Direct Observation and Chemistry of Biradicals from Photochemical Decarbonylation of α-Perphenylated Cycloalkanones[1]

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Abstract: Photolysis of solutions of 2,2,6,6-tetraphenylcyclohexanone (**1**) yields 1,1,5,5-tetraphenylpent-1-ene and 1,1,2,2-tetraphenylcyclopentane in a 2:1 ratio with a quantum yield of 0.9 ± 0.2. Photolysis of 2,2,5,5-tetraphenylcyclopentanone (**2**) yields 1,1-diphenylethylene and 1,1,2,2-tetraphenylcyclobutane in approximately equal amounts with a quantum yield of about 0.5. The corresponding $Ph_2\dot{C}(CH_2)_n\dot{C}Ph_2$ triplet biradicals, **5** ($n = 3$) and **8** ($n = 2$), which are derived by a Norrish type I cleavage of the triplet ketones **1** and **2** followed by very rapid decarbonylation, have been identified in laser flash photolysis experiments, e.g., $\lambda_{max} = 334$ nm (strong) and 475 nm for **5** with the major contribution to the latter band being due to biphotonic processes. The yield of **8** was only about 3% of that of **5** which we attribute to additional singlet-state processes in the more strained 5-membered ring. The lifetimes of these biradicals are surprisingly long, 0.9 ± 0.2 μs for **5** and 0.5 ± 0.1 μs for **8**, and are determined by irreversible intersystem crossing to the singlet state. The 2:1 disproportionation–combination ratio for **5** is not the same as the 0.1 ratio estimated for two 1,1-diphenylethyl radicals, a result which we attribute to conformational restrictions on the transition states for chemical reaction of the biradical. It is pointed out that the considerably shorter lifetime of biradicals that contain a heteroatom between their termini, such as Paterno–Buchi biradicals, can be most simply explained by the fact that the heteroatom reduces the distance between the biradical termini and also reduces steric hindrance to the close approach of the termini.

The chemistry and kinetic behavior of photogenerated biradicals have been the subjects of increasing attention during the last few years.[3–6] Much of this attention has been concentrated on 1,4-ketyl–alkyl biradicals, reflecting the facts that these can be readily generated with the Norrish type II photoreaction and that the reactivity and optical absorption properties of the ketyl radical site facilitate the detection and characterization of the biradical.[3,5–7]

Another well-documented biradical source is the Norrish type I reaction of cycloalkanones; these biradicals have been the subject of several CIDNP studies during the last decade[8–12] but have only recently been detected with laser flash photolysis techniques.[13,14] Typical lifetimes for triplet 1,6-biradicals such as $(CH_3)_2\dot{C}(CH_2)_4\dot{C}O$ or $Ph\dot{C}H(CH_2)_4\dot{C}O$ are around 50 ns and show little solvent or temperature sensitivity. In these systems the decarbonylation of the acyl site is expected and confirmed to be slow compared with the biradical lifetime.[15] In contrast, the decarbonylation reaction of α-perphenylated cycloalkanones is expected to be very fast, due to the stabilization of the resulting benzylic radical center.[16,17] On photolysis such ketones are therefore expected to form α,α,ω,ω-tetraphenyl-α,ω-diyl biradicals very rapidly. These biradicals, which can be anticipated to have strong

Scheme I

3   **5**   **4**
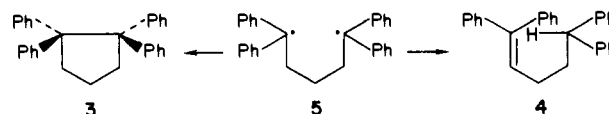
absorptions in the UV region, are rather unusual[18] in that they have two identical termini. This feature allows one to compare the *chemical* decay modes, e.g., disproportionation/combination ratios, of the radical sites in the biradical with the decay products formed by the bimolecular self-reactions of structurally related monoradicals. Such studies throw light on the conformational preferences involved in the decay of the biradical and in the decay of two free monoradicals.

The presence of identical termini in a biradical is also of interest with regard to its effect, if any, on the lifetime of the biradical. Although several biradical lifetimes have been determined, they have mostly been for Norrish type II biradicals.[3,5] Certainly there have not been enough lifetime measurements to allow much generalization and/or prediction of general trends. This is important because the lifetime of a biradical will determine whether it is likely, or even possible, for it to undergo a radical–molecule reaction.

There is easy access to α-perphenylated ketones via reaction of the potassium enolate of a cycloalkanone with either triphenyl bismuth carbonate or a tetraphenylbismuthonium ester.[22] Thus, 2,2,6,6-tetraphenylcyclohexanone (**1**) was prepared from cyclohexanone with triphenylbismuth carbonate (93%) or tetraphenylbismuthonium tosylate (80%). In similar fashion, arylation of 2,2-diphenylcyclopentanone with tetramethylbismuthonium

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(18) We are aware of only three other nonconjugated biradicals having identical termini which have been studied by time-resolved techniques: $Ph\dot{C}(OH)CH_2CH_2\dot{C}(OH)Ph$,[19] 1,4-dinaphthyl-2,3-(carbonylmethyl)butane-1,4-diyl,[20] and a diacenaphthylene dimer.[21]
(19) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126.
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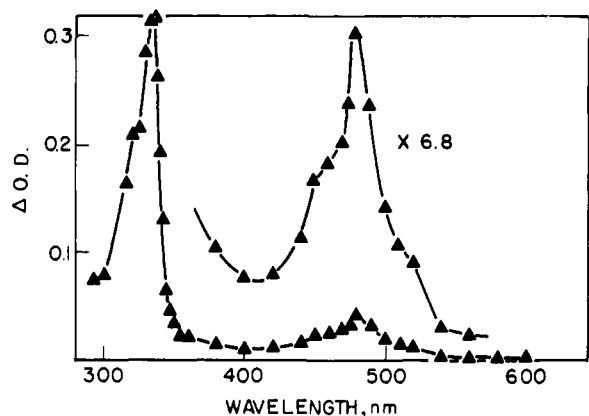
Figure 1. Spectrum obtained following laser excitation (308 nm) of **1** in benzene at 300 K. The long-wavelength band (expanded) is mostly due to a biphotonic process (see text).

trifluoroacetate furnished the tetraphenylcyclopentanone (**2**) (74%).
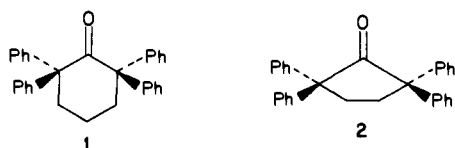
The chemistry of the biradicals formed by photolysis of α-perphenylated cyclohexanone and cyclopentanone has been examined by product studies and quantum yield measurements, and their kinetics have been studied with laser flash photolysis techniques.

Results

2,2,6,6-Tetraphenylcyclohexanone (1). Preparative Photochemistry. Irradiation of 2,2,6,6-tetraphenylcyclohexanone in tetrahydrofuran at 15 °C led to the formation of two major hydrocarbon photoproducts which were separated by a combination of column chromatography and careful fractional crystallization. The less polar of these, isolated in a combined yield of 20%, was shown by spectroscopic techniques to be the symmetrical coupling product, 1,1,5,5-tetraphenylcyclopentanone (**3**). This structure has now been confirmed by an independent crystallographic study.[23] The more polar hydrocarbon isomer, isolated in a combined yield of 25%, was readily identified on the basis of its ^{1}H and ^{13}C NMR spectra as 1,1,5,5-tetraphenylpent-1-ene (**4**), the product of intramolecular hydrogen atom abstraction by the biradical (**5**) (Scheme I). The ratio of the two products was unaffected by use of benzene as solvent at a comparable temperature. Photolysis of **1** in tetrahydrofuran at −78 °C led to a change in the isomer distribution with preponderant formation of the disproportionation product (**4**) (**3:4** = 1:7). However, in view of the relatively poor mass balance of isolated products, it was decided to examine the photolysate directly by NMR spectroscopy before purification and separation. This study, performed in perdeuteriobenzene at room temperature, confirmed not only that the starting ketone was completely consumed but also that **3** and **4** were the only products of reaction. The ratio of **3:4** was 1:2 before isolation and 1:1 after separation, suggesting that olefin **4** was a relatively labile substance. A series of blank experiments established that **3** and **4** are non-interconvertible primary photoproducts in this reaction.

Quantum Yield for Photodecomposition of 1. The photodecomposition of **1** in benzene at 310 K was examined with use of RPR-3000 lamps for irradiation and the Norrish type II photodecomposition of valerophenone [Φ(acetophenone) = 0.30][24] as an actinometer. The quantum yield obtained, $\Phi_{-ketone}$ = 0.9 ±

0.2, provides conclusive evidence that the laser flash photolysis experiments are actually monitoring the main photoprocess taking place.

Laser Flash Photolysis of 1. Laser excitation of **1** in benzene or 1:4 benzene:methanol at 300 K with the pulses from an excimer (308 nm) laser produces intense transient absorptions showing λ_{max} 475 and 334 nm (strong), Figure 1. The strong band is almost identical with that observed in the diphenylmethyl radical for which we have measured λ_{max} 332 nm.[25] The signals in Figure 1 are assigned to the biradical **5**, produced via decarbonylation of **6**, initially formed in the Norrish type I cleavage of 2,2,6,6-tetraphenylcyclohexanone. Recent studies on the phenylacetyl radical and related molecules suggest that the lifetime for the decarbonylation of **6** should be substantially shorter than 100 ns.[16,17]

6
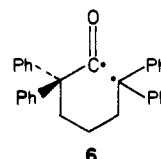
The presence of a band in the visible region of the spectrum (λ_{max} 475 nm) is common in benzylic radicals,[28,29] although its intensity (in monoradicals) is usually close to 1% of that for the UV band. However, the intensity of the visible band in Figure 1 is ~10% of that for the UV band. Following this unusual observation, we examined in some detail the dependence of the ratio of transient optical densities for the 475- and 332-nm bands on the energy of the 308-nm laser pulse. Our experiments clearly demonstrated that this ratio was dependent on laser power and indicated a contribution to the visible band from a biphotonic process. Extrapolation to "zero" laser power suggests that the optical density for the 475-nm band is about 1–3% of that of the 332-nm band. The 475-nm band may be similar to the signals observed by Meisel et al.[30] in the decay of excited triphenylmethyl or by us[31] in the case of Ph₂ĊH. The 475 nm band must be mainly due to a short-lived product or one of its excited states.

In view of the results mentioned above all kinetic measurements on **5** were carried out with the short-wavelength signal. The lifetime of **5** at 300 K is 0.9 ± 0.2 μs in benzene or 1:4 benzene:methanol when monitored in the 320–330 nm region.[32] The signal does not decay to the original (or preexcitation) level, indicating some absorption by the products of reaction in this wavelength region. A few experiments using a nitrogen laser (337.1 nm) for excitation led to results in agreement with those obtained with the 308-nm laser.

In order to establish that the signals observed arise from a triplet precursor, we added to the system a well-known triplet quencher, 2,5-dimethyl-2,4-hexadiene. This produced a decrease of the signals at 332 and 475 nm but no change in the observed lifetimes. This is consistent with the assignment of these absorptions to the biradical, **5**; i.e., while the biradical is not quenched by dienes, its precursor (the ketone triplet) is quenched, thus leading to a decrease in the yield of biradical formation. Stern–Volmer analysis of the intensity of the biradical signals led to $k_q\tau_T$ = 0.83 M^{-1} in 1:4 benzene:methanol at 300 K, where k_q is the rate constant

(23) Details of the crystallographic analysis, kindly carried out by Dr. E. Gabe and Mrs. F. Lee (NRCC), will be published separately.

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(25) The positions of these bands, and particularly their short-wavelength side, are normally somewhat dependent upon the precursor used since the technique measures ΔOD, not OD. In any event, the biradical absorptions agree well with those from Ph₂CH obtained via the carbene[26] (Ph₂CN₂ in cyclohexane) or the ketone[27] (Ph₂CHCOCHPh₂ in benzene).

(26) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 283.

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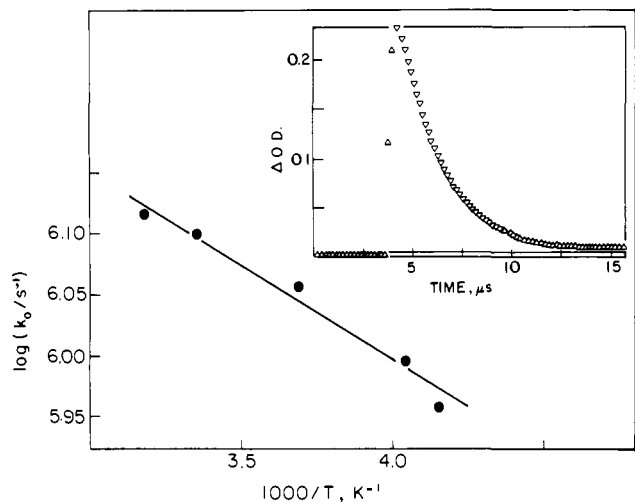
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(32) Lifetimes monitored at 480 nm were usually 10–15% longer than those measured in the UV region due to the presence of the additional, biphotonically produced transient, with a lifetime of 1.3 μs.

Figure 2. Arrhenius plot for the decay of **5** in 1:4 benzene:methanol and (insert) representative decay trace monitored at 325 nm.

for triplet quenching and τ_T the triplet lifetime. If we take k_q = 6–7 × 10⁹ M^{-1} s⁻¹, we obtain $\tau_T \sim$ 0.1 ns, which confirms that the observed long-lived signals are not due to the excited carbonyl triplet but rather to the biradical. These are formed so rapidly that they can be reexcited within the duration of a single laser pulse (≤5 ns).

It is now well established that triplet biradicals are readily quenched by paramagnetic substrates.[3] Biradical **5** is no exception; addition of di-*tert*-butylnitroxide (DTN) or oxygen leads to a marked decrease of the biradical lifetime. Kinetic analysis gives k_s (the rate constant for scavenging) of (1.36 ± 0.03) × 10⁹ M^{-1} s⁻¹ for DTN in benzene at 300 K. The lifetime in an air-saturated solution was 93 ns, suggesting $k_{O_2} \sim$ 5 × 10⁹ M^{-1} s⁻¹.

In the case of other biradicals, particularly those derived from the Norrish type II reaction, it has been generally observed that when the biradical lifetime is controlled by irreversible triplet-to-singlet intersystem crossing, the biradical decay shows unusual but very characteristic Arrhenius parameters.[7,14,19] Lifetimes of **5** were measured in 1:4 benzene:methanol (monitoring at 325 nm) in the 213 to 314 K range. The data can be represented by

$$-\log(\tau_B/s^{-1}) = (7.10 \pm 0.50) - (1330 \pm 590)/\theta$$

where θ = 2.3RT in cal/mol and the errors are reported as ±2σ. Figure 2 shows the corresponding plot and a typical decay trace. These parameters seem consistent with intersystem crossing as the main factor controlling the biradical lifetimes (see Discussion).

2,2,5,5-Tetraphenylcyclopentanone (2). Preparative Photochemistry. Photolysis of 2,2,5,5-tetraphenylcyclopentanone (**2**) in tetrahydrofuran at 15 °C afforded two major products which were readily separated by preparative TLC. The more polar hydrocarbon, isolated in 35% yield, was readily identified as 1,1-diphenylethylene (**7**) by comparison with an authentic sample, thus indicating an alternative mode of decomposition for the 1,4-biradical (**8**) (Scheme II). The less polar photoproduct, isolated in 23% yield, is spectrally consistent with the symmetrical cyclobutane (**9**). This assignment has also been confirmed in a crystallographic study.[23] The large ring strain involved in an intramolecular disproportionation (i.e., in an intramolecular H-atom abstraction) presumably precludes this mode of decay. A blank experiment involving photolysis of **7** indicated that **9** could not be derived via this reaction product.

Quantum Yields for 2. The quantum yield for ketone disappearance for **2** was measured simultaneously with that from **1**. The quantum yield for **2** was about one-half of that for **1**. It seems clear that this difference in quantum yield is not sufficient to explain the much larger difference in signal intensity observed in the laser experiment (vide infra).

Laser Flash Photolysis of 2. Photolysis of the cyclopentanone (**2**, 0.005 M) in 1:3 benzene:methanol at 308 nm yielded a weak transient with λ_{max} 335 nm and a lifetime of 0.5 ± 0.1 μs. The
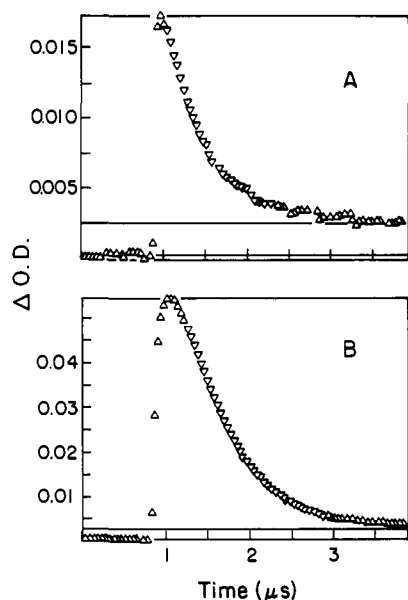
Figure 3. Traces obtained at 330 nm during the direct photolysis of **2** (top) and the acetone sensitized decomposition of **9** (at 308 nm; T = 300 K; solvent = benzene).

formation of this transient occurred within the duration of the laser pulse (<5 ns), and to our surprise the signals were only about 3% as intense as those obtained from **5**, based on a parallel series of carefully matched experiments. Quenching experiments with di-*tert*-butylnitroxide led to k_s = (2.1 ± 0.3) × 10⁹ M^{-1} s⁻¹ in benzene at 300 K.

Sensitized Photodecomposition of 9. Laser photolysis (308 nm) of acetone in acetonitrile containing 0.0065 M 1,1,2,2-tetraphenylcyclobutane produced a transient (λ_{max} 335 nm, τ = 0.5 μs). We attribute this signal to biradical **8**, formed by acetone triplet sensitized decomposition of **9**. The signal is not due to acetone triplet since, in the absence of the cyclobutane, the signal from triplet acetone was at least 10 times less intense and had a lifetime in excess of 1.6 μs. It appears that **8** is formed more efficiently in the sensitized decomposition of the cyclobutane than in the direct photodecomposition of the parent ketone.

The traces in this system were different from those obtained by irradiation of **2** in that the buildup of signal was not instantaneous. Figure 3 shows traces obtained with both biradical sources. The slower signal growth in Figure 3 (bottom) is attributed to the sensitization process which is not instantaneous on this time scale.

Our attempts to generate **5** by sensitized decomposition of **3** were complicated by underlying transient signals which were formed together with the expected biradical signal.

Disproportionation of 1,1-Diphenylethyl. In order to compare the behavior of radical centers in monoradicals and in biradicals (vide infra) we decided to measure the value of k_d/k_c (disproportionation-to-combination ratio) for the 1,1-diphenylethyl radical, which can serve as a (rough) model for the biradicals examined here.

No information on the value of k_d/k_c for $Ph_2\dot{C}CH_3$ appears to have been reported. However, the rate constant for the thermal decomposition of 2,2,3,3-tetraphenylbutane (TPB) to yield these radicals had been determined from 60 to 90 °C by Ziegler and co-workers in 1942.[33–35] The diphenylethyl radicals were trapped

$$CH_3CPh_2CPh_2CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2CH_3\dot{C}Ph_2 \qquad (1)$$
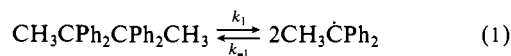
$$k_1 = 10^{16.43} \exp(-30.7 \text{ (kcal/mol)}/RT)$$

(33) Ziegler, K.; Seib, A.; Knoevenagel, K.; Herte, P.; Andreas, F. *Annalen* **1942**, *551*, 150.

(34) For a recent review of the products and kinetics of hydrocarbon thermolysis see: Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 429.
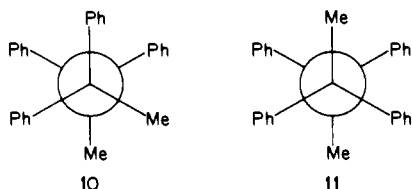
by O_2 to prevent the back reaction. The rate of the forward reaction at 60 °C has been confirmed by other groups.[36-38] Our own measurements (by NMR) on TPB decomposition were carried out under vacuum at 80 °C in benzene. They gave $k_1 = 2.7 \times 10^{-4}$ s^{-1}, a value 10 times slower than those reported in the presence of oxygen.[33,36-38] By combining our data with Ziegler's we can estimate $k_d/k_c \sim 0.1$ at 80 °C. The NMR product data on the 1,1,5,5-tetraphenyl-1,5-diyl biradical indicate that the intramolecular value of $k_d/k_c \sim 2.0$ at room temperature.

Discussion

Temperature Dependence and Quantum Yields. Biradicals **5** and **8** are believed to be triplet species whose lifetimes are controlled by the rate of intersystem crossing to the singlet state from which products are ultimatley formed. The virtual temperature independence found for the decay of **5** substantiates this hypothesis. The preexponential factor for decay ($10^{7.1}$ s^{-1}) is itself inconsistent with the idea that product formation is rate determining since it is certainly lower than would be expected for cyclization or fragmentation. However, this preexponential factor is entirely consistent with a biradical lifetime that is determined by the spin-forbidden nature of the intersystem crossing decay process. In fact, all biradicals for which the temperature dependence for decay have been examined have systematically shown preexponential factors of 10^7 s^{-1} or slightly higher.[7,14,19,39] Small activation energies such as the one obtained for **5** have previously been interpreted as a reflection of the fact that the most favorable conformation for intersystem crossing was different from, and higher in energy than, the most favorable conformation for the ground-state biradical. Thus, the activation energy does not reflect an energy requirement for intersystem crossing but rather an energy requirement in order that a certain conformation can be achieved.

The weak signals observed in the case of the cyclopentanone are rather surprising. If earlier experience with extinction coefficients for biradicals is valid, there is no reason to expect $\epsilon_5 \gg \epsilon_8$. Thus, one must conclude that the weak signals reflect a low concentration (and thus yield) for biradical formation. Since the signals differ by a factor of ~30, while the overall quantum yields differ only by a factor of ~2, one must assume that **5** is formed from the excited state with at least 15 times more efficiency than **8**. We can only speculate at this point that the increased ring strain in the case of the cyclopentanone induces more singlet-state processes, which do not lead to long-lived biradicals.

Disproportionation–Combination Ratios. As pointed out earlier the value of k_d/k_c for 1,1-diphenylethyl radicals is about 0.1 while, for the intramolecular decay of **5**, $k_d/k_c \sim 2.0$ at room temperature (based on NMR). This difference is probably due mainly to physical restrictions imposed by the biradical's "backbone" on the possible transition states for its decay, these special restrictions being absent in the self-reactions of the two monoradicals. For example, for two $Ph_2\dot{C}CH_3$ radicals to form their principal product, i.e., to combine, there are two potential transition-state conformations, **10** and **11**. However, the staggered conformation **10** suffers from similar limitations (phenyl–phenyl interactions) to those that prevent the head-to-head coupling of two $Ph_3\dot{C}$ radicals. It therefore seems likely that only one rotamer radical pair (**11**) can actually collapse to tetraphenylbutane. A conformation

10   **11**

analogous to **11** cannot possibly be achieved by our 1,5 biradical, and therefore the biradical and monoradical processes are simply not comparable. Product ratios should not be expected, nor in the present case are they found, to follow the same pattern of reactivity observed in monoradicals.

Fischer[40,41] has developed a model for the reaction of two *tert*-butyl radicals which is based on partitioning the surface of an oblate spheroid (which serves as the *tert*-butyl model) into two reactive zones leading to combination or disproportionation. Similar ideas could be applied to the case of a biradical where the "backbone" makes the conformations that *can* be explored different from those available to a pair of monoradicals.

Conformation Effects on Biradical Lifetimes. The biradical lifetimes measured for **5** and **8** are among the longest ones known for each "distance" between the termini. They are comparable to lifetimes for other biradicals with highly delocalized radical centers, such as **12** and **13** which are in the 0.20–0.32 μs range.[20,21]

12   **13**
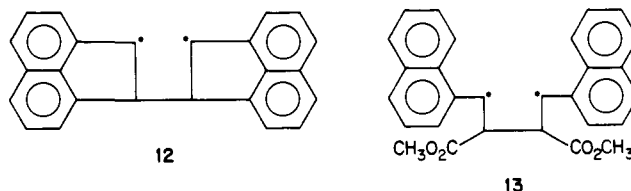
Comparison of the biradical lifetimes found for **5** and **8** with data in the literature and with lifetimes measured for Norrish type I biradicals derived from cycloalkanones[42] implies that for a given "distance" between the two spin centers in "all-carbon" nonconjugated frameworks the lifetimes follow the following order: benzylic–benzylic > alkyl–ketyl > acyl–alkyl ~ acyl–benzylic. Furthermore, for a given series of biradicals, their lifetime increases with an increase in the number of carbon atoms between the termini, presumably because of the change in distance between the reactive sites. However, biradicals containing a heteroatom between the termini, such as Paterno–Buchi biradicals, tend to have considerably shorter lifetimes than their "all-carbon" analogues.[43,44] Various explanations for this observation have been advanced.[43,44] Specifically, it has been suggested that the reduced lifetimes may be due (i) to electron delocalization onto the heteroatom which effectively reduces the distance between the unpaired electrons, (ii) to enhanced spin–orbit coupling, and (iii) to variations in the singlet–triplet splitting in the biradical. One aspect that has been ignored by these "explanations" is that the "accelerating" effect of intervening heteroatoms is also present in free radical cyclizations, where intersystem crossing cannot play a role. For example,[45,46] the cyclization of **14** is ~2 orders of magnitude faster than those of **15**. Similarly, **16** cyclizes 12 times faster than **17**.

14   **15**   **16**   **17**
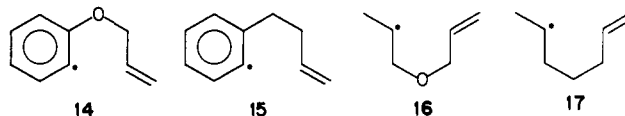
We propose that the most probable explanation for the reduced lifetimes of heteroatom[47] containing biradicals relative to their all-carbon analogues is the same as that which applies to the cyclizations of heteroatom containing monoradicals relative to their all-carbon analogues. That is, the heteroatom[47] reduces the distance between the biradical termini (because carbon–hetero-

(35) The structure of tetraphenylbutane has been confirmed by NMR and UV. See: Hook, S. C. W. *Tetrahedron Lett.* **1975**, 3321.

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(47) In this context "heteroatom" refers to the first row elements, oxygen and nitrogen. Increased rather than reduced lifetimes would be expected for a heteroatom such as silicon because this would increase the distance between the termini.

α-Perphenylated Cycloalkanones

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Scheme II
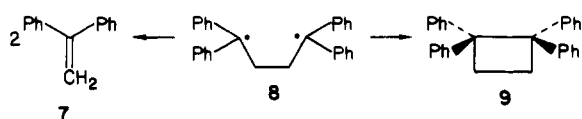
atom bond lengths are less than carbon–carbon bond lengths) and reduces steric hindrance to the close approach of the termini because the number of H–H eclipsing interactions is reduced.

Experimental Section

Materials. 2,2-Diphenylcyclopentanone was prepared via condensation of benzhydryl cyanide with 3-chloropropionitrile as described by Easton and Nelson.[48] Triphenylbismuth, triphenylbismuth dichloride, triphenylbismuth carbonate, tetraphenylbismuthonium tosylate, and trifluoroacetate were prepared by previously reported methods.[49,50]

2,2,6,6-Tetraphenylcyclohexanone. Method A. From Triphenylbismuth Carbonate (in Collaboration with Dr. M. T. Barros Popoula). A solution of cyclohexanone (300 mg, 3 mmol) in tetrahydrofuran (5 mL) was added dropwise to a stirred suspension of potassium hydride (960 mg, 24 mmol) in tetrahydrofuran (15 mL) at room temperature under an argon atmosphere. After 1 h the reaction mixture was cooled to 0 °C in an ice bath and triphenylbismuth carbonate (12 g, 24 mmol) was added in five successive portions over a 30-min period. The reaction mixture was then stirred and heated at 60 °C for 18 h and filtered through a pad of Celite, and the solvent was removed in vacuo. The residue was taken up in dioxan (20 mL), heated to 80 °C, and stirred with sodium dithionite (10 g) to destroy organobismuth compounds. After 3 h, the mixture was filtered through Celite, and solvent was removed in vacuo. Chromatography of the residue on a silica column (30 g, eluant hexane) gave the desired ketone (1.15 g, 93%), mp 222–224 °C (from dichloromethane–hexane): IR (CHCl₃) 1705, 1450, 1320, 1125, 920 cm⁻¹; ¹H NMR (80 MHz, CDCl₃) δ 7.26–6.74 (20 H, m), 2.60–1.77 (6 H, m); MS *m/e* 403 (M⁺ + 1), 402 (M⁺), 375, 374. Anal. Calcd for C₃₀H₂₆O: C, 89.5; H, 6.5; O, 4.0. Found: C, 89.5; H, 6.5; O, 4.0.

Method B. From Tetraphenylbismuthonium Tosylate. A solution of cyclohexanone (300 mg, 13 mmol) in anhydrous tetrahydrofuran (1 mL) was added dropwise, under argon, to a magnetically stirred suspension of potassium hydride (720 mg, 18 mmol) in tetrahydrofuran (10 mL). After 0.5 h at room temperature, the mixture was placed in an ice bath and tetraphenylbismuthonium tosylate (10.3 g, 15 mmol) was added in three successive portions at half-hour intervals, after which stirring was continued at room temperature for 24 h. Trichloroacetic acid was then added, and the reaction mixture was heated at 40 °C for 1 h to destroy organobismuth compounds. Water was added, and tetrahydrofuran was removed in vacuo. The aqueous phase was then thoroughly extracted with dichloromethane, and the combined organic extracts were washed sequentially with water and brine and dried over sodium sulfate. Removal of solvent and recrystallization of the residue from dichloromethane–ether gave the title compound (0.97 g, 80%), whose spectroscopic and physical properties were identical with those reported above.

2,2,5,5-Tetraphenylcyclopentanone. To a stirred suspension of potassium hydride [20% dispersion in oil (1.4 g, 7 mmol)] in dry tetrahydrofuran (60 mL) at room temperature under a nitrogen atmosphere was added 2,2-diphenylcyclopentanone[48] (359 mg, 1.52 mmol). The mixture was stirred for 1 h and then cooled in an ice bath. Tetraphenylbismuthonium trifluoroacetate (2.5 g, 3.97 mmol) was then added in two portions over a 30-min interval and stirring was continued for 2 h at 0 °C and then overnight at room temperature. Filtration through Celite (eluant, ether) followed by evaporation gave a residual semisolid which was purified by silica gel column chromatography to give, in order of increasing polarity, triphenylbismuth (eluant hexane) and 2,2,5,5-tetraphenylcyclopentanone (435 mg, 74%) as colorless plates, mp 180–182 °C (from dichloromethane–hexane): IR (CHCl₃) 1730 cm⁻¹; NMR (80 MHz, CDCl₃) δ 2.74 (4 H, s), 7.05 (20 H, s); MS, *m/e* 388 (M⁺), 360 (M⁺ – CO, 100%). Anal. Calcd for C₂₉H₂₄O: C, 89.6; H, 6.2. Found: C, 89.7; H, 6.4.

Preparative Photochemistry. All photochemical experiments were carried out under an argon atmosphere with a 100 Watt Hanovia medium pressure lamp and a Pyrex filter.

Photolysis of 2,2,6,6-Tetraphenylcyclohexanone. A solution of 2,2,6,6-tetraphenylcyclohexanone (700 mg, 1.74 mmol) in tetrahydro-

furan (650 mL) was irradiated at 15 °C for 2.5 h at which time aliquot monitoring by analytical TLC indicated complete reaction. Removal of solvent and column chromatography of the residue gave, in order of increasing polarity, 1,1,2,2-tetraphenylcyclopentane (116.6 mg, 20%) which was purified by recrystallization from hexane to give large plates (mp 134–135 °C: IR (CHCl₃) 3050, 2900, 1600 cm⁻¹; NMR (80 MHz, CDCl₃) δ 1.55–1.2 (2 H, m), 2.6–2.3 (4 H, m), 7.0 (20 H, m, w₁/₂, 3 Hz); ¹³C NMR (80 MHz, CDCl₃) δ 20.4, 41.3, 63.2, 125.3, 126.8, 130.8, 147.4; UV (cyclohexane) λ_max 223 (ε 27 220), 250 (340), 225 (620), 262 (820), 267 (990), and 273 nm (800); MS, *m/e* 374 (M⁺), 130, 115, 91; anal. calcd for C₂₉H₂₆: C, 93.0; H, 7.0; found: C, 93.14; H, 6.93) and 1,1,5,5-tetraphenylpent-1-ene (25%) after recrystallization from cold hexane as needles (mp 80–81 °C; IR (CH₂Cl₂) 3000, 2900, 1600 cm⁻¹; NMR (80 MHz, CDCl₃) δ 2.2–2.4 (4 H, m), 3.9 (1 H, m), 6.1 (1 H, m), 7.2 (20 H, m); ¹³C NMR (80 MHz, CDCl₃) δ 28.26, 36.07, 50.90, 126.17, 126.76, 126.95, 127.33, 127.70, 127.97, 128.22, 128.50, 129.34, 129.92, 140.15, 142.32, 142.88, 144.93; UV (cyclohexane) λ_max 220 (ε 32 840), 248 (19 490), 255 (19 940), and 260 nm (18 670); MS, *m/e* 374 (M⁺), 208, 193, 165, 91; anal. calcd for C₂₉H₂₆: C, 93.0; H, 7.0; found: C, 93.18; H, 7.13).

Repetition of the above experiment at –78 °C for 1.75 h gave from 2,2,6,6-tetraphenylcyclohexanone (143 mg, 0.356 mmol) 1,1,2,2-tetraphenylcyclopentane (9 mg, 7%) and 1,1,5,5-tetraphenylpent-1-ene (65 mg, 49%). The ratio of the two isomers obtained at 15 °C was unaffected by use of benzene as solvent. A series of blank NMR experiments established that no thermal (heating of a 1:1 mixture of isomers in toluene at 115 °C for 2 h) or photochemical (irradiation of a 1:1 mixture of the two isomers in benzene for 2 h in the presence and in the absence of 2,2,6,6-tetraphenylcyclohexanone) interconversion of the two photoproducts was occurring. 2,2,6,6-Tetraphenylcyclohexanone was also demonstrated to be thermally stable for 2 h at 115 °C in toluene solution.

Photolysis of 2,2,5,5-Tetraphenylcyclopentanone. A solution of 2,2,5,5-tetraphenylcyclopentanone (143 mg, 0.37 mmol) in dry freshly distilled tetrahydrofuran (100 mL) was irradiated at 15 °C for 3.5 h at which time analytical TLC showed reaction to be complete.

Removal of solvent and purification of the residual oil by preparative TLC (silica, eluant hexane) gave 1,1-diphenylethylene (46 mg, 35%) identical in all respects with an authentic sample and 1,1,2,2-tetraphenylcyclobutane (31 mg, 23%) as white plates, mp 121–123 °C (from hexane–ether): NMR (80 MHz, CDCl₃) δ 3.16 (4 H, s), 6.88 (20 H, s); MS, *m/e* 360 (M⁺), 180 (M⁺ – Ph₂CCH₂, 100%). Anal. Calcd for C₂₈H₂₄: C, 93.3; H, 6.7. Found: C, 93.44; H, 6.75. Irradiation of 1,1-diphenylethylene under the above conditions did not lead to formation of 1,1,2,2-tetraphenylcyclobutane.

Determination of Quantum Yields. These were measured in benzene at 36 °C with RPR 3000 lamps for irradiation of deoxygenated samples contained in Pyrex cells. The disappearance of 2,2,6,6-tetraphenylcyclohexanone was monitored by gas chromatography (OV-101, 5 ft, 5%). Valerophenone, which in this solvent yields acetophenone with Φ = 0.30, was used as an actionometer.[24]

Laser Flash Photolysis. The samples were contained in 3 × 7 or 7 × 7 mm² cells made of rectangular or square Suprasil tubing and were deoxygenated by bubbling oxygen-free nitrogen. Most experiments used the pulses (308 nm, ~5 ns, up to 80 mJ/pulse) from a Lumonics TE-860/2 excimer laser operated with Xe/HCl mixtures. The 337.1-nm line used in a few experiments was from a Molectron UV-24 (~8 ns, up to 10 mJ/pulse) laser. The system has been fully interfaced with a PDP 11/23 computer which controls the experiment and provides suitable processing, storage, and hardcopy facilities. Further details have been given elsewhere.[51]

Spectra. 2,2,6,6-Tetraphenylcyclohexanone presents a well-defined n,π* absorption band, considerably red shifted with respect to other nonconjugated ketones. This characteristic allowed excitation with a nitrogen laser (337 nm) even at low substrate concentrations. The fluorescence spectrum shows λ_max 358 nm. Comparison of fluorescence and absorption spectra suggests a singlet energy of around 87 kcal/mol.

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