We consider these lifetime data as experimental verification of Salem's orbital orientation rule.[4] It should be possible to devise long-lived, localized triplet diradicals by incorporating the radical sites into planar and rigid molecular skeletons.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support and thank Dr. K. E. Gilbert for providing us preliminary results on the molecular mechanics calculations.

UV-Laser Photochemistry of the Azoalkane 1-Phenyl-2,3-diazabicyclo[2.2.2]oct-2-ene: Detection and Lifetime Determination of the Triplet Diradical 1-Phenyl-1,4-cyclohexadiyl by Time-Resolved UV Spectroscopy (Flash Photolysis) and by Trapping with Molecular Oxygen

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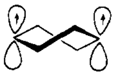
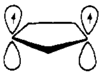
The short lifetime (τ_T) of the triplet diradical 1,4-cyclohexadiyl (**1**) compared to the relatively long-lived 1,3-cyclopentadiyl (**2**)

1a

τ_T~0.1 ns



1b



2

τ_T~100 ns

was previously[2] rationalized in terms of Salem's orbital orientation rule.[3] It was argued that in its boat conformation the 1,4-cyclohexadiyl (**1a**) suffers fast intersystem crossing through favorable orientation of the orbital lobes for spin-orbit coupling, resulting in a short lifetime and thus inefficient trapping by $^3O_2$. In analogy to the planar 1,3-cyclopentadiyl (**2**), the twist-boat conformation of the 1,4-cyclohexadiyl (**1b**) should be a relatively long-lived triplet diradical, since the parallel radical lobes constitute an unfavorable arrangement for intersystem crossing. Indeed, theoretical work[4] on the tetramethylene fragment predicts a triplet ground state, provided the radical lobes are aligned parallel, i.e., analogous to the twist-boat conformation of the 1,4-cyclohexadiyl (**1b**). Presently we provide experimental evidence that phenyl stabilization promotes conformational relaxation to the favored twist-boat triplet ground state, resulting in the long-lived 1-phenyl-1,4-cyclohexadiyl (**3b**). The generation of the 1,4-diradical **3** via photolysis (Coherent Supergraphite CR 18 argon ion laser) and product formation (with and without oxygen trapping) is summarized in Scheme I, together with the rate constants used to derive eq 1.[2a]

Direct laser photolysis of azoalkane **4**[5] in benzene at 364 nm gave diene **5**, presumably via the singlet diradical **S-3**. Control experiments showed that prolonged photolysis gave about 5% of the unknown bicyclo[2.2.0]hexane **6** as secondary product.[6] Under benzophenone sensitization (333 nm) small amounts of the bicyclo[2.1.1]hexane **7** were formed.[7] In the presence of molecular oxygen (10 atm), the benzophenone-sensitized laser photolysis (333 nm) in $CFCl_3$ at −10 °C gave besides the hexadiene **5** the peroxides **8** (1.3%), **9** (4.6%), and **10** (5.7%), isolated by means of flash chromatography on silica gel at −25 °C.[6] An authentic sample of the cyclic peroxide **8** was prepared by photooxygenation of 1-phenyl-1,3-cyclohexadiene[8] and diimide reduction.[9]

The benzyl chromophore should allow for a direct detection of the diradical **3** by UV spectroscopy.[10] This was achieved by kinetic and spectrographic nanosecond flash photolysis at ambient temperature using a XeF excimer laser (351 nm, 100 mJ, 25 ns).[11] No transient was observed after direct excitation of the azoalkane **4** ($5{\cdot}10^{-2}$ M, CH_3CN). In the presence of benzophenone and **4**, in concentrations ($5{\cdot}10^{-3}$ M and $2{\cdot}10^{-3}$–$1{\cdot}10^{-2}$ M, respectively) such that most of the 351-nm radiation was absorbed by the former, the first-order decay curves in the visible region indicated that triplet benzophenone (λ_{max} 530 nm) was quenched by **4** with a rate constant of ca. $6{\cdot}10^9$ M^{-1} s^{-1}. Transient absorption spectra, taken with a suitable delay such that essentially all the triplet benzophenone had decayed, showed an absorption band in the range of 300–330 nm which disappeared more slowly. Kinetic traces in that wavelength region were clearly biphasic and could be fitted quite well with a dual exponential rate law; the faster decay rate was within the limits of error equal to the single exponential decay rate determined in the visible region. The second transient is attributed to the triplet diradical **T-3**. Its decay rate grew linearly with increasing oxygen pressure, affording $k(O_2)$ = $1.6(\pm0.1){\cdot}10^{10}$ M^{-1} s^{-1} and $2.2(\pm0.2){\cdot}10^{10}$ M^{-1} s^{-1}, respectively, in C_6H_6 and CH_3CN. *We conclude that the rather long-lived diradical **T-3** (τ = 275 ± 15 and 248 ± 15 ns in C_6H_6 and CH_3CN, respectively) reacts with triplet oxygen at an essentially diffusion-controlled rate.*

To determine the triplet lifetime of the 1,4-diradical **T-3** by the quantitative oxygen-trapping technique, the benzophenone-sensitized photolysis was conducted in benzene at varying oxygen concentrations as previously described.[2a] According to the kinetic expression (eq 1), the slope ($6.2(\pm1.0){\cdot}10^{-4}$ M^{-1}) and intercept (2.8 ± 0.1) were obtained from a $1/(1 - X_H)$ vs $1/[O_2]$ plot. The trapping factor was calculated to be T_f = 0.36 ± 0.01 as the reciprocal intercept. Clearly, spin-catalyzed intersystem crossing (k_c) by $^3O_2$ dominates trapping (k_t) for this triplet diradical. The triplet lifetime was calculated from the slope, employing the $k(O_2)$ value from the flash photolysis results. The agreement in the triplet lifetimes in benzene from oxygen trapping (τ_T = 280 ± 40 ns) and flash photolysis (τ_T = 275 ± 15 ns) is most gratifying. This fact underscores the reliability of the oxygen-trapping method for estimating lifetimes of triplet diradical transients and validates the assumption of diffusion control in the oxygen trapping rate.[12]

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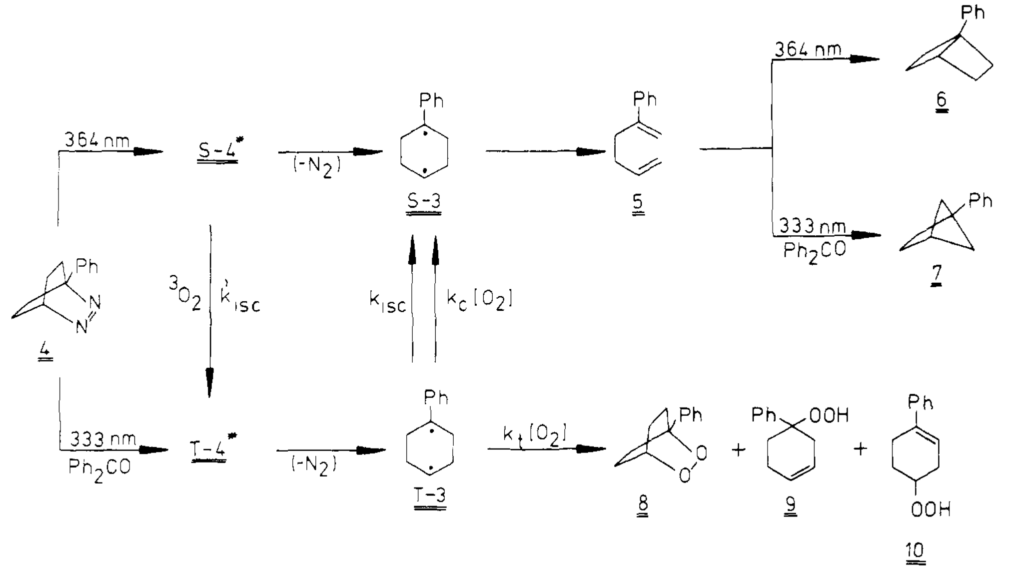
Scheme I

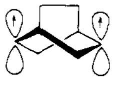


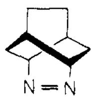
$$\frac{1}{X_P} = \frac{1}{1-X_H} = \frac{1}{T_f} + \frac{1}{k_t\tau_T[O_2]} \quad (1)^a$$

[a] X_P = mole fraction of peroxide (trapped product); X_H = mole fraction of hydrocarbons (untrapped product); $T_f = k_t/(k_t + k_c)$ is the trapping factor; k_t = rate constant for oxygen trapping; k_c = rate constant for spin-catalyzed intersystem crossing; $\tau_T = 1/k_{ISC}$ is the triplet lifetime; k_{ISC} = rate constant for inherent intersystem crossing.

The phenyl-substituted triplet 1,4-cyclohexadiyl **T-3** ($\tau_T \sim 300$ ns) is several 1000-fold longer lived than the parent triplet diradical **T-1** ($\tau_T \sim 0.1$ ns). Stabilization by phenyl conjugation alone can hardly account for such a massive effect, as evidenced by Norrish type II triplet diradicals[13] or by 1,5-diradicals.[14] We suggest that Salem's orbital orientation rule[3] is the reason for this large differentiation in the triplet lifetimes.[2] On photoextrusion of the nitrogen from the bicyclic azoalkane precursor, the 1,4-cyclohexadiyl is initially born in the boat conformation. In the absence of stabilization of the radical centers, efficient spin-orbit coupling[3] in the boat conformation of the parent triplet diradical **1a** leads to significant amounts (ca. 33%) of bicyclo[2.2.0]hexane as product. However, phenyl stabilization of the radical site in **3a** increases its lifetime and therewith provides sufficient time for the species to relax to the preferred twist-boat conformation **3b**, as suggested by theoretical work on tetramethylene.[4] Intersystem crossing is now slow because the parallel arrangement of the radical lobes in **3b** is not conducive for spin-orbit coupling.[3] Molecular distortions to the chair conformation induces spin inversion, but the resulting singlet exclusively fragments into the 1,5-hexadiene **5** rather than cyclizing to the bicyclo[2.2.0]hexane **6**. The intervening σ-bond is better aligned for fragmentation in the chair than in the twist-boat conformation **3b**.

It is of interest to report that the triplet 1,4-cyclohexadiyl **11**, derived from the known[15] azoalkane **12**, can be trapped with $^3O_2$.


11



12

This is the *first* bicyclic, localized triplet diradical that could be trapped with molecular oxygen![2] Presumably its appreciable lifetime derives from its essentially rigid twist-boat conformation, as confirmed by molecular mechanics calculations.[16]

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Stiftung Volkswagenwerk for generous financial support.

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Radical Anions in Hydrocarbon Media. Interaction between Unsolvated and/or Solvated Radical Anions and Metal Alkoxides. Evidence for Cation-Dependent Clustering of Ketyl Anions at High Concentrations

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Almost all the chemistry of radical anions (RA) can be understood on the basis of their ability to donate an electron plus a metal cation and as such can be considered as homogeneous sources of metals. It is this property which makes them increasingly useful reagents in organic and organometallic synthesis.[1] A serious problem associated with their employment in organometallic preparations, however, is the instability of the organometallic products in the ethereal solvents[2] which are necessary for the preparation of RA.[3] We now report a method of solubilizing unsolvated RA in hydrocarbon media thus broadening their synthetic and catalytic potentials. We also present physical evidence concerning the state of aggregation of RA at concentrations which, perhaps, are not accessible by other relevant techniques.[4] Previously, only dilute solutions of unsolvated

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