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Intramolecular and Intermolecular Reactivity of Localized Singlet Diradicals: The Exceedingly Long-Lived 2,2-Diethoxy-1,3-diphenylcyclopentane-1,3-diyl

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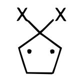
Abstract: The direct and benzophenone-sensitized photodenitrogenation of the diethoxy-substituted diazene **3** in nonprotic solvents, e.g. *n*-hexane, benzene, and acetonitrile, afforded exclusively the housane **4** through the intermediary 2,2-diethoxy-1,3-diphenylcyclopentane-1,3-diyl diradical **2b**. Alternatively, in the presence of methanol, the formation of the adduct **6** competed through trapping of the allylic cation **5**. The intervention of the intermediates was corroborated by laser-flash photolysis experiments of the diazene **3**. The diradical intermediate was characterized by its strong transient absorption at 545 nm, which decayed with a first-order lifetime in the microsecond range. The diradical lifetimes increased in the order *n*-hexane (0.52 μs), benzene (0.88 μs), acetonitrile (1.01 μs), and chloroform (3.73 μs). The singlet ground state of the 2,2-diethoxy-substituted 1,3-diradical **2b** is suggested by the absence of EPR signals at low temperature, the lack of quenching by molecular oxygen, and the calculated (UB3LYP/6-31G*) singlet preference of ca. 4 kcal mol^{-1} for 2,2-dihydroxy-1,3-diphenyl-1,3-cyclopentanediyl as a model. Trapping of the 1,3-diradical **2b** by external additives, e.g., olefins, dienes, and TEMPO, was not observed. In protic solvents, a decrease of the diradical lifetimes with increasing acidity was noted, e.g., the lifetime in acetic acid dropped to 70 ns. Moreover, a concomitant growth of an additional transient at 470 nm was found in acidic solvents, which was assigned to the allylic cation **5**. The factors governing the intramolecular and intermolecular chemical reactivity of the localized singlet diradical **2b** are discussed.

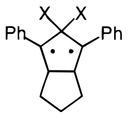
Introduction

The theoretical and experimental examination of localized singlet diradicals presents a topic of considerable current interest.[1−4] 2,2-Difluoro substitution in 1,3-cyclopentanediyl diradicals has been theoretically predicted[1] to promote a singlet ground state for the parent **1a** and this has been experimentally confirmed[2] for the 1,3-diphenyl derivative **2a**. Similarly, the most recent theoretical and experimental results suggest that 2,2-disilyl[3] or 2-spiroepoxy[4] substitution facilitates also a singlet ground state in such diradicals, e.g., derivatives **1c** and **1d**. The hitherto known singlet diradicals suffer some drawbacks, however, which have encumbered a detailed characterization of their intermolecular and intramolecular chemistry. On one hand, the difluoro-substituted diradical **2a,** while spectroscopically detectable, possesses a still too short lifetime (80 ns in *n*-pentane and 6 ns in acetonitrile)[2] to allow intermolecular chemistry to compete efficiently; moreover, its housane product does not persist near ambient temperature such that its comprehensive characterization has been difficult.[2] On the other hand, the spiroepoxy case **1d**, for which intermolecular trapping by methanol has been demonstrated through product studies,[4] lacks a chromophore for spectroscopic detection.



1a: X = F **1c**: X = SiR_3

1b: X = OH **1d**: X = 



2a: X = F

2b: X = OEt

Herein, we present a detailed spectroscopic characterization and product studies for the most persistent localized singlet diradical known to date, namely the 2,2-diethoxy-1,3-diphenyl-1,3-cyclopentanediyl (**2b**). Despite the seemingly innocuous substitution (as opposed to the previously employed fluoro[1,2] and silyl[3] substituents), the lifetimes of this diradical are orders of magnitude longer (3.7 μs in chloroform!) than those of the difluoro derivative **2a**. This has enabled us to study the factors that govern the intramolecular and intermolecular reactivity of this singlet diradical in detail.

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[1] (a) Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425. (b) Borden, W. T. *Chem. Commun.* **1998**, 1919.

[2] Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Heubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutzow, D.; Wirz, J. *J. Am. Chem. Soc.* **1998**, *120*, 593.

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[4] Abe, M.; Adam, W.; Nau, W. M. *J. Am. Chem. Soc.* **1998**, *120*, 11304.

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Scheme 1

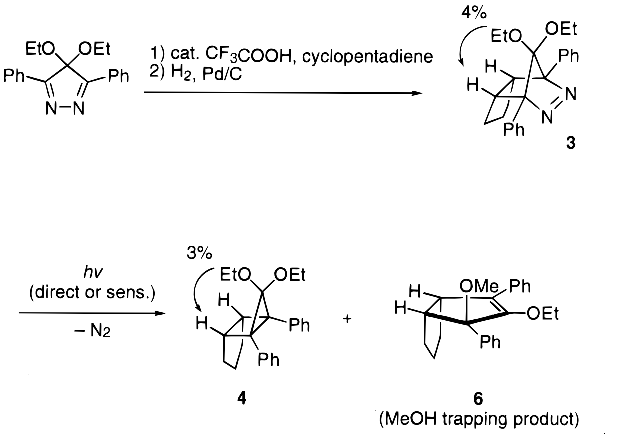


Table 1. Product Distributions for Photodenitrogenation of Diazene **3**[a]

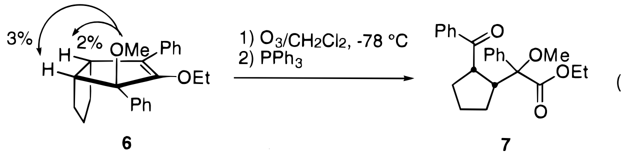
entry	solvent	yields of **4**[b]	ratios of **4**/**6**[c]
1	benzene	97	
2	*n*-hexane	98	
3	CH_3CN	95	
4	MeOH	88	92/8
5	MeOH/CF_3CH_2OH[d]	72	77/23
6[e]	MeOH	90	93/7
7[e]	MeOH/CF_3CH_2OH[d]	73	75/25

[a] The photodenitrogenation of diazene **3** (27 mM) was performed at 25 °C with a high-pressure Hg lamp (300 W, 320−380 nm band-path filter); diazene consumption was 100%. [b] Yields of isolated product after chromatography on silica gel. [c] The ratios of **4**/**6** (normalized to 100%) were determined on the basis of ^{1}H NMR (270 MHz) peak areas; reproducibility was ±0.9% for independent experiments. [d] A 1:1 mixture of MeOH/CF_3CH_2OH was used as solvent. [e] With benzophenone (270 mM) as triplet sensitizer.

Results

Photoproducts of Diazene 3. Diazene **3** was prepared from 4,4-diethoxy-3,5-diphenyl-4*H*-pyrazol[5] through the Hünig route[6] (Scheme 1). On direct photolysis with a high-pressure Hg lamp in benzene, *n*-hexane, or acetonitrile, diazene **3** ($\epsilon = 116$ $M^{-1}cm^{-1}$ at $\lambda_{max} = 364$ nm) afforded quantitatively housane **4** (> 95%, entries 1−3 in Table 1, Scheme 1). The anti configuration of **4** was established by NOE effects (cf. Scheme 1). For photodenitrogenations in the presence of methanol (entries 4−7), the methanol adduct **6** was observed by NMR spectroscopy along with housane **4**. Since the latter persisted in the presence of methanol and even trifluoroethanol, the methanol adduct **6** is not formed by reaction with housane **4** (vide infra). Trapping by methanol was more efficient in CF_3CH_2OH (entries 5 and 7). The ratios of **4**/**6** in the direct and triplet (benzophenone) sensitized photodenitrogenation were the same within experimental error (compare entries 4,5 with 6,7).

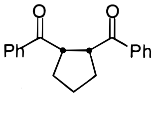
The structure of the methanol trapping adduct **6** was established on the basis of NMR spectra (^{1}H and ^{13}C DEPT). It was formed as a single diastereomer and its exo configuration was readily determined by means of ^{1}H NMR-NOE measurements for the MeOH/CF_3CH_2OH photolysate (cf. NOE effects in eq 1). The bridgehead and methoxy protons are well distinguished from the protons of housane **4** in d_6-benzene. The observed stereochemistry was expected from an exo attack of methanol on the intermediary allylic cation **5** (cf. Discussion). Since adduct **6** was too labile for isolation by silica gel or alumina chromatography, additional structural evidence was obtained by chemical transformation to the keto ester **7** (8% yield from diazene **3**) in the ozonolysis of the crude photolyzate in MeOH/CF_3CH_2OH (eq 1); housane **4** persisted under the ozonolysis conditions.



(1)

Diradical Trapping Experiments. Additional trapping experiments were performed to obtain evidence for the involvement of singlet diradical **2b** as an intermediate in the photolysis of diazene **3**. For example, the photodenitrogenation was performed in the presence of an excess (up to 0.5 M) of alkenes and conjugated dienes, e.g., vinyl ether, acrylonitrile, furan, etc.[7] However, only housane **4** was observed quantitatively in the photolyzates. Similarly, trapping experiments of the diradical (photolysis of diazene **3** or thermolysis of housane **4** at 65 °C for 24 h) with the radical scavengers TEMPO[8a] (1.1 M in $CHCl_3$ or benzene) and tributyltin hydride[8b] (neat) provided only housane **4** in >90% yield.

Trapping experiments with molecular oxygen ($^3O_2$) were pursued with particular interest, because oxygen is well-known to be an excellent scavenger of virtually all carbon-centered radicals and is sterically the least hindered trapping agent. High oxygen concentrations were achieved in a 1:5 mixture of *n*-hexane and perfluorodecalin ($C_{10}F_{18}$), in which the solubility of dioxygen is much higher than that in *n*-hexane alone.[9] An elevated temperature was needed to achieve homogeneous conditions[10] and the oxygen concentration was found to be 81.5 ± 2.0 mM at 4 atm and 65 °C.[11] After irradiation of diazene **3** for 4 h under O_2 (4 atm), the oxygenated products **8** (5%), **9** (6%), and **10** (10%) were isolated in addition to housane **4** (72%).



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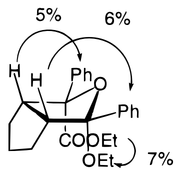

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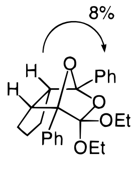

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(5) Gerninghaus, C.; Kümmell, A.; Seitz, G. *Chem. Ber.* **1993**, *126*, 733.

(6) Beck, K.; Hünig, S. *Chem. Ber.* **1987**, *120*, 477.

(7) Intermolecular reactions of non-Kekulé (delocalized) singlet diradicals: (a) Berson, J. A. *Acc. Chem. Res.* **1997**, *30*, 238. (b) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659. (c) Bush, L. C.; Heath, R. B.; Feng, X. W.; Wang, P. A.; Maksimovic, L.; Song, A. I.; Chung, W.-S.; Berinstein, A. B.; Scaiano, J. C.; Berson, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 1406. (d) Heath, R. B.; Bush, L. C.; Feng, Wu, X.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.* **1993**, *97*, 13355. Note that orbital-symmetry considerations suggest an allowed cycloaddition of conjugated dienes, e.g., furan, with the singlet diradical, and a forbidden one for monoolefins.

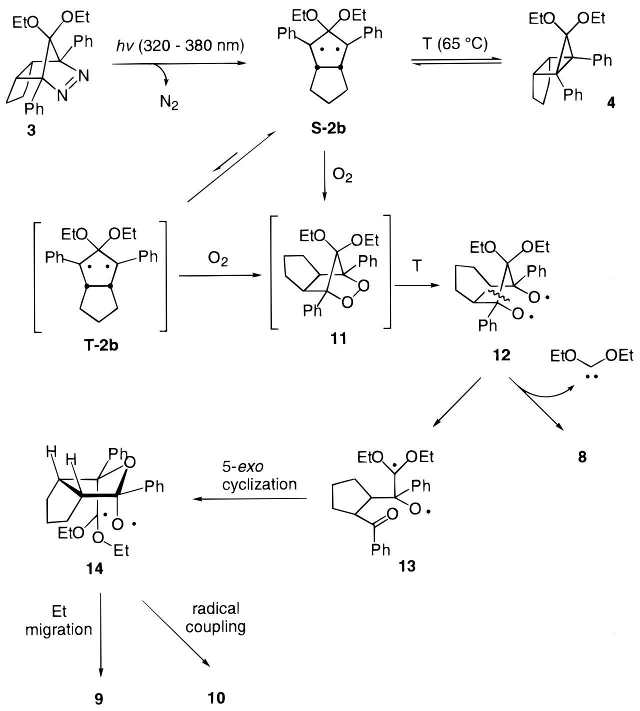
(8) (a) The rate constant for reaction of benzyl radicals with TEMPO in benzene has been reported to be 1.8×10^8 M^{-1} s^{-1}, cf.: Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983. (b) The rate constant for reaction of benzyl-type radicals with tributyltin hydride has been reported to be 3.6×10^4 M^{-1} s^{-1}, cf.: Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19.

(9) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 289.

(10) Klement, I.; Lütjens, H.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1454.

(11) The previously reported method was employed to determine the dioxygen solubility: Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929.

Scheme 2



The stereochemical assignments of the acid-labile products **9** and **10** were made by NOE measurements in C_6D_6 (cf. NOE effects above). In the oxygenated product **9**, significant NOE enhancements between the aromatic protons and the bridgehead protons, and also between the protons of the carboethoxy and ethoxy groups, were found, while for the ortho ester **10** strong NOE effects between the aromatic protons and the bridgehead ones, but *no* NOE enhancement between the bridgehead protons and the ethoxy group, were observed. The cis configuration of the 1,2-dibenzoylcyclopentane (**8**) was deduced by comparison with the spectral data of its known trans isomer.[12]

A control experiment was performed to check the thermal stability of housane **4**. After 18 h at 65 °C, housane **4** was also converted to the oxygenated products **8** (23%), **9** (23%), and **10** (43%). To perform the trapping experiments at ambient temperature (25 °C) at which housane **4** persists, benzotrifluoride ($CF_3C_6H_5$) was added to a suspension of diazene **3** in *n*-hexane/$C_{10}F_{18}$ to achieve homogeneous conditions also at ambient temperature ($C_{10}F_{18}$/*n*-hexane/$C_6H_5CF_3$ = 5/1/1). The oxygen concentration in this solvent system was found to be 58 ± 2 mM at 25 °C and 4 atm.[11] After direct or benzophenone-sensitized irradiation (320−380 nm) for 4 h (conversion 100%), housane **4** was obtained almost quantitatively (93%).

The combined results suggest that housane **4** undergoes ring opening to diradical **2b** and subsequent oxygen trapping at 65 °C (Scheme 2). The observed oxygen trapping during the high-temperature photolysis proceeds presumably also through the intermediary housane since a control experiment at ambient temperature did not afford any oxygen-trapping product. While the experiments establish oxygen trapping of diradical **2b**, it cannot be decided whether the singlet or the triplet state of the diradical is being trapped (Scheme 2).

With respect to the mechanism for formation of the oxygenated products **8**−**10** (Scheme 2), we assume homolytic decomposition of endoperoxide **11** at the elevated temperature (65 °C). Related bicyclic 1,2-dioxolanes have been reported to be quite unstable due to ring strain,[13] e.g., the thermally labile 1,2-dioxolane 2,3-dioxabicyclo[2.2.1]heptane decomposes readily even at 50 °C. This may explain the failure to detect the presumed intermediary endoperoxide **11**. The decomposition of the latter may involve α cleavage at one of the oxyl radical centers to form diradical **13**, which cyclizes[14] to the 1,5 diradical **14**. The tricyclic ortho ester **10** results from radical coupling of the 1,5 diradical **14** and the bicyclic product **9** is presumably produced by ethyl migration. The *cis*-1,2-dibenzoylcyclopentane (**8**) is probably formed from the elimination of diethoxycarbene in the 1,5-dioxyl diradical **12** (double α cleavage).[15] However, trapping of this carbene by electron-deficient olefins, e.g., acrylonitrile and fumaronitrile, was not observed.

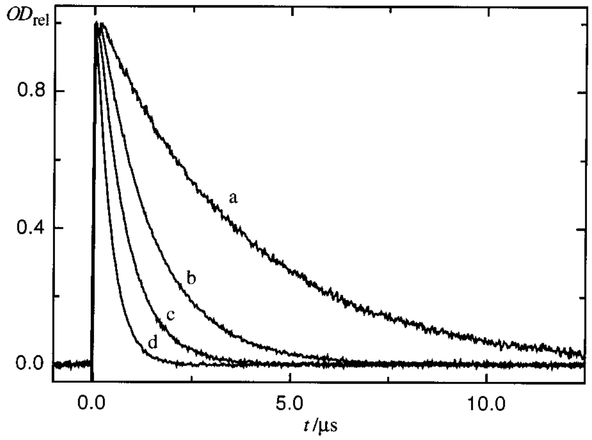


Figure 1. Transient decay traces of the singlet diradical **2b** (λ_{obs} = 545 nm), generated by photolysis from the diazene **3** (λ_{exc} = 351 nm) in (a) chloroform, (b) methanol, (c) acetonitrile, and (d) *n*-hexane.

Transient Absorption Spectroscopy. The transient absorption spectra and decay traces of diazene **3** were measured in various solvents by means of laser-flash photolysis (λ_{exc} = 351 nm, 20 ns pulse). These experiments could not be performed in the most polar (water) and least polar (perfluorohexane) solvents due to insolubility. In solvents of higher acidity than acetic acid, e.g., trifluoroacetic acid, rapid decomposition of the diazene **3** occurred. In the other solvents, a strong transient absorption was observed at around 545 nm, which decayed with clean first-order kinetics (Figure 1) and displayed a linear Arrhenius temperature dependence (Figure 2). The lifetimes were unaffected by the presence of oxygen (1 atm of air or oxygen atmosphere), even in chloroform and in the fluorocarbon solvent mixture used for the preparative trapping experiments ($C_{10}F_{18}$/*n*-hexane/$C_6H_5CF_3$ = 5/1/1). The transient lifetimes and activation parameters are summarized in Table 2.

The quantitative formation of the corresponding housane **4**, which in contrast to that derived from diradical **2a** is persistent near ambient temperature, allows the assignment of this transient as the intermediary singlet diradical **2b**. The singlet multiplicity is further indicated by the following facts and analogies: (a) the absorption maximum (λ_{max} = 545 ± 5 nm in all solvents) is very similar to that of the difluoro-substituted diradical **2a** (λ_{max} = 530 nm);[2] (b) the absorption obtained on photolysis in

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(12) Fuson, R. C.; Fleming, C. L.; Warfield, P. F.; Wolf, D. E. *J. Org. Chem.* **1945**, *10*, 121.

(13) (a) Balci, M. *Chem. Rev.* **1981**, *81*, 91. (b) Coughlin, D. J.; Salomon R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2761. (c) Adam, W.; Duran, N. *J. Am. Chem. Soc.* **1977**, *99*, 2729. (d) Clennan, E. L.; Foote, C. S. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; p 276.

(14) (a) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 230. (b) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674.

(15) For a related extrusion of silylene in the thermolysis of an endoperoxide see: Satoh, T.; Moritani, I.; Matsuyama, M. *Tetrahedron Lett.* **1969**, 5113. Nakadaira, Y.; Nomura, T.; Kanouchi, S.; Satoh, R.; Kabuto, C.; Sakurai, H. *Chem. Lett.* **1983**, 209.

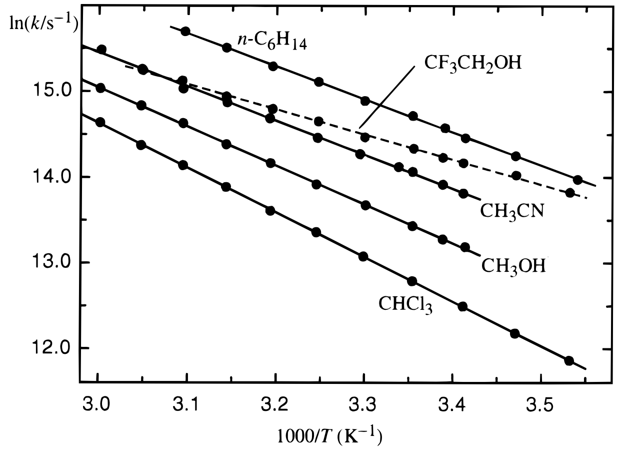

Figure 2. Arrhenius plots for the decay rate constants (ln k) of the singlet diradical **2b** (λ_{obs} = 545 nm), generated by photolysis of the diazene **3** (λ_{exc} = 351 nm) in a variety of solvents.

Table 2. Solvent Effect on the Lifetimes and Activation Parameters for Decay of Singlet Diradical **2b**

solvent	$E_T(30)^a$	τ (**2b**)/μs^b	E_a/(kcal mol^{-1})^c	log(A/s^{-1})^c
n-hexane	33.1	0.52	7.6	12.0
CCl_4	33.6	0.82		
benzene	34.8	0.88		
1,4-dioxane	36.0	0.91		
ethyl acetate	38.1	0.72		
$CHCl_3/CDCl_3$	39.1	3.73	10.3	13.2
CH_2Cl_2	41.1	1.55		
CH_3CN	46.0	1.01	8.0	12.0
iPrOH	48.6	1.29		
EtOH	51.9	1.54		
CH_3CN (10% H_2O)	54^d	1.19		
CH_3CN (20% H_2O)	55^d	1.32		
MeOH	55.5	1.89 [≈2.0]^e	9.0	12.5
MeOH/$CF_3CH_2OH^f$	[57.5]^g	2.37 [≈3.1]^e		
CF_3CH_2OH	59.5	0.64 [≈2.0]^e	5.8^h	10.5^h
CH_3COOH	51.7	0.07 [≈1.0]^e		

[a] From ref 23. [b] Lifetime of the singlet diradical **2b** determined by laser flash photolysis (λ_{obs} = 545 nm, λ_{exc} = 351 nm, 20 ns pulse); due to the strong temperature dependence, all values were obtained in thermostated cells at 20.0 ± 0.2 °C; 5% error. [c] Determined from Arrhenius plots of the lifetimes of the singlet diradical **2b** at ca. 10 temperatures between 10 and 60 °C; statistical error in the data is ca. 0.1 kcal mol^{-1} for E_a and 5% for log$A$. [d] From: Balakrishnan, S.; Easteal, A. J. *Aust. J. Chem.* **1981**, *34*, 943−947. [e] Values in brackets are the extrapolated lifetimes used in Figure 4 (correction for the interference from allylic cation formation) taken as 1/k_4 according to eq 3e with ϕ_5 from Table 3. [f] 1:1 mixture by volume. [g] Estimated to be the average of the values in the neat solvents. [h] Arrhenius plots for the growth kinetics of the allylic cation **5** at 470 nm provided consistent results.

a 2-methyltetrahydrofuran glass was thermally persistent at 77 K and resembled that of the transient in solution (λ_{max} = 566 nm), but it was EPR silent;[16] (c) the lifetime of the transient was insensitive to the presence of molecular oxygen; and (d) the activation parameters are similar to those for the decay of the difluoro-substituted diradical **2a**,[2] in particular, the high (ca. $10^{12}-10^{13}$ s^{-1}) preexponential Arrhenius factor (Table 2) is indicative of a spin-allowed reaction, namely ring closure to housane **4**.

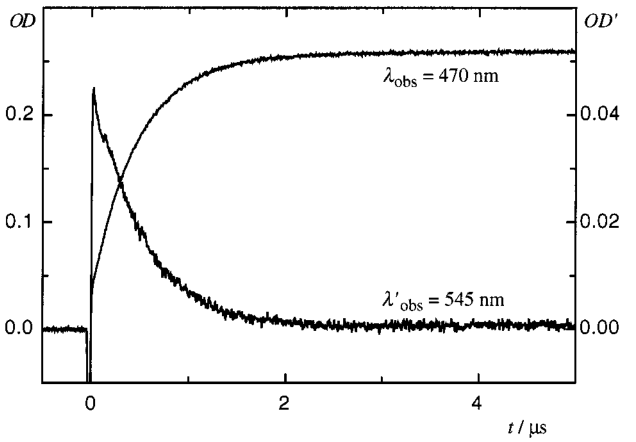

Figure 3. Transient decay trace of the singlet diradical **2b** (λ_{obs} = 545 nm, lower trace, OD′ scale), generated by photolysis of the diazene **3** (λ_{exc} = 351 nm) in trifluoroethanol and the concomitant growth of absorbance of the allylic cation **5** (λ_{obs} = 470 nm, OD scale).

Table 3. Lifetimes and Relative Absorbances of Transients (Singlet Diradical **2b** at 545 nm and Allylic Cation **5** at 470 nm) Formed in the Photolysis of Diazene **3** in Protic Solvents

solvent	τ(**2b**)/μs^a	τ(**5**)^b	OD$_{rel}^c$	ϕ_5^d	ϕ_4^e
MeOH	1.89	23 μs	0.33	0.04 [0.08]	0.96 [0.92]
MeOH/ $CF_3CH_2OH^f$	2.37	230 μs	2.0	[0.23]^g	[0.77]^g
CF_3CH_2OH	0.64	~10 min^h	6.0	0.69	0.31
CH_3COOH	0.07	71 μs	ca. 8	0.92	0.08

[a] From Table 2, the same lifetime was measured for the growth of the allylic cation **5** at λ_{obs} = 470 nm, λ_{exc} = 351 nm. [b] Lifetime for the decay of the allylic cation **5** determined by laser-flash photolysis (λ_{obs} = 470 nm, λ_{exc} = 351 nm, 20 ns pulse) at 20.0 ± 0.2 °C. [c] Ratio of the absorbances at 470 and 545 nm (OD_{470}/OD_{545}), determined from the initial maximum absorbance at 545 nm and the absorbance maximum in the plateau region at 470 nm, cf. Figure 3, under identical experimental conditions (same pulse energy, etc.). [d] Efficiency of allylic cation **5** formation obtained from eq 2; the values in brackets were acquired from product studies (trapping of the allylic cation with methanol). [e] Taken as $1 - \phi_5$. [f] 1:1 mixture by volume. [g] This ratio (from product studies) was used as reference to determine the extinction coefficients from eq 2, which were subsequently employed to calculate the efficiencies in the other solvents, cf. text. [h] Measured with conventional UV spectrophotometry.

In nonprotic solvents, the transient at 545 nm was the only detectable species. In protic solvents, however, the decay of the transient at 545 nm was accompanied by an isokinetic growth at 470 nm (Figure 3). The tail absorption of the 545 nm transient was very small at this wavelength. Moreover, the activation parameters, determined independently from the growing and decaying absorption, were the same within error. This provides evidence that the transient at 545 nm is the *precursor* of the transient at 470 nm. The secondary transient species at 470 nm decayed also with first-order kinetics (Table 3). In the case of trifluoroethanol, the transient persisted long enough to allow, after laser excitation, measurement of its slow decay by conventional UV spectrophotometry in the presence of air.

The transient at 470 nm was assigned to the allylic cation **5** on the basis of the following observations: (a) its lifetime was not influenced by molecular oxygen;[17a] (b) the observed absorption maximum is very similar to that of the allylic cation derived from the difluoro-substituted diradical **2a** (470 nm)[2] and to that of the related acyclic *E,E*-1,3-diphenylallyl cation (490 nm);[18] (c) the lifetime in methanol was much shorter than that

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(16) In contrast to diradical **2a**, which proved to be relatively photostable in MTHF glass at 77 K, the diradical **2b** underwent very efficient photodecomposition upon broad-band UV−visible irradiation with a medium-pressure mercury lamp. In fact, due to the high extinction coefficient of **2b**, it was only observable when special precautions were taken to exclude visible light (cobalt glass filters, Schott UG 1) or, alternatively, when 351 nm laser excitation was employed for the generation from the diazene **3**.

(17) (a) Miranda, M. A.; Pérez-Prieto, J.; Font-Sanchis, E.; Kónya, K.; Scaiano, J. C. *J. Phys. Chem. A* **1998**, *102*, 5724. (b) Mayer, R.; Fabian, J.; Viola, H.; Jakisch, L. *Phosphorus Sulfur* **1987**, *31*, 109.

in the less nucleophilic solvents trifluoroethanol and acetic acid (Table 3); and (d) the methanol trapping product **6** is formed (vide infra).

The chemical trapping in the presence of methanol suggests that the corresponding faster first-order decays are attributable to pseudo-first-order reactions with methanol. The lifetimes in *neat* methanol and acetic acid (Table 3) then suggest that the *apparent* reaction rate constants (k_r) of the allylic cation **5** with methanol and the less nucleophilic acetic acid are ca. 1.8 and 0.8×10^3 M^{-1} s^{-1}, taking k_r to be the inverse of $\tau \times$ [solvent]. For trifluoroethanol one obtains a lower limit of <0.6 M^{-1} h^{-1}, based on the very long first-order lifetime. These rate constants for nucleophilic trapping are orders of magnitude lower than those recently measured or estimated for the *E*,*E*-1,3-diphenylallyl cation, e.g., 1.3×10^5 M^{-1} s^{-1} with methanol and 8.0×10^3 M^{-1} s^{-1} with trifluoroethanol,[18] which indicates a dramatic stabilization of the allylic cation **5** by the electron-donating ethoxy and alkyl groups.

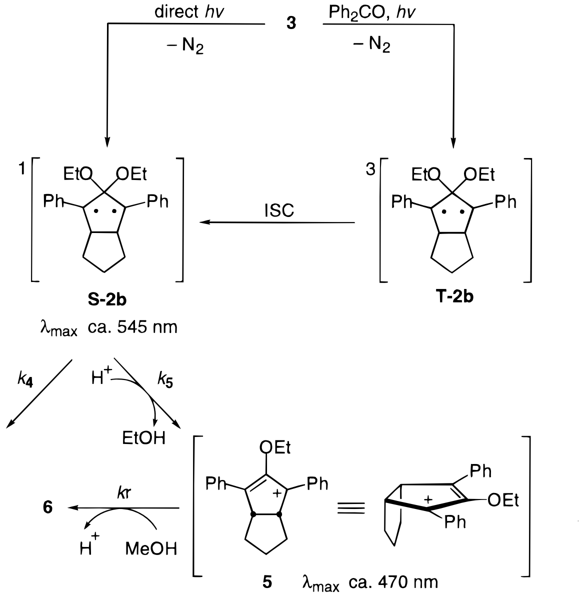
The extinction coefficients of the singlet diradical **2b** at 545 nm and that of the allylic cation **5** at 470 nm were determined in a 1:1 mixture of methanol/trifluoroethanol relative to that of triplet benzophenone in benzene at 525 nm (7800 ± 800 M^{-1} cm^{-1}) as actinometer.[18] The quantum yield for the formation of the diradical **2b** was assumed to be unity and that for the allylic cation **5** was taken as 23%, based on the relative yield of methanol trapping product in the same solvent mixture (see above). Extinction coefficients of 3350 M^{-1} cm^{-1} for **2b** and 27000 M^{-1} cm^{-1} for **5** were obtained. These agree well with the previously estimated value of 10^4 M^{-1} cm^{-1} for both **2a**[2] and the parent *E*,*E*-1,3-diphenylallyl cation.[17b] The efficiencies for allylic cation formation in other protic solvents were obtained from the experimental ratio of the absorbances of the diradical and the allylic cation (Table 3). Correction for the known extinction coefficients was made according to eq 2 and a possible solvent dependence of the extinction coefficients was neglected.

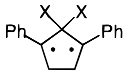
$$\phi_5 = [\mathrm{OD}_5 \times \epsilon_{2b}]/[\mathrm{OD}_{2b} \times \epsilon_5] \tag{2}$$

For methanol as solvent, the efficiency for allylic cation formation calculated from eq 2 (4%) agreed reasonably well with that obtained from chemical trapping (8%). The efficiency of allylic cation formation in neat trifluoroethanol (no trapping) was estimated from transient absorption to be 69%. In the most acidic solvent examined, acetic acid, the allylic cation **5** is nearly quantitatively formed (92%). The efficiency for the formation of housane **4** (ϕ_4, Table 3) was taken to be $1 - \phi_5$, in agreement with the observed product distributions.

Calculation of the Diradical Ground State. Our previously employed and tested[4] density function theoretical procedure (UB3LYP/6-31G*)[19] was used to assess the effect of 2,2-dihydroxy substitution on the singlet−triplet energy gap (ΔE_{ST}) of 1,3-cyclopentanediyl diradicals. The calculated data (not corrected for the small[4] zero-point vibrational energy differences) for the 2,2-dihydroxy diradical **1b** ($\Delta E_{ST} = -7.38$ kcal mol^{-1}) and its 1,3-diphenyl derivative **15b** ($\Delta E_{ST} = -3.96$ kcal mol^{-1}) resemble the corresponding values for the 2,2-difluoro derivatives **1a** ($\Delta E_{ST} = -7.07$ kcal mol^{-1})[4] and **15a** ($\Delta E_{ST} = -4.72$ kcal mol^{-1}, this work), which indicate a singlet ground state in all cases. The calculated singlet preference for the 2,2-dihydroxy diradical **1b** is larger than that for the 2-monoalkoxy (spiroepoxy) case **1d** ($\Delta E_{ST} = -1.00$ kcal mol^{-1}).[4]

Scheme 3





15a: X = F
15b: X = OH

Diradical **15b** should be an excellent model system for the experimentally examined system **2b**, since the effect of the 4,5-annelated cyclopentane ring is expected to have a minor effect. Note that the 4,5-ethano bridge in 1,3-cyclopentanediyl diradicals is a much weaker through-bond coupler than the 2-methano bridge.[20]

Discussion

The photolysis of diazene **3** is proposed to proceed through the pathways in Scheme 3. The involvement of the singlet diradical **2b** and the allylic cation **5** has been established by their transient spectra and kinetics, as well as product studies (cf. Results). For example, intervention of the allylic cation **5** has been confirmed by trapping with methanol. Diradical **2b** and the previously reported derivative **2a**[2] bear a number of similarities, namely their strong transient absorption in the visible region[21] and their competitive follow-up reactions,

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[18] Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.

[19] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) The calculations were performed within Gaussian 94; Frich, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94; Gaussian, Inc.: Pittsburgh, PA, 1995.

[20] (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 5409. (b) Dixon, D. A.; Dunning, T. H., Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

[21] A CF_2-induced mixing of the parity-forbidden transition of benzyl radicals at 460 nm with allowed transitions at higher energies has been held responsible for the strong, bathochromically shifted absorption band in the singlet diradical **2a** (ref 2). An alternative interpretation, already under discussion in the previous work, would involve a transition between the symmetric and antisymmetric SOMO orbitals, which is allowed for singlet diradicals. With respect to the latter possibility, the bathochromic shift for the diethoxy-substituted diradical **2b** versus the difluoro-substituted diradical **2a** (by ca. 15 nm) could be due to a smaller singlet−triplet energy splitting (cf. calculated values for diradicals **15a,b** in Results).

namely cyclization to the housane and heterolytic cleavage to the allylic cation **5** (Scheme 3). However, the two singlet species **2a** and **2b** display three important differences: (i) in contrast to the housane derived from diradical **2a**, that of diradical **2b** persists at ambient temperature which facilitates reliable product studies; (ii) the lifetimes of diradical **2b** are up to 2 orders of magnitude longer than those of diradical **2a** (Table 2), which dramatically increases the dynamic range for intermolecular trapping; and (iii) heterolytic cleavage (ethoxide ion expulsion) of diradical **2b** to yield the allylic cation **5** competes only in acidic protic solvents (Table 3). In contrast, diradical **2a** undergoes this competitive reaction even in nonpolar solvents.[2] The exceptional properties of diradical **2b** render this intermediate first choice to examine the intermolecular and intramolecular reactivity of localized singlet diradicals, in regard to both product studies and spectroscopic measurements.

Ground-State Multiplicity and Persistence of Diradical 2b. The singlet ground state of the localized diradical **2b** has been established by product studies and, in analogy to the difluoro derivative **2a**, by transient absorption spectroscopy (cf. Results). The assignment of a singlet ground state is supported by density-functional calculations (UB3LYP/6-31G*), which reveal a singlet ground state for the 2,2-dihydroxy diradical **1b** and also the 2,2-dihydroxy-1,3-diphenyl derivative **15b**. Interestingly, the singlet spin-state preference resulting from 2,2-dihydroxy substitution is calculated to be as large as for 2,2-difluoro substitution (cf. Results).

In view of the seemingly innocuous alkoxy substitution in diradical **2b** compared to the strongly electron-withdrawing fluoro- or electron-donating silyl substituents (theory has suggested that these serve best to promote singlet diradical character),[1,3] the exceptional persistence of diradical **2b** comes much as a surprise. This happenstance demands an adequate theoretical rationalization. Comparison of the activation parameters in *nonpolar* solvents (*n*-hexane for **2b**, Table 2, and cyclohexane for **2a**)[2] suggests that the higher persistency of diradical **2b** versus **2a** originates mainly from a decreased preexponential factor [$\log(A/\mathrm{s}^{-1}) = 12.0$ versus 12.8] and not from an increased activation barrier ($E_A = 7.6$ versus 7.8 kcal mol^{-1}). This implies that an entropic rather than an enthalpic effect is responsible. In addition, the ethoxy substituents are expectedly poorer leaving groups and render diradical **2b** more reluctant to undergo heterolytic cleavage to the allylic cation.

Intramolecular Reactivity: Heterolytic Cleavage of the Singlet Diradical 2b to the Allylic Cation 5. The formation of allylic cation **5** was corroborated by chemical trapping experiments (cf. Results). Its ease of formation increased with the *acidity* of the solvent,[22] as evidenced by efficiencies, e.g., acetic acid > trifluoroethanol > methanol (Table 3). The presence of a protic solvent alone, e.g., in acetonitrile−water mixtures, did not promote formation of the allylic cation **5**. Evidently, the elimination of the ethoxide ion is assisted by protons (formation of the better leaving group EtOH), as shown in Scheme 3. As may be seen in Table 2, the lifetime of the singlet diradical **2b** is correspondingly *shortened* in acidic solvents, most prominently in acetic acid (70 ns). Under acidic conditions, it is expected that proton-catalyzed heterolytic cleavage competes with housane **4** formation. This change in mechanism manifests itself not only in a shortened transient lifetime, but also in a reduced activation energy (Table 2). The examined temperature range (10−60 °C) was too small, however, to observe significant curvature of the Arrhenius plots and thereby to discriminate between the activation parameters for the two competitive processes. Moreover, there was little variation in the absorbance ratios with temperature, which precluded further analysis.

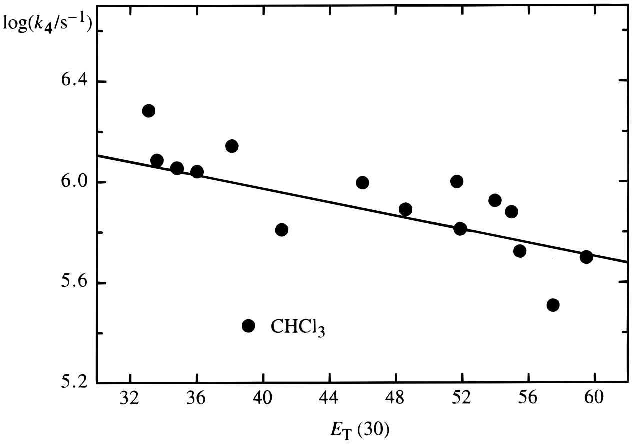

Figure 4. Correlation of the rate constant for housane **4** formation from the singlet diradical **2b** (log k_4) versus the $E_T(30)$ solvent polarity parameter; the data are taken from Table 2 and corrected where appropriate, as discussed in the text.

Intramolecular Reactivity: Ring Closure to Housane 4. Significant solvent effects were observed on the lifetimes of the singlet diradical **2b.** The lifetimes and activation energies decreased in the order chloroform > methanol > acetonitrile > *n*-hexane. The rate of ring closure of diradical **2b** to the corresponding housane **4** (k_4) decreased roughly with solvent polarity, as confirmed by the moderate correlation with the E_T(30) parameter[23] in Figure 4 [$\log(k_4) = 6.5 \pm 0.3 - (1.3 \pm 0.5)E_T(30)$, $r = 0.55$, $n = 16$].

The values for the rate constants k_4 were obtained as the inverse of the diradical lifetime, i.e., $1/\tau = k_{\mathrm{obs}} = k_4$, unless formation of the allylic cation **5** decreased the housane **4** yield below unity. In the latter case, the values for k_4 and k_5 may be obtained by correction of the observed diradical lifetime for the efficiencies of formation of the allylic cation **5** (ϕ_5) and the housane **4** (ϕ_4, Table 3) according to the simple relations in eqs 3a−e. The “apparent” lifetimes of the singlet diradical **2b** were taken as the inverse of k_4, i.e., they are those expected if the formation of the allylic cation **5** were not to occur in protic solvents, cf. values in brackets in Table 2.

$$k_{\mathrm{obs}} = 1/\tau = k_4 + k_5 \tag{3a}$$

$$\phi_5 = k_5/(k_4 + k_5) \tag{3b}$$

$$\phi_4 = 1 - \phi_5 = k_4/(k_4 + k_5) \tag{3c}$$

$$k_5 = \phi_5/\tau \tag{3d}$$

$$k_4 = k_{\mathrm{obs}} - k_5 = k_{\mathrm{obs}} - \phi_5/\tau \tag{3e}$$

The strong solvent dependence of the lifetime of the singlet diradical **2b** is unprecedented and tentatively attributed to a stabilization of its dipolar mesomeric structures **II** and **III** in

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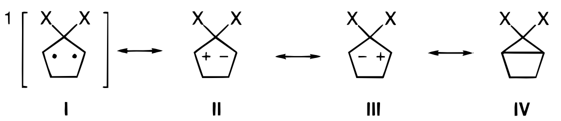
[22] Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents; Physical Properties and Methods of Purification*; John Wiley & Sons: New York, 1986.

[23] (a) Reichardt, C.; Harbusch-Görnert, E. *Lieb. Ann. Chem.* **1983**, 721. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.

polar solvents. In contrast, the lifetimes of closely related triplet diradicals do not display a significant solvent dependence.[24b]



In Table 2 and Figure 4, the high persistence of the diradical **2b** in chloroform (and to a lesser degree also in methylene chloride) stands out: Although the polarity of chloroform lies between that of dioxane and acetonitrile, the lifetime of diradical **2b** in chloroform is four times longer! Presumably the weak hydrogen-bonding (yet nonprotic) properties of the C−H bonds in chloroform[25] stabilize the singlet diradical **2b**.[26] Evidently, in addition to the bulk polarity, specific interactions with the solvent molecules may stabilize the localized singlet diradical **2b**.

Intermolecular Reactivity. All our extensive efforts to trap the localized singlet diradical **2b** by external additives and, thus, to explore the intermolecular reactivity of a localized singlet diradical met with failure. Even at very high concentrations ($\geq$0.5 M) of trapping agents (diylophiles, TEMPO, tributyltin hydride) no new products except housane **4** were detected. Not even in the time-resolved spectroscopic experiments, in which the exceedingly long lifetime (e.g., in chloroform ca. 3.7 μs) should facilitate the observation of subtle effects, did we obtain clear-cut evidence for trapping by external additives. These results suggest, if a lower limit of 0.60 μs is assumed for the lifetime of the singlet diradical **2a** (Table 2) and if a conservative estimate of 10% for the detection limit of trapping products is made, that the trapping rate constants are less than 4×10^5 M^{-1} s^{-1}. Such low values contrast sharply with those for *delocalized* (non-Kekulé) singlet diradicals, for which trapping by diylophiles is efficient and occurs with rate constants up to 10^8 M^{-1} s^{-1}, e.g., for acrylonitrile.[7c,d]

Strikingly, no dioxygen trapping products could be isolated even when the photolysis of diazene **3** was carried out at ambient temperature in a fluorocarbon solvent mixture to ensure a very high molecular oxygen concentration of ca. 60 mM. By employing the experimental lifetime of the singlet diradical in $C_{10}F_{18}$/*n*-hexane/$C_6H_5CF_3$ = 5/1/1 ($\tau = 0.74$ μs) and assuming a detection limit to 10%, this failure of diylophilic trapping suggests an oxygen-scavenging rate constant below 3.0×10^6 M^{-1} s^{-1}. The absence of trapping of the singlet diradical **2b** in chloroform under oxygen (1 atm) implies an even lower value of 1.4×10^6 M^{-1} s^{-1}, estimated on the basis that 5% trapping would have been detectable in laser flash photolysis. While these low values are reasonable in comparison to non-Kekulé (delocalized) singlet diradicals, which display values of 10^4−10^7 M^{-1} s^{-1},[7d] they are, nevertheless, surprising if one considers the presence of benzylic radical sites in this intermediate.

It should be noted that dioxygen trapping *was* observed upon photolysis of diazene **3** at elevated temperature (cf. Results). Unfortunately, the housane is oxidized at this temperature, such that oxygen trapping may have also taken place through equilibration with the energetically disfavored (by ca. 4 kcal mol^{-1} according to calculations for **15b**) triplet diradical **T-2b** (Scheme 2). The latter is expected to be 3 orders of magnitude ($k_r \geq 10^9$ M^{-1} s^{-1})[24] more reactive than the singlet diradical **2b**. Presently we have no experimental criteria to exclude the intervention of the triplet pathway.[27]

The estimated lower limits of the rate constants for intermolecular reactions of the localized singlet diradical **2b**, e.g., $\leq 1.4 \times 10^6$ M^{-1} s^{-1} for reaction with triplet molecular oxygen and $\leq 4 \times 10^5$ M^{-1} s^{-1} for trapping by alkenes, dienes, TEMPO, etc., characterize such singlet diradicals as exceptionally unreactive. We take the sluggish intermolecular chemical reactivity as experimental evidence that the electronic configuration of the singlet 1,3-diphenyl-1,3-cyclopentanediyl structure **I** has significant or even major contributions from the zwitterionic forms **II** and **III** or the covalent mesomer **IV**. In fact, such singlet diyls may well be viewed as planarized housanes with a "central π bond" and an activation barrier of ca. 8 kcal mol^{-1} toward rehybridization to the bent housane.

Conclusions

The three important conclusions from the present work on localized singlet 1,3-diphenyl-1,3-cyclopentanediyl diradicals are the following: (1) simple 2,2-dialkoxy substitution is sufficient to promote a singlet ground state and an extraordinary persistence; (2) the intramolecular reactivity of localized singlet diradicals may be affected by the medium, whereby nonpolar solvents accelerate cyclization to the housane, while acidic solvents accelerate cleavage to the allylic cation; and (3) the localized singlet diradicals are reluctant to undergo intermolecular trapping reactions, which may be indicative of significant zwitterionic and covalent contributions. The experimental findings, along with the observation of the strong long-wavelength absorption of such localized singlet diradicals,[21] challenge more detailed theoretical investigations. The present state of the art displays the lack of a comprehensive theoretical understanding of localized singlet diradicals, which presents an obstacle in the design of appropriate experimental test cases for further investigation.

Acknowledgment. We express our gratitude to the Deutsche Forschungsgemeinschaft, the Volkswagen Foundation, the Fonds der Chemischen Industrie, and the Swiss National Science Foundation for generous financial support. This work was supported in part by the grant-in-aid for Scientific Research on Priority Areas "Molecular Physical Chemistry" from the Ministry of Education, Science, Sports, and Culture of Japan. M.A. thanks the Alexander-von-Humboldt Foundation for a postdoctoral fellowship (1997−1998) and Prof. M. Nojima for his encouragement.

Note Added in Proof: The generous gift (Dr. M. Tinkl, CIBA SC) of a high-pressure cuvette (up to 10 atm) for transient absorption measurements has enabled us to obtain a value of 8.4×10^5 M^{-1} s^{-1} for the oxygen trapping rate constant in $C_{10}F_{18}$/*n*-hexane/$C_6H_5CF_3$ = 5/1/1 at ambient temperature. This

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[24] (a) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165. (b) Kita, F.; Adam, W.; Jordan, P.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1999**, *121*, 9265.

[25] For solvent parameters on hydrogen-donating ability (α values) cf. textbooks and: Daniel, D. C.; McHale, J. L. *J. Phys. Chem. A* **1997**, *101*, 3070.

[26] The supposition that the "lower concentration" of C−H bonds in chloroform may be responsible (C−H and O−H bonds could serve to promote this chemical reaction by electronic-to-vibrational energy transfer, akin to the deactivation of singlet molecular oxygen, cf.: Gorman, A. A.; Rodgers, M. A. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, pp 229−247), is discarded in view of the absence of a deuterium isotope effect and the "normal" behavior (short lifetime) in carbon tetrachloride (Table 2).

[27] Oxygen trapping of related triplet diradicals has been previously observed in the thermally induced ring opening of the parent 1,3-diphenylbicyclo[2.1.0]pentane (Adam, W.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1989**, *111*, 6896); however, unlike for the latter housane, NMR coalescence experiments could not be employed to evaluate the bond dissociation of the housane **4** to its diradical **2b** due to its unsymmetric structure, i.e., anti and syn diastereomers.

result is in line with our assumed lower limit. This finding has once more encouraged the search for oxidation products in preparative trapping experiments and, indeed, 2% of one oxidation product, *cis*-1,2-dibenzoylcyclopentane (**8**), could be isolated along with 91% housane **4** after photolysis of diazene **3** in $CDCl_3$ under 4 atm of oxygen at ambient temperature.

Supporting Information Available: Experimental Section (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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