handicap; however, some progress has been made to fill this gap (Table II). For those cases that exhibit low oxygen trapping yields, the extent of involvement of spin-catalyzed ISC is worrisome. The application of the cyclopropylcarbinyl "free-radical clock" in combination with the oxygen trapping studies, as applied with the diradical **8** (Table III), can help to assess the degree of involvement of oxygen-catalyzed ISC. The intervention of relatively long-lived diazenyl diradicals[26] could be troublesome in that their trapping by oxygen might contribute to the formation of peroxide products. Furthermore, the diazenyl diradicals might exhibit very different ISC characteristics than the nitrogen-free triplet diradicals and, thus, distort the triplet lifetime data. However, this latter limitation also applies to other methods.

In conclusion, it would seem that the advantages of this oxygen trapping technique override these limitations. Thus, the first experimental support for the Salem–Rowland orbital orientation rule for ISC figures as the most evident success of this technique. Since no chromophores are needed in the diradicals to assess their lifetimes, it is possible to study localized hydrocarbon diradicals unperturbed by substituents. Such studies open the way for testing theoretical models of ISC in parent triplet diradicals, provide an experimental check on the results of complex potential energy surface calculations, and provide reaction products that can be correlated with important reaction intermediates that are postulated in many photochemical as well as thermal transformations. Besides theoretical insights, a detailed understanding of diradical behavior should greatly facilitate the development of new materials with novel optical, electronic, or magnetic properties,[29] and more rational diradical synthetic strategies.[30] For instance, the realization of two-photon processes involving the excitation of photochemically generated, long-lived diradicals is vitally dependent upon an understanding of diradical lifetime properties.[31]

Registry No. Oxygen, 7782-44-7.

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