Photochemical Generation and Methanol Trapping of Localized 1,3 and 1,4 Singlet Diradicals Derived from a Spiroepoxy-Substituted Cyclopentane-1,3-diyl

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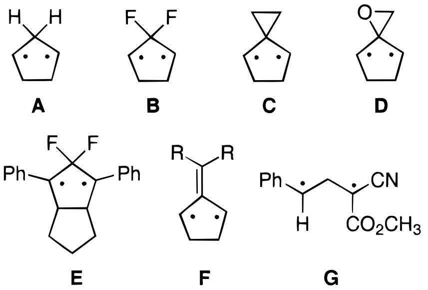
Received June 29, 1998

Abstract: The direct and benzophenone-sensitized photodenitrogenation of the azoalkane 2,3-diazabicyclo-[2.2.1]hept-2-ene-7,3′-spiro-2′,2′-diphenyloxirane **1** at ambient temperature (ca. 15 °C) in benzene afforded exclusively the 6-oxabicyclo[3.2.0]hept-1-ene **3**. The labile oxetane **3** is proposed to be formed by the selective cleavage of the C−O bond in the epoxy ring of the initially photogenerated, spiroepoxy-substituted, localized cyclopentane-1,3-diyl diradical **1,3-DR** to the **1,4-DR** diradical and subsequent cyclization of the latter. Even at −100 °C, the highly strained (strain energy estimated to be ca. 94 kcal/mol) spiroepoxy housane **2** could not be observed by ^{1}H NMR (600 MHz) spectroscopy. In MeOH, instead of the oxetane **3**, the two regioisomeric MeOH adducts **6** (trapping product of the diradicals **1,3-DR** and **1,4-DR**) and **6′** (methanolysis product of **3**) were obtained in high yields. For the first time methanol trapping of a cyclopentane-1,3-diyl singlet diradical was achieved; the required dipolar character is presumably induced in this symmetric species by the polar methanol medium. Computational work (UB3LYP/6-31G*) reveals that the **S-1,3-DR** singlet diradical possesses a singlet ground state (ΔE_{ST} ca. 1 kcal/mol), for which ring closure (E_A ca. 2.6 kcal/mol) to the spiroepoxy housane **2** requires more activation than epoxide-ring opening (E_A ca. 0.7 kcal/mol); the **T-1,3-DR** triplet species ring-opens spontaneously (E_A ca. 0 kcal/mol) to the corresponding **T-1,4-DR**. Stereoelectronic effects dictate the appropriate conformational alignment of the C−O bond with the radical p orbital in the **1,3-DR** for the selective cleavage of the C−O rather than C−C bond in the epoxy ring.

Introduction

For localized cyclopentane-1,3-diyl diradicals, the balance between *through-space* and *through-bond* coupling of the nonbonding molecular orbitals (NBMO's, Ψ_S and Ψ_A) affects the singlet−triplet energy gap ($\Delta E_{ST} = E_S - E_T$) and thus determines the spin multiplicity.[1] When the two are of approximately equal strength, a triplet ground-state applies; otherwise the singlet is preferred. In such localized 1,3 diradicals (structures **A**−**D**) the *through-bond* interaction is a sensitive function of the substituents X at the carbon atom between the two radical sites (Figure 1).[2] For X = H (**A**) the *through-bond* interaction of the symmetric NBMO (Ψ_S) with the σ C−H (pseudo-π) orbital dominates, while for X = F (**B**) it is the interaction with the σ^* C−F orbital due to the greater electronegativity of fluorine. These interactions either increase or decrease the energy of Ψ_S, and thus the small or large energy gap between the NBMOs results in a triplet or singlet ground state for the diradicals **A** and **B**.[2d]



For the parent cyclopentane-1,3-diyl **A** (X = H), the triplet state is favored by 1.10−1.35 kcal/mol according to high-level ab initio calculation (Table 1).[3] Indeed, the triplet ground state was confirmed by EPR spectroscopy, the first fully characterized localized triplet diradical.[4] Geminal fluorine substitution in the derivative **B** favors the singlet state by 6.1 to 9.7 kcal/mol according to calculations (Table 1).[5] The singlet ground state in the case of the fluorine-substituted derivative **B** was recently substantiated by time-resolved spectroscopy for the diphenyl derivative **E**.[6] This constitutes the first sufficiently persistent (ca. 80 ns lifetime in *n*-pentane at room temperature) *localized singlet* 1,3 diradical that has been spectroscopically character-

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(1) (a) *Diradicals*; Borden, W. T. Ed.; Wiley-Interscience: New York, 1982. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

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(5) Xu, J. D.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 5425.

10.1021/ja9822761 CCC: $15.00

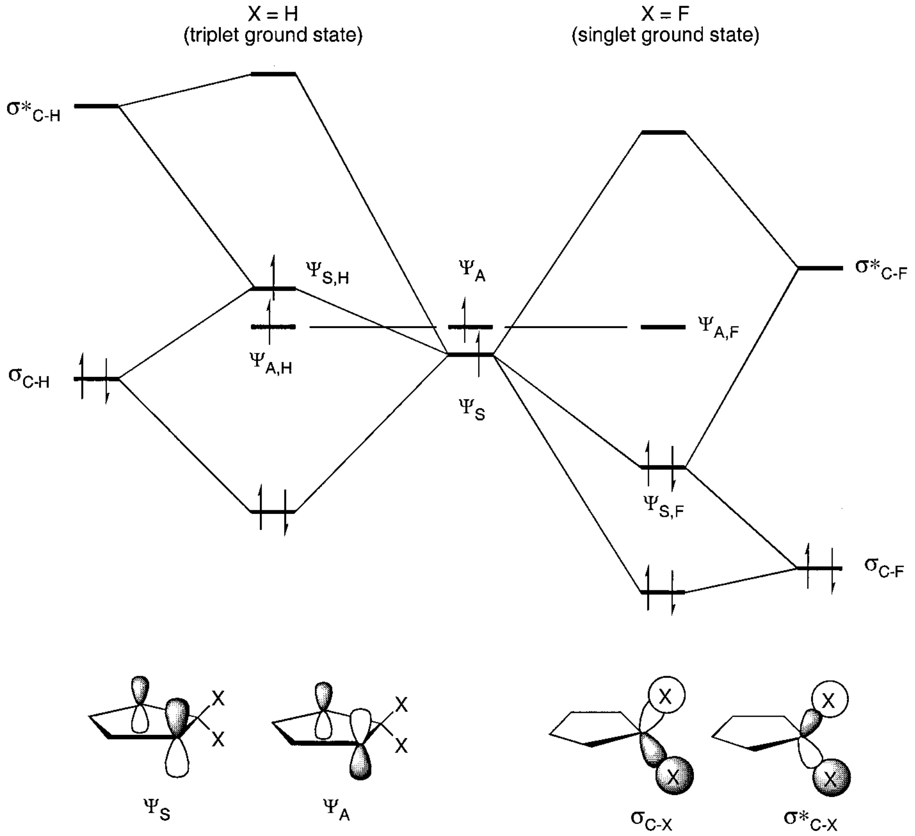


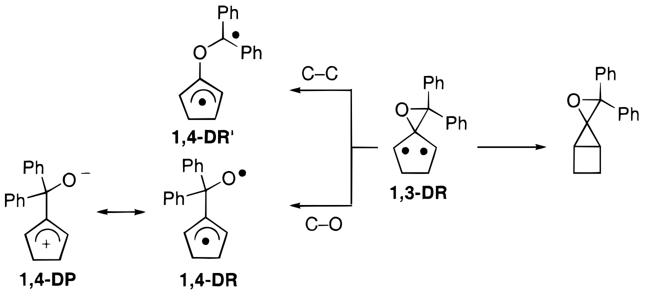
Figure 1. The effect of *through-bond* interaction of the methylene bridge in cyclopentane-1,3-diyl diradicals on the nonbonding molecular orbitals (NBMOs, Ψ_S and Ψ_A); a triplet ground state (X = H) or a singlet ground state (X = F) is preferred as a consequence of the *through-bond* interaction by the σ and σ^* C−X orbitals with the symmetric NBMO (Ψ_S).

Table 1. Singlet-Triplet Energy Gaps (ΔE_{ST}) of Localized Cyclopentane-1,3-diyl Diradicals

		$\Delta E_{ST} = E_S - E_T$	
diradical	UB3LYP/6-31G*^{a}	calcd, lit.	exp
A	1.12 [1.20]	1.10 to 1.35^b	T^c
B	−7.07 [−6.48]	−(6.1 to 9.7)^d	S^e
C	1.85 [1.80]	1.5^f	T^g
D	−1.00 [−0.71]^{h,i}	−	S^i

[a] C_{2v}-symmetric structures **A**−**C**, C_S-symmetric structure **D** from this work; values in brackets are corrected for zero-point vibrational energy differences. [b] Reference 3b. [c] Reference 4. [d] Reference 5. [e] 1,3-Diphenyl derivative **E** from ref 6. [f] Reference 10, footnote 21. [g] Reference 10, inferred from the triplet diradical formed by cyclopropane ring opening. [h] Vertical energy gap at the singlet geometry (the triplet diradical is a dissociative state). [i] This work.

Scheme 1. Possible Transformation of the Spiroepoxy-Substituted Cyclopentane-1,3-diyl Diradical 1,3-DR



ized.[7,8b] However, attempts to trap it by methanol or diylophiles failed, because fast fluoride ion elimination competed especially in polar solvents. Nevertheless, alcohol trapping of singlet diradicals has been reported, e.g., for the delocalized non-Kekulé-type trimethylenemethanes **F**[8] and the localized donor/acceptor-substituted trimethylene **G**.[9]

Figure 1 illustrates that through the proper selection of substituents X, the *through-bond* coupling may be manipulated such that either a triplet or a singlet ground-state prevails. An attractive pair is given by the spirocyclopropyl- and spiroepoxy-substituted cyclopentane-1,3-diyls **C** and **D**. For **C**, both ab initio calculations and EPR-spectroscopic data[10] suggest a triplet ground state (Table 1), while for **D**, a singlet ground state has been established in the present work.

The diphenyl derivative **1,3-DR** has been examined in the present study. As displayed in Scheme 1, a variety of competitive transformations may be anticipated. Besides cyclization of the singlet cyclopentane-1,3-diyl to the highly strained housane, attractive alternatives are epoxide-ring opening by cleavage of the C−O or C−C bond to afford the respective diradicals **1,4-DR** and **1,4-DR′**. The following pertinent ques-

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(6) 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.

(7) For delocalized singlet diradicals see Bushby, R. J. *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1211 and also see ref 8b.

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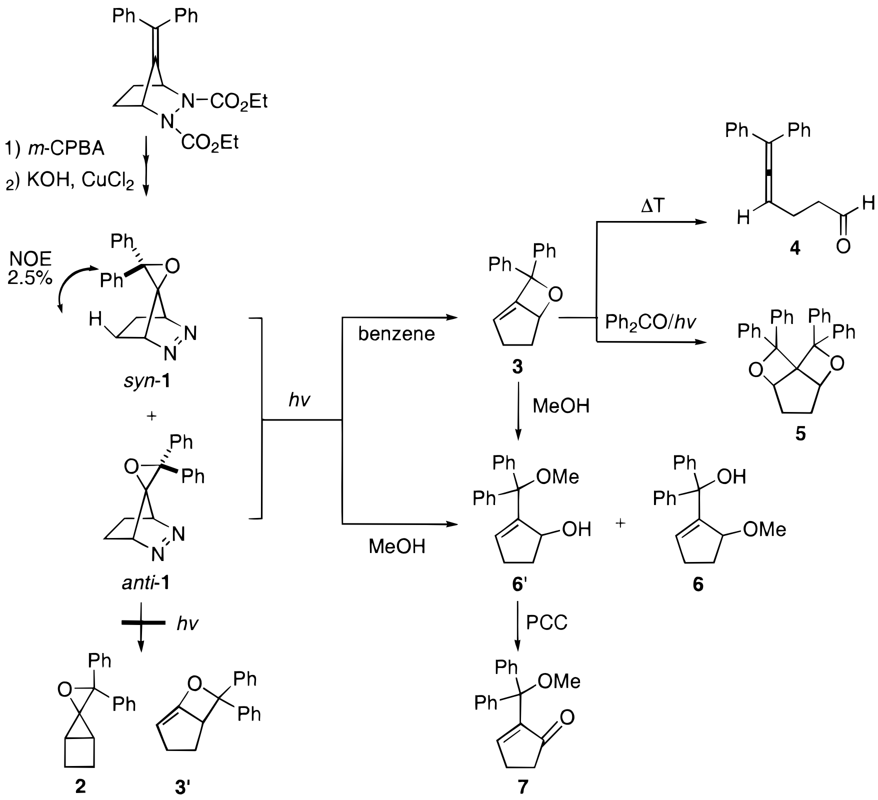
(10) Jain, R.; McElwee-White, L.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 552.

Scheme 2. Synthesis of Diazene **1** and Its Photolysis Products



tions shall be addressed: Which reaction channel in Scheme 1 dominates? What differences in the chemical reactivity manifest the singlet and triplet spin states of the various diradicals? Do the singlet species possess dipolar character? Can such localized singlet diradicals be trapped by methanol?

Results

Preparation of the Diazene 1 and Its Photodenitrogenation. The spiroepoxy diazene **1** was prepared from the hydrazide[11,12] as depicted in Scheme 2. The configurations of the diastereomers *syn*-**1** ($\lambda_{max} = 344$ nm, ϵ 230) and *anti*-**1** ($\lambda_{max} = 352$ nm, ϵ 90), which could be separated by silica gel chromatography, were determined by NOE experiments. The stereoisomer with appreciable (2.5%) NOE enhancement between the *exo* hydrogen atoms and the aromatic ones was assigned to the *syn* configuration.

The azoalkane **1** was photochemically denitrogenated at 15 °C by means of an argon-ion laser (Scheme 2). The 6-oxabicyclo[3.2.0]hept-1-ene **3** was formed exclusively (>95%) in benzene (5.2×10^{-2} M), independently of the diazene **1** configuration. Also the irradiation conditions had no influence, since the direct irradiation (333 and 351 nm, 15 min, conversion 100%) or benzophenone (5.2×10^{-2} M) sensitization (364 nm, 5 min, conversion ca. 30%) gave exclusively the labile oxetane **3**. A control experiment without Ph_2CO (364 nm, 60 min, conversion only 5%) established that the photodenitrogenation of the diazene **1** at 364 nm is triplet-sensitized in the presence of Ph_2CO.[13]

The strained oxetane **3**, which could be recrystallized from *n*-hexane at −15 °C, was fully characterized by spectroscopy (NMR, IR) and elemental analysis (see Supporting Information). This photoproduct did not persist under acidic conditions or at temperatures above 40 °C. Thus, the thermal decomposition of the oxetane **3** (60 °C in benzene, 45 h) led to the allene **4** (78%, conversion 100%), while prolonged irradiation gave the symmetrical adduct **5** (65%, conversion 100%)[15] by photochemical cycloaddition with Ph_2CO. These two transformations clearly establish the 6-oxabicyclo[3.2.0]heptene structure for the labile oxetane **3**. Not even traces of the regioisomeric 7-oxabicycloheptene **3′** were formed.

To check for the intervention of the housane **2** (Scheme 2), the photoreaction (333 and 351 nm, 30 min, conversion 40%) was performed at −98 °C in a 10:1 mixture of d_8-toluene/d_6-benzene, and the reaction mixture was directly analyzed by 600-MHz ^{1}H NMR and 150-MHz ^{13}C NMR spectroscopy. Even at this low temperature, only the additional signals of the oxetane **3** were observed.[16] These results suggest that the housane **2**, if formed at all, does not persist even at −98 °C to allow NMR-spectral detection. The formation of the oxetane **3** establishes that the C−O bond of the epoxy ring rather than the C−C bond (Scheme 1) suffers ring-opening in the diradical **1,3-DR**, which is assisted through heterolytic cleavage to the 1,4 dipole **1,4-DP**.[19] Had homolysis taken place, C−C bond fragmentation to the regioisomeric 1,4-diradical (**1,4-DR′**) should have been

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[11] Marullo, N. P.; Alford, J. A. *J. Org. Chem.* **1968**, *33*, 2368.

[12] Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, S. R.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725.

[13] The triplet energies of diazabicyclo[2.2.1]hept-2-ene (DBH) derivatives are around 60 kcal/mol (ref 14) and that of Ph_2CO is 68 kcal/mol; thus, the sensitized process is energywise feasible.

[14] Engel, P. S.; Horsey, D. W.; Scholz, J. N.; Karatsu, T.; Kitamura, A. *J. Phys. Chem.* **1992**, *96*, 7524.

[15] The regioisomer was observed as a minor product by ^{1}H NMR spectroscopy; the product ratio was ca. 91:9.

[16] Although for the corresponding spirocyclopropane-substituted 1,3 diradical the housane persists (ref 17), the failure to observe the housane **2** derives presumably from the fact that epoxide ring is cleaved ca. 100 times faster than the cyclopropane ring (ref 18).

[17] (a) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1969**, *730*, 82. (b) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1970**, *733*, 44. (c) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303.

[18] Krosley, K. W.; Gleicher, G. J. *J. Phys. Org. Chem.* **1993**, *6*, 228.

Table 2. Photoreactions of the Spiroepoxy Azoalkane **1** in Methanol[a]

			product distribution (%)[b]	
entry	**1**	conditions	**6′** (= **3**)	**6**
1	*syn*	333/351 nm	78	22
2	*anti*	333/351 nm	79	21
3	*syn*	Ph_2CO (0.05 M), 364 nm	91	9
4	*anti*	Ph_2CO (0.05 M), 364 nm	91	9
5[c]	*syn*	1,3-cyclohexadiene (1 M), 333/351 nm	80	20
6[d]	*syn*	333/351 nm	73	27
7[d]	*syn*	Ph_2CO (0.05 M), 364 nm	87	13
8[e]	*syn*	333/351 nm	90	10

[a] At 15 °C, 36.0 μmol **1** in 0.7 mL of degassed C_6H_6/MeOH (1:1), unless otherwise noted; azoalkane consumption was >95% and the mass balance >88%, except for entry 5 (75%). [b] Relative yields (normalized to 100%) are based on ^{1}H NMR (200 MHz) peak areas of the methyl singlets (δ 3.22 ppm for **6** and 3.05 ppm for **6′**); the reproducibility was ±0.8% for independent experiments. [c] O_2 (up to 2 atm) showed no effect on the product ratios. [d] The photoreactions (**1**, 36.0 μmol) were run at 15 °C in 0.7 mL of degassed MeOH. [e] The photoreaction (**1**, 36.0 μmol) was run at 15 °C in 0.7 mL of degassed C_6H_6/MeOH (9:1).

favored due to the stabilization of the unpaired electron at the benzylic site by phenyl conjugation (Scheme 1).[20]

Time-resolved (nanosecond time scale) laser-flash spectroscopy was performed to detect intermediates (λ_{exc} = 351 nm, 25-ns pulse); however, no transient with significant absorption above 300 nm was observed. This result rules out that the regioisomeric 1,4-diradical **1**,**4-DR′**, derived from C−C-bond cleavage of the epoxide ring (Scheme 1), is formed as an intermediate since such diradicals should be sufficiently long-lived and should show sufficiently strong absorption in the UV region (benzyl chromophore) to allow detection by laser flash photolysis.[5,6] Furthermore, no paramagnetic species could be detected by EPR spectroscopy under matrix isolation (MTHF, at 77 K), which indicates that a diradical with a triplet ground state does not intervene under these conditions.[4,10]

Methanol-Trapping Experiments. The 1,4-diradical (**1**,**4-DR**, Scheme 1) is expected to possess pronounced dipolar (zwitterionic) character due to the localized negative charge on the electronegative oxygen atom and allylic stabilization of the positive charge.[19a,21] Consequently, to provide evidence for dipolar character in the 1,4-diradical (**1**,**4-DR**), the photoreactions of azoalkane **1** were performed in the presence of MeOH to trap such intermediates. As shown in Table 2, in 1:1 MeOH/C_6H_6 the methanol adducts **6** and **6′** (see Scheme 2) were obtained instead of the oxetane **3**. The structure of adduct **6′** was determined by oxidation to the ketone **7** (56%) with pyridium chlorochromate (PCC); the regioisomer **6** expectedly resisted oxidation (see Supporting Information). A control experiment showed that the oxetane **3** was exclusively (96%) converted to the MeOH adduct **6′**. Even in the triplet-sensitized denitrogenation (entries 3, 4, 7), the MeOH adduct **6** was observed but by 10% (absolute) less than in the direct photolysis (cf. the **6**:**6′** product ratios in Table 2). In pure MeOH (entries 6 and 7), a small increase in the **6** trapping product was observed in both the direct and sensitized photolysis, while in 10% MeOH (entry 8), a significant drop in the amount of the MeOH adduct **6** was found in the direct photolysis.

In the presence of 1,3-cyclohexadiene (entry 5)[22] or oxygen (up to 2 atm) as triplet quenchers almost the same product ratio as in the direct photolysis (entry 1) was observed. The insensitivity toward addition of triplet quenchers rules out the intervention of a long-lived azoalkane triplet state. In fact, since 2,3-diazabicyclohept-2-ene and its derivatives, except some special cases,[23] do not undergo intersystem crossing (ISC),[24] we assume that the chemical reactivity derives from the singlet-excited azoalkane $^{S}\mathbf{1}^{*}$.

Quantum-Chemical Calculations. The assessment of the ground-state multiplicity of diradicals has remained a computational challenge over the years.[3,5] High-level, ab initio calculations with configuration interaction for the proper description of such open-shell species and electron correlation, e.g., the CISD and CASPT2 methods with large basis sets, are expensive and inapplicable for the large systems as examined herein.[3,5] Also, experimental studies on absolute singlet−triplet energy gaps may show a considerable scatter and have often borne out surprising effects,[25] which render the selection of a reliable computational procedure, i.e., one which reproduces experimental findings, quite difficult.

Density functional theory (DFT) is well-known to handle properly both open-shell and closed-shell structures,[26a] and we have employed this method for the diradical intermediates **A**−**D**. Although the question has been raised whether spin-projected rather than uncorrected energies should be employed in the calculation of diradicals by density functional theory,[26] we find that the uncorrected DFT energies reproduce adequately the experimental data. Hence, the UB3LYP/6-31G* level of theory (in Gaussian 94)[27] provides excellent results on the singlet−triplet gaps of diradicals for some experimentally examined 1,3-cyclopentanediyl systems (Table 1).

The calculations confirm a triplet ground state for the parent 1,3-cyclopentanediyl and a singlet ground state for the 2,2-difluoro derivative. The calculated singlet−triplet energy gaps for these model species agree well with the data from the highest-level computations (Table 1). For the spiroepoxy diradical **D**, the singlet ground state is favored by 1.0 kcal/mol (0.7 kcal/mol when corrected for the zero-point vibrational energies). The preference for singlet-spin multiplicity is much less pronounced than for the 2,2-difluoro case, as would be expected from the reduced *through-bond* interaction imposed by one alkoxy versus two fluoro groups.

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(19) For dipolar character in singlet diradicals see (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. (b) Jean, Y.; Salem, L. *J. Chem. Soc., Chem. Commun.* **1971**, 382. (c) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Sevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279.

(20) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. (b) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687. (c) Stogryn, E. L.; Gianni, M. H. *Tetrahedron Lett.* **1970**, 3025. (d) Ayral-Kaloustian, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 314.

(21) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; pp 195−258.

(22) The triplet energy of 1,3-cyclohexadiene is 52 kcal/mol (Kellogg, R. E.; Schwenker, R. P. *J. Chem. Phys.* **1964**, *41*, 2860); that of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) derivatives is ca. 60 kcal/mol (ref 14), and thus the triplet quenching is feasible.

(23) (a) Adam, W.; Nau, W. M.; Sendelbach, J.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 12571. (b) Adam, W.; Fragale, G.; Klapstein, D.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc*. **1995**, *117*, 12578.

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(25) See, for example, Matsuda, K.; Iwamura, H. *J. Am. Chem. Soc.* **1997**, *119*, 7412.

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(27) Gaussian 94. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian Inc.: Pittsburgh, PA, 1995 Revision A.1.

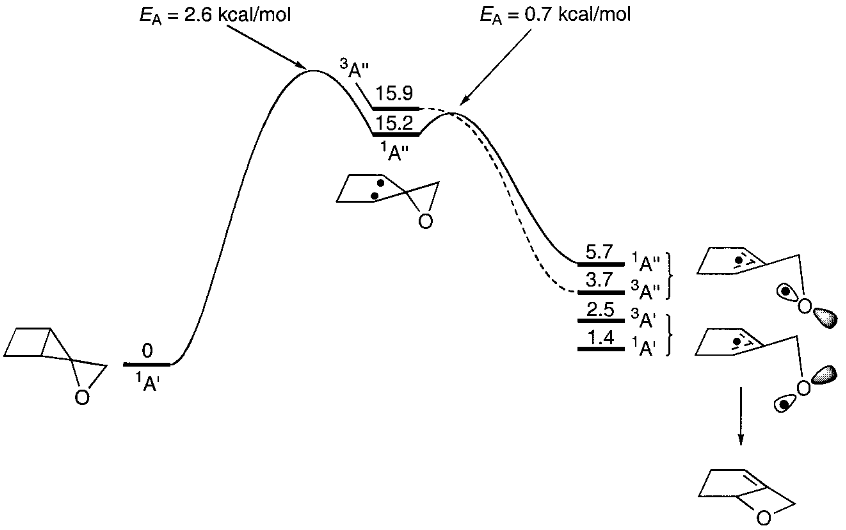

Figure 2. Calculated energy profile (B3LYP/6-31G*) for the reactions of the spiroepoxy-substituted cyclopentane-1,3-diyl diradical **D**; the energies are relative to the housane.

The reaction pathways (Figure 2) for the singlet and triplet states of the spiroepoxy diradical **D** (without the phenyl substituents) were also examined computationally at the same level of theory. All geometries were restricted to C_S symmetry for reasons of computational economy. Vibrational frequencies and zero-point vibrational energy (ZPE) contributions were also calculated (cf. Supporting Information). The ZPE corrections, which varied up to 3.5 kcal/mol, are included in the relative energy values given in Figure 2. Minima and transition state structures were identified by the absence or presence of one imaginary vibrational frequency. Exceptions were the singlet and triplet 1,4 diradicals 1A″ and 3A′, which indicated an out-of-plane movement (one small imaginary frequency with A″ symmetry) as a consequence of the imposed symmetry constraints.

The singlet cyclopentane-1,3-diyl diradical **D** is found to be an intermediate with a finite lifetime, which in principle should be trappable. For ring closure to the housane, the singlet diradical requires an activation energy (E_A) of 2.6 kcal/mol, while for ring opening to the 1,4-allylic diradical, only 0.7 kcal/mol is necessary. The bond dissociation energy of the spiroepoxide housane to the singlet diradical **D** amounts only to 15.2 kcal/mol (corrected for ZPE contributions, Figure 2), which is much below the value calculated here for the parent housane (ca. 38 kcal/mol) and even the spirocyclopropane housane (ca. 29 kcal/mol). The low bond dissociation energy may account for the fact that the singlet diradical is a real minimum rather than a transition state.[3b,5]

In contrast to the singlet diradical, the triplet diradical, when calculated at the geometry of the singlet diradical, is not a stationary state, but undergoes spontaneous (no activation) ring opening to the 1,4 diradical (A″), since the triplet diradical lies at the same energy (or slightly above without ZPE corrections) as the transition state for epoxide ring opening of the singlet species (Figure 2). Hence, the calculated singlet−triplet energy gap (Table 1) refers to the geometry of the singlet diradical (vertical singlet−triplet energy). Note that the singlet and triplet 1,4 diradicals may adopt two different electronic states with the unpaired electron on the oxygen atom located within the plane of symmetry (A″) or orthogonal to it (A′); all states are close in energy (Figure 2). The A′ singlet state was calculated as the most stable electronic configuration due to the admixture of dipolar character (cf. Discussion).

Discussion

The mechanism in Scheme 3 is proposed to account for all the pertinent experimental and computational results: (a) The DFT calculations suggest that the epoxy substitution at the C-2 position in the cyclopentane-1,3-diyl diradical places the singlet state below the triplet by 1.0 kcal/mol (0.7 kcal/mol with ZPE correction); the singlet state **S-1**,**3-DR** possesses a small, but significant, activation energy (0.7 kcal/mol) for epoxide-ring opening and a larger one (2.6 kcal/mol) for the formation of the housane **2**; for the triplet state **T-1**,**3-DR**, no barrier was found. (b) C−O bond cleavage of the epoxy ring to the **1**,**4-DR** was observed to give exclusively the oxetane **3** in the direct and triplet-sensitized photolyses; the regioisomeric **1**,**4-DR′** diradical derived from C−C bond cleavage of the epoxy ring was not observed by time-resolved (nanosecond) spectroscopy. (c) The housane **2** was not detected even at −98 °C. (d) The dipolar intermediate **1**,**4-DP** was trapped by MeOH to afford the methoxy alcohol **6**; its yield was appreciably higher (10% absolute) in the direct photolysis compared to the triplet-sensitized irradiation.

The denitrogenation of the singlet-excited spiroepoxy diazene ^{S}**1*** in the direct irradiation leads first to the singlet 1,3-diradical **S-1**,**3-DR** (Scheme 1). With very few exceptions, intersystem crossing (ISC) in such diazenes does not occur;[23,24] a long-lived diazene triplet state is also ruled out since no triplet quenching was observed (Table 2, entry 5). ISC from the singlet diradical **S-1**,**3-DR** to the triplet species **T-1**,**3-DR** is expected to be inefficient since the singlet state of the parent epoxy-substituted diradical lies below the triplet (Figure 2). The fate of the singlet 1,3 diradical **S-1**,**3-DR** is ring opening to the 1,4 diradical **S-1**,**4-DR** by C−O bond breakage, a process that requires some activation (0.7 kcal/mol, Figure 2). This is considerably more attractive than ring closure to the highly strained housane **2** (a strain energy as high as ca. 94 kcal/mol has been estimated;[28] the bond dissociation energy was calculated to be only 15.2 kcal/mol), for which an activation energy of ca. 2.6 kcal/mol was computed (DFT). Thus, the difference in these activation

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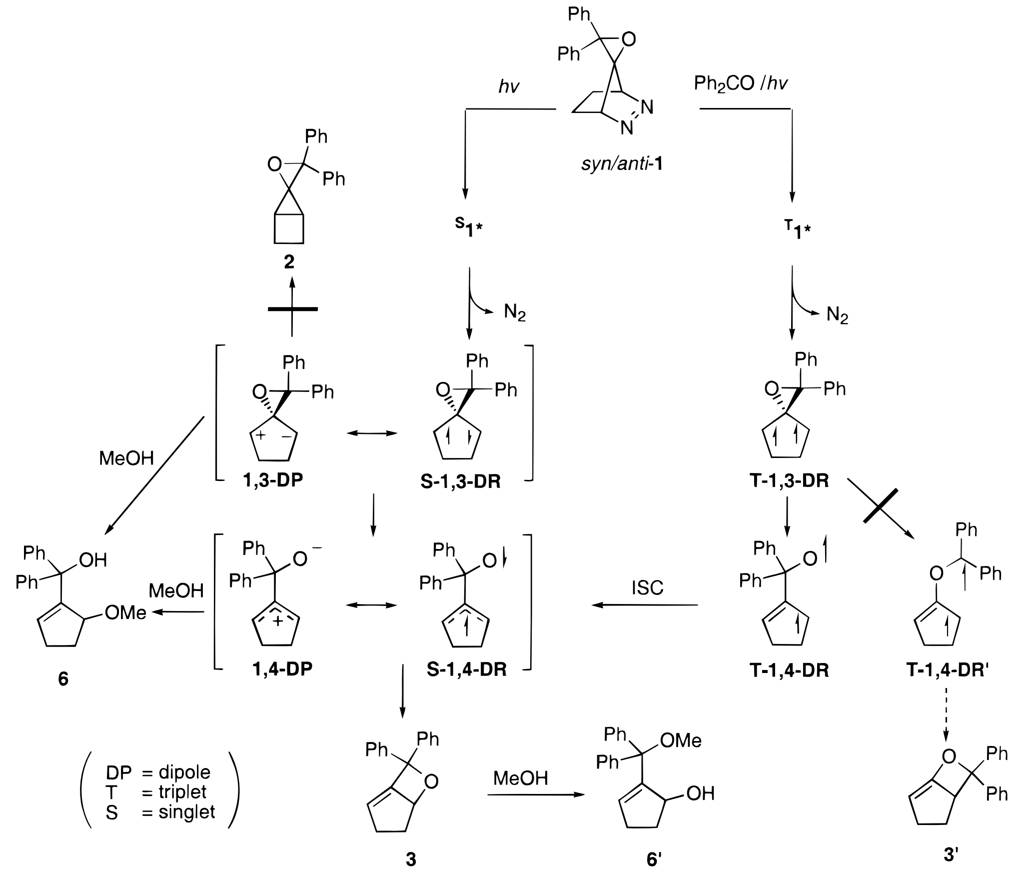
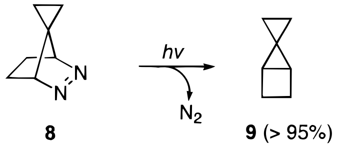
[28] The strain energy of spiroepoxybicyclo[2.1.0]pentane (ca. 94 kcal/mol) was estimated as the sum of its calculated (AM1 method, ref 29) heat of formation (*syn*: 42.5 kcal/mol, *anti*: 42.3 kcal/mol) and that of an unstrained C_6H_8O analogue (−51.6 kcal/mol, ref 30) by using group-additivity values (ref 31). The strain energy of the housane **9** (ca. 89 kcal/mol) was estimated similarly by adding its heat of formation (−65.6 kcal/mol) to that of an unstrained C_7H_{10} analogue (−23.0 kcal/mol, ref 31).

Scheme 3. Mechanism of the Direct and Benzophenone-Sensitized Photolysis of the Spiroepoxy-Substituted Diazene **1**



energies establishes that epoxide-ring opening is preferred over housane formation. Entropic factors also favor the epoxide-ring opening, as the calculated entropies of the transition states for housane formation (77.9 cal mol^{-1}K^{-1}) and epoxide ring opening (79.7 cal mol^{-1}K^{-1}) confirm.

The failure to detect the housane **2** even down to −98 °C (cf. NMR experiments) provides circumstantial evidence for this mechanistic interpretation. For comparison, the related spirocyclopropane azoalkane **8** cleanly affords the corresponding housane **9** in the direct photolysis (eq 1),[17] which persists even at +100 °C.



(1)

The allylic diradical **S-1,4-DR** also possesses a singlet ground state (A′). In this case, admixture of dipolar character is held responsible for the singlet preference. The dipolar character is most pronounced in the A′ state of the diradical, which displays an increase of the charge density on the oxygen atom (−0.34) compared to the triplet A′ (−0.29) state. This charge separation is accompanied by a concomitant decrease in oxygen spin density, i.e., singlet A′ (0.82) has a lower oxygen spin density than the triplet A′ (0.90) state. We consider this trend significant, since the computational results refer to a gas-phase model; in solution, solvent polarity should promote a more pronounced charge separation and hence increase the preference for a singlet ground state of the diradical **1,4-DR**. Such dipolar stabilization of the 1,4 singlet diradical provides an additional incentive (besides loss of strain energy, Figure 2) for the epoxide-ring opening in **S-1,3-DR**. The final product of the 1,4 diradical in benzene is the oxetane **3** from cyclization.

The triplet diradical **T-1,3-DR**, produced in the benzophenone-sensitized photolysis, exhibits analogous chemistry, i.e., epoxide-ring opening. ISC in **T-1,3-DR** should be energywise a feasible process, since the resulting singlet diradical **S-1,3-DR** is the ground state; however, the calculations predict a spontaneous (no activation energy) epoxide-ring opening of the triplet diradical (Figure 2), and the spin-forbidden ISC process is too slow to compete. Hence, we assume that all oxetane **3** product in the sensitized photolysis derives from the sequence **T-1,3-DR** →**T-1,4-DR** →**S-1,4-DR** →**3**.

What appears at first sight puzzling is why the **T-1,3-DR** triplet diradical prefers cleavage of the C−O instead of C−C bond in the epoxide-ring so that the regioismeric oxetane **3′** is not observed. Also, time-resolved spectroscopy failed to detect its precursor, the **T-1,4-DR′** species, an attractive structure in view of stabilization of the spins by allyl and benzyl conjugation. Since both the C−C and the C−O ring-opening reactions are symmetry-allowed for the A″ **1,3-DR** species, other factors must be responsible for this preference. The UB3LYP/6-31G* computations for the parent system **D** and, more definitively, the AM1 calculations[29] for the diphenyl derivative provide a clue in that the energy-favored conformation (Scheme 4) of the diradical **1,3-DR** aligns the C−O bond better (more axially) for cleavage than the C−C one. Additionally, the bond strength for a C−O bond is ca. 6 kcal/mol lower than for a C−C bond.[31]

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(29) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

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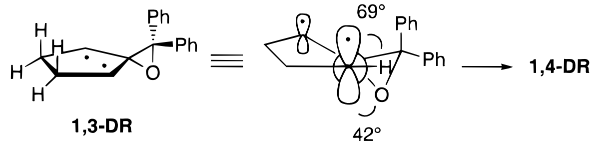
Scheme 4. AM1-Optimized Conformation of the Spiroepoxy-Substituted Diradical 1,3-DR



Moreover, the anomeric effect (in radicals the C−O bond prefers an axial alignment with a radical center[32] due to the stabilizing interaction of the radical p orbital with σ^* C−O bond) and steric repulsion (geminal diphenyl substitution) are presumably responsible for the preferred conformation in Scheme 4. Consequently, scission of the C−O bond is kinetically favored and the **1**,**4-DR** diradical is exclusively generated.[33]

The most convincing evidence for the dipolar character **1**,**4-DP** in the singlet 1,4 diradical **S-1**,**4-DR** (Scheme 3) comes from methanol trapping experiments. As much as 10−30% (Table 2) of the methoxy alcohol **6** was obtained as diradical-trapped product; the remainder is the regioisomeric methoxy alcohol **6′**, which derives from methanolysis of the oxetane **3** (cyclization product). Thus, the product ratio **6**:**6′** serves as a convenient monitor to assess the competition between trapping (regioisomer **6**) and cyclization (regioisomer **6′**) of the 1,4 diradical **S-1**,**4-DR**. However, if the **S-1**,**4-DR** were the only source of the trapping product **6**, the **6**:**6′** ratio would have to be the same in the direct and triplet-sensitized photolyses. Yet, significantly more (ca. 12% absolute) methanol trapping is observed in the direct process (Table 2). The differences in the **6**:**6′** product ratio for the singlet and triplet processes confirm that the ISC step **T-1**,**3-DR** →**S-1**,**3-DR** must be inefficient because otherwise no differentiation between trapping and cyclization would be observed for the direct and sensitized photolyses. Indeed, the DFT calculations support this interpretation, since the triplet diradical undergoes spontaneous (no activation energy) epoxide-ring opening.

The additional methanol product **6** is proposed to come from direct trapping of **S-1**,**3-DR**. While such a reaction constitutes an unprecedented event for a localized cyclopentane-1,3-diyl diradical, we reiterate that the calculations suggest that the **S-1**,**3-DR** species should be a minimum-energy structure (0.7 kcal/mol activation energy for ring opening) with a finite lifetime to allow trapping. Whether the polar methanol medium induces zwitterionic character in the **S-1**,**3-DR** singlet diradical and stabilizes it is open to debate,[8a] but certainly in such a symmetrical species charge separation is necessary for trapping by methanol. The structural and electronic differences between the 1,3 and 1,4 diradicals **S-1**,**3-DR** and **S-1**,**4-DR** must be clearly recognized, since only the latter one may exist as a bona fide 1,4 dipole with the negative charge stabilized by the electronegative oxygen atom and the positive charge by allyl resonance.

We conclude that in agreement with theoretical predictions, our experimental results confirm that the electronegative oxygen atom in the spiroepoxy group at the C-2 position of the cyclopentane-1,3-diyl diradical promotes a singlet ground state. The fate of the singlet diradical **S-1**,**3-DR** is not to cyclize to the housane **2**, but to open up the epoxide ring by C−O bond scission to the 1,4 diradical **S-1**,**4-DR**. For the cyclopentane-1,3-diyl triplet diradical **T-1**,**3-DR**, which was generated by benzophenone-sensitized photolysis, the selective C−O bond cleavage also takes place to give 1,4-diradical **T-1**,**4-DR**, despite the fact that the regioisomeric **T-1**,**4-DR′** derived from the C−C bond cleavage would be the thermodynamically better stabilized triplet. Conformational effects align the C−O better than the C−C bond and account for this ring-opening selectivity in the **1**,**3-DR** diradical. The methanol-trapping experiments in the direct and the triplet-sensitized photolyses (Table 2) provide the first experimental evidence for dipolar character in the localized **1**,**3-DR** and **1**,**4-DR** cyclopentanediyl diradicals, but only for the latter is a genuine 1,4 dipole likely.

Acknowledgment. This paper is dedicated to Prof. M. V. George (Trivandum) on the occasion of his 70th birthday. We express our gratitude to the Deutsche Forschunggemeinschaft, Volkswagen Foundation, the Fonds der Chemischen Industrie, and the Swiss National Science Foundation for generous financial support. M.A. thanks the Alexander-von-Humboldt Foundation for a postdoctoral fellowship (1997-1998).

Supporting Information Available: Experimental data and computational details, i.e., absolute energies, Cartesian coordinates, etc. (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9822761

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