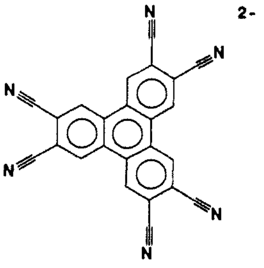
thermally accessible triplet.[57] Sufficiently strong donors that stabilize these dianions and could form the desired ···$D^{2+}A^{\cdot 2-}D^{2+}A^{\cdot 2-}D^{2+}A^{\cdot 2-}$··· structure are unknown. Hexacyanotriphenylene, **14**, or dodecacyanodecacyclene, **15**, dianions, however, might be suitable compounds to prepare as a component for an s/p-orbital-based ferromagnet.



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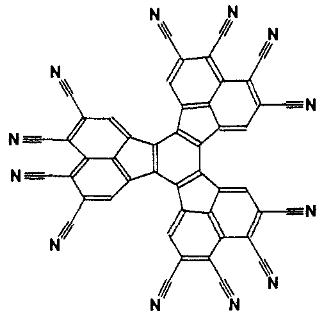

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Stable organic triplet ground-state species are of fundamental scientific interest and the possibility that they might be a viable components for s/p-orbital-based molecular ferromagnet enhances their scientific/technological value. Dications and dianions of six-membered-ring systems with 3-fold symmetry designed to frustrate the singlet ground state should be investigated.

Acknowledgment. We express our appreciation to the colleagues who helped us in several experimental areas: D. Wipf in synthesis, W. Marshall in X-ray diffraction, R. S. McLean in magnetic susceptibility, S. Hill and W. Barney in EPR, D. B. Chase in Raman and IR spectroscopies, F. Davidson and D. Ovenall in NMR, and E. Matthews and R. Richardson in electronic and vibrational spectroscopies. Thanks are due also to Prof. H. van Willigen (University of Massachusetts, Boston) for having taken several ENDOR spectra, to Prof. R. Breslow (Columbia University) for kindly providing a preprint prior to publication, and to K. Preston and J. R. Morton (NRC, Ottawa) for many insightful discussions.

Registry No. HOC, 92187-27-4; $[\mathrm{HOC}]^{\bullet+}[\mathrm{BPh}_4]^-$, 114491-13-3; $[\mathrm{HOC}]^{\bullet+}[\mathrm{BF}_4]$, 123265-28-1; $[\mathrm{HOC}]^{\bullet+}[\mathrm{PF}_6]^-$, 123265-12-3; $[\mathrm{HOC}]^{\bullet+}[\mathrm{SbF}_6]^-$, 114530-89-1; $[\mathrm{HOC}]^{\bullet+}[\mathrm{AsF}_6]^-$, 123265-13-4; $[\mathrm{HOC}]^{\bullet+}[\mathrm{F_3CSO_3}]^-$, 123265-14-5; $[\mathrm{HOC}]^{\bullet+}[\mathrm{TCNE}]^{\bullet-}$, 123265-15-6; $[\mathrm{HOC}]^{\bullet+}[\mathrm{TCNQ}]^{\bullet-}$, 123265-16-7; $[\mathrm{HOC}]^{2+}[n\text{-}\mathrm{C_4(CN)_6}]^{2-}$, 123265-17-8; $[\mathrm{HOC}]^{\bullet+}[\mathrm{DDQ}]^{\bullet-}$, 123265-18-9; $[\mathrm{HOC}]^{2+}[\mathrm{TCNQF_4}]^{2-}$, 123265-19-0; $[\mathrm{HOC}]^{2+}\{\mathrm{C_3[C(CN)_2]_3}\}^{2-}$, 123265-20-3; $[\mathrm{HOC}]^{2+}\{[\mathrm{TCNE}]^{\bullet-}\}_2$, 123265-21-4; $[\mathrm{HOC}]^{2+}\{[\mathrm{FB_4}]^-\}_2$, 117346-46-0; $[\mathrm{HOC}]^{2+}\{[\mathrm{PF_3}]^-\}_2$, 117346-47-1; $[\mathrm{HOC}]^{2+}\{[\mathrm{AsF_6}]^-\}_2$, 123265-22-5; $[\mathrm{HOC}]^{2+}\{[\mathrm{F_3CSO_3}]^-\}_2$, 123265-23-6; $[\mathrm{HOC}]^{2+}\{[\mathrm{SbF_6}]^-\}_2$, 123265-25-8; $[\mathrm{HOC}]^{2+}\{\mathrm{Ni[S_2C_2(CF_3)_2]_2}^{\bullet-}\}_2$, 123265-26-9; $[\mathrm{HOC}]^{2+}\{[\mathrm{C(CN)_3}]^-\}_2$, 121919-38-8; $[\mathrm{HOC}]^{2+}\{\mathrm{C_3[C(CN)_2]_3}^{\bullet-}\}_2$, 123289-02-1; $[\mathrm{HOC}]^{2+}\{\mathrm{C[C(CN)_2]_3}\}^{2-}$, 123289-01-0; $[\mathrm{HOC}]^{\bullet 3+}\{[\mathrm{PF_6}]^-\}_3$, 123265-24-7; $[\mathrm{HOC}]^{\bullet 3+}\{[\mathrm{SbF_6}]^-\}_3$, 123265-27-0; $[\mathrm{HOC}]^{4+}\{[\mathrm{SbF_6}]^-\}_4\cdot\mathrm{MeCN}$, 118399-45-4; $[\mathrm{HOC}]^{\bullet+}$, 92187-28-5; $[\mathrm{HOC}]^{2+}$, 92187-29-6; $[\mathrm{HOC}]^{3+}$, 92187-30-9; $[\mathrm{HOC}]^{4+}$, 92187-31-0; 2a,4a,6a,8a,10a,12a-hexaazacoronene-1,3,5,7,9,11(2*H*,4*H*,6*H*,8*H*,10*H*,12*H*)-hexone, 92187-33-2.

Supplementary Material Available: Figures showing stereoviews and anion labeling and tables listing anion bond distances and angles, fractional coordinates/anisotropic thermal parameters, intermolecular separations, electronic absorption maxima and their extinction coefficients, and deviations from least-squares planes for HOC, $[\mathrm{HOC}][\mathrm{BF_4}]$, $[\mathrm{HOC}][\mathrm{F_3CSO_3}]$, $[\mathrm{HOC}][\mathrm{TCNE}]$, $[\mathrm{HOC}][\mathrm{BF_4}]_2$, $[\mathrm{HOC}][\mathrm{PF_6}]_2$, $[\mathrm{HOC}]\{\mathrm{Ni[S_2C_2(CF_3)_2]_2}\}_2$, $[\mathrm{HOC}][\mathrm{C(CN)_3}]_2$, $[\mathrm{HOC}]\{\mathrm{C[C(CN)_2]_3}\}$, $[\mathrm{HOC}][\mathrm{PF_6}]_3$, $[\mathrm{HOC}][\mathrm{SbF_6}]_3$, and $[\mathrm{HOC}][\mathrm{SbF_6}]_4\cdot\mathrm{MeCN}$, as well as optimized structures for $[\mathrm{HOC}]^n$ (n = 0, 1+, 2+, 3+, 4+) (119 pages); tables of calculated and observed structure factors (58 pages). Ordering information is given on any current masthead page.

Photochemistry of Diphenylketyl Radicals in Polar Solvents[1]

R. W. Redmond, J. C. Scaiano,* and L. J. Johnston*

Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada K1A 0R6. *Received May 18, 1989*

Abstract: The photolysis of diphenylketyl radicals in acetonitrile leads to their photobleaching with a quantum yield of 0.10. The decay of the excited radicals occurs by four different pathways: (a) doublet–doublet fluorescence; (b) radiationless decay; (c) electron photoejection, which accounts for 20% of the observed bleaching; and (d) O–H bond cleavage leading to benzophenone, which is presumed to account for the remaining 80% of the bleaching. The electrons produced in acetonitrile are trapped by ground-state benzophenone to yield its radical anion (λ_{max} 710 nm); addition of electron scavengers (N_2O or acetone) prevents the formation of $Ph_2CO^{\bullet-}$.

The photochemistry and photophysics of a number of radicals have recently attracted considerable attention.[2-11] For example, the fluorescence lifetimes and quenching behavior of a variety of arylmethyl-type radicals have been examined. The majority of these radicals do not undergo any net photochemistry from their excited states, although quenching of the excited states with various substrates may often lead to different products from those formed from the ground-state radical. In contrast, several ketyl radicals do yield products upon excitation.[12-15] The diphenylketyl radical

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has so far been the most extensively examined. The radical shows a readily detectable fluorescence with a maximum at ~575 nm and with a lifetime of 3–4 ns in a variety of solvents.[13,14,16,17] The fluorescence lifetime has a substantial temperature dependence and is considerably lengthened by deuterium substitution at the hydroxyl position (10 ns) although only minor effects are induced by substitution on the aromatic ring.[13]

Excitation of the diphenylketyl radical in its visible absorption band leads to efficient bleaching in both cyclohexane and toluene, although there is no evidence for the formation of any additional transients in these solvents.[12] Two-laser-product studies have recently demonstrated that the efficient photodecomposition of the diphenylketyl radical involves cleavage of the O–H bond to generate benzophenone plus a hydrogen atom (reaction 1).[12] A

$$\mathrm{Ph_2\dot{C}OH^* \rightarrow Ph_2CO + H^\bullet} \qquad (1)$$

decrease in the normal ketyl radical products and a concomitant increase in unreacted benzophenone were observed when the radical (generated by photoreduction of benzophenone) was photolyzed. The proposed pathway was further confirmed by the Raman detection of hydrogen gas as a product when the radical was photolyzed in cyclohexane; both this and the increased yield of dicyclohexyl observed in the two-laser experiment were consistent with hydrogen abstraction from the solvent by the hydrogen atom. A quantum yield of 0.27 ± 0.06 was measured for the loss of a hydrogen atom. This number, in combination with an extrapolated fluorescence quantum yield, indicated that 70% of the excited radicals decayed by a nonradiative pathway.

In the course of our examination of the photochemistry of the diphenylketyl radical, we had observed that results somewhat different from those described above were obtained upon excitation of the radical in acetonitrile.[12] In this case, the radical was readily bleached by 515-nm dye laser excitation and there was evidence for the formation of a new transient that absorbed at longer wavelengths than the radical. Two possible candidates for this additional species were the solvated electron or the benzophenone radical anion. We have now examined the behavior of the diphenylketyl radical in considerable detail and carried our exploratory work on several of its substituted analogues in several polar solvents; the results are reported herein.

Results

Generation of Ketyl Radicals. Diphenylketyl radicals may be readily generated by hydrogen abstraction by triplet benzophenone from an appropriate hydrogen donor (reaction 2) or by hydrogen abstraction from benzhydrol by *tert*-butoxyl radicals produced by photolysis of di-*tert*-butyl peroxide (reaction 3, $k_q = 6.9 \times 10^7$ M^{-1} s^{-1}).[18]

$$\mathrm{Ph_2CO^* + RH \rightarrow Ph_2\dot{C}OH + R^\bullet} \qquad (2)$$

$$\mathrm{Ph_2CHOH + Bu^tO^\bullet \rightarrow Ph_2\dot{C}OH + Bu^tOH} \qquad (3)$$

The present experiments have mostly used benzophenone with 1,4-cyclohexadiene as the hydrogen donor, for which $k_2 = 2.9 \times 10^8$ M^{-1} s^{-1}.[19] Excimer laser irradiation (308 nm) was used for both methods, and the resulting radical was then excited with pulses from a dye laser (515 nm) or, for fluorescence measurements, a nitrogen laser at 337 nm.

Bleaching of Diphenylketyl Radicals. The parent diphenylketyl radical was generated by reaction of benzophenone triplets with 1,4-cyclohexadiene in acetonitrile and then excited with a 515-nm dye laser pulse. The dye pulse led to efficient and irreversible bleaching (Figure 1) of the ketyl radical at both 550 and 330 nm with the concomitant production of a new transient at longer wavelength. The new species has a broad maximum at 710 nm (Figure 1, inset) and decays with mixed first–second-order kinetics with a half-time of ~1.8 μs (Figure 2A). An experiment in which the concentration of 1,4-cyclohexadiene was varied from 0.1 to 0.5 M gave no observable reduction in either the amplitude or lifetime of the new transient, indicating that neither it nor its precursor was affected by the presence of diene.

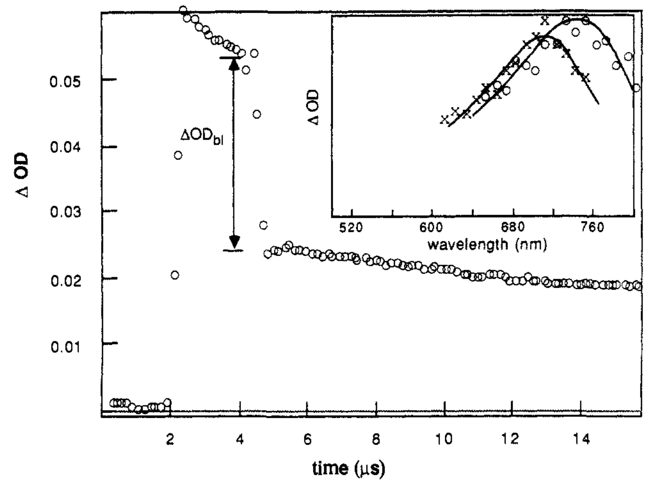

Figure 1. Transient absorption observed at 550 nm following 308 + 515 nm photolysis of 5 mM benzophenone in acetonitrile containing 10^{-2} M 1,4-cyclohexadiene, illustrating the photobleaching of the benzophenone ketyl radical. Inset: Transient absorption spectra observed 200 ns after the 515-nm pulse in 308 + 515 nm photolysis of 5 mM benzophenone (×) and 5 mM 4,4′-dichlorobenzophenone (○) in acetonitrile containing 10^{-2} M 1,4-cyclohexadiene.

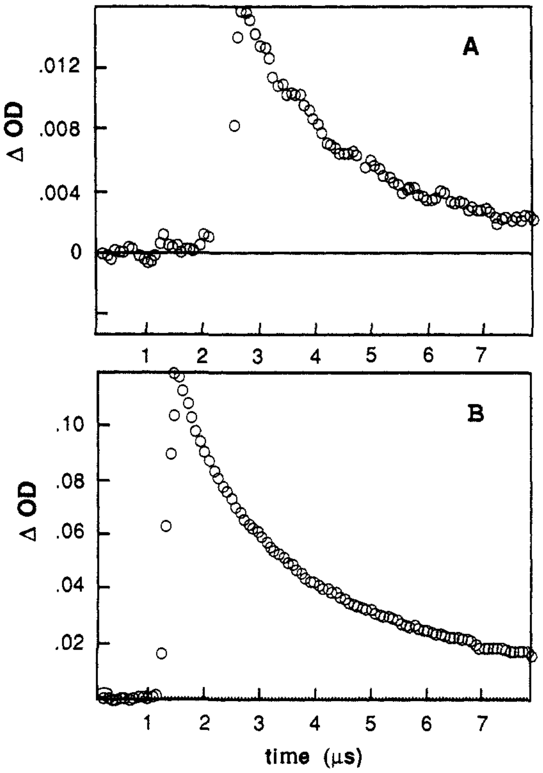

Figure 2. (A) Transient absorption observed at 720 nm following 308 + 515 nm photolysis of 5 mM benzophenone in acetonitrile containing 10^{-2} M 1,4-cyclohexadiene. (B) Transient absorption observed at 720 nm following 308-nm photolysis of 5 mM benzophenone in acetonitrile containing 5 mM DABCO.

Excitation of the ketyl radical in several other polar solvents was also examined, again with benzophenone plus cyclohexadiene

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as the radical source. In methanol there was reasonably efficient bleaching, but there was little or no absorption in the 700-nm region. In both 2-propanol and 1,4-dioxane, bleaching of the ketyl radical led to the formation of a weakly absorbing transient at ~700 nm. This species was considerably longer lived than that observed in acetonitrile. In 9:1 acetonitrile/water, the amount of ketyl radical bleaching was substantially reduced, as was the intensity of the 700-nm species. However, this effect is readily explicable on the basis of the previously observed quenching of the excited state of the radical by water.[13]

Excitation of the diphenylketyl radical generated from benzhydrol in acetonitrile via reaction 3 yielded somewhat different results. In the presence of 0.43 M di-*tert*-butyl peroxide, over 80% of the initial radical could be bleached, with the full power from the dye laser (200–300 mJ). There was also a slow regrowth of the radical that had previously been established to occur via reaction of the excited radical with peroxide to give *tert*-butoxyl radicals, which then abstract hydrogen from benzhydrol to regenerate the ground-state ketyl radical (reactions 4 and 3, $k_4 = 1.9 \times 10^9\ M^{-1}\ s^{-1}$).[12] However, there was no evidence for the

$$Ph_2\dot{C}OH^* + Bu^tOOBu^t \rightarrow Ph_2CO + Bu^tO^\bullet + Bu^tOH \qquad (4)$$

formation of the new long-wavelength species in this case. Although this suggested that benzophenone was necessary for the production of the new transient, we were somewhat concerned that the majority of the excited radicals were expected to be quenched by peroxide at the relatively high concentrations used. Therefore, the same experiment was repeated with 0.11 M peroxide; similar results were also obtained under these conditions. With use of the known rate constant for reaction 4 and our measured lifetime (4.8 ns) for the excited diphenylketyl radical in acetonitrile, one can estimate that approximately 80% of the radicals would be quenched by peroxide at the higher peroxide concentration and 50% at the lower.

The bleaching of the ketyl radical was carried out in the presence of a variety of substrates that are known to react with the solvated electron. Deaerating the benzophenone plus 1,4-cyclohexadiene solution with nitrous oxide almost completely removed the absorption at 710 nm, although the bleaching efficiency was not substantially changed. The addition of ~1 M acetone to a nitrogen-deaerated sample completely removed the 710-nm transient, again without decreasing the amount of bleaching of the ketyl radical. Acetone is known to react with the hydrated electron with a rate constant of $6 \times 10^9\ M^{-1}\ s^{-1}$.[20] Similar results were also observed in the presence of 0.5 M trifluoroacetic acid, although it should be noted that the acid would be expected to quench the solvated electron and to protonate the radical anion.

The bleaching of the ketyl radicals generated from several substituted benzophenones was also examined in acetonitrile. The radical from 4,4′-dichlorobenzophenone was efficiently bleached with the concomitant formation of a new species absorbing at longer wavelengths. In this case, the λ_{max} was shifted to slightly longer wavelength (740 nm), as shown in the inset in Figure 1. The ketyl radicals from both 4,4′-difluorobenzophenone and 4,4′-dimethoxybenzophenone showed very inefficient bleaching in acetonitrile, despite the fact that in cyclohexane they both show bleaching yields that are comparable to that of the unsubstituted ketyl.

Direct Generation of Benzophenone Radical Anions. Several benzophenone radical anions were produced via electron-transfer quenching of triplet benzophenone with 1,4-diazabicyclo[2.2.2]octane (DABCO) in acetonitrile (reaction 5, for which $k_q \sim 4 \times 10^9\ M^{-1}\ s^{-1}$).[21] The benzophenone radical anion showed a broad

$$Ph_2CO^* + DABCO \rightarrow Ph_2CO^{\bullet-} + DABCO^{\bullet+} \qquad (5)$$

absorption with λ_{max} at 720 nm (Figure 3) in good agreement with the previously reported spectrum.[22] The radical anion did not show a clean first-order decay (Figure 2B), a fact readily explicable on the basis of decay of the anion via electron back-transfer to the DABCO radical cation. Such a process would be expected to follow second-order kinetics, and except for a small faster component at the beginning of the decay, a reasonable second-order fit (correlation coefficient 0.996) could be obtained for the trace shown in Figure 2B. The second-order kinetics result from the fact that the radical ions are present in equimolar concentrations throughout their decay. The decay kinetics for the DABCO radical anion were similar to those observed for the new transient produced by the bleaching of the diphenylketyl radical (Figure 2A). Furthermore, the decay of the radical anion was not affected by the presence of nitrous oxide. Radical anions from 4,4′-dichlorobenzophenone and 4,4′-dimethoxybenzophenone had λ_{max} values of 750 (Figure 3) and 680 nm, respectively. These solvent shifts are in qualitative agreement with those observed previously for substituted benzophenone radical anions in 9:1 acetonitrile/water containing 0.02 M sodium hydroxide, although the magnitude of the observed shifts was larger in the aqueous solvent.[21] The earlier work had reported λ_{max} values of 625, 680, and 615 nm for the radical anions from benzophenone, 4,4′-dichlorobenzophenone, and 4,4′-dimethoxybenzophenone.[21]

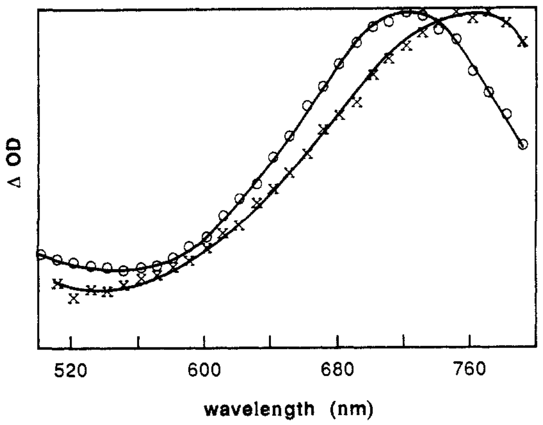
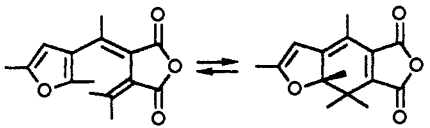


Figure 3. Transient absorption spectra of radical anions measured 1 μs after 308-nm excitation of 5 mM benzophenone (O) and 5 mM 4,4′-dichlorobenzophenone (X) in acetonitrile containing 5 mM DABCO.

Bleaching Efficiencies. The quantum yield for bleaching of the ketyl radical in acetonitrile was measured with Aberchrome-540 as a two-laser actinometer.[23] Aberchrome-540 is the commercial name for fulgide I, which is isomerized to II (reaction 6) with a quantum yield of 0.20 in toluene and has been widely used as an actinometer for steady-state irradiations.[24] Reaction 6 has been shown to be photoreversible with a quantum yield that depends linearly upon the irradiation wavelength. We have recently shown that this reaction may be conveniently used as an actinometer for the measurement of transient extinction coefficients and for the determination of bleaching quantum yields for transients in two-laser experiments.[23] The latter requires the parallel generation of both the colored form (II) of Aberchrome and the transient to be bleached with the first laser pulse and the matching of the optical densities of these two at the wavelength and time of the second laser. Both the transient of interest and



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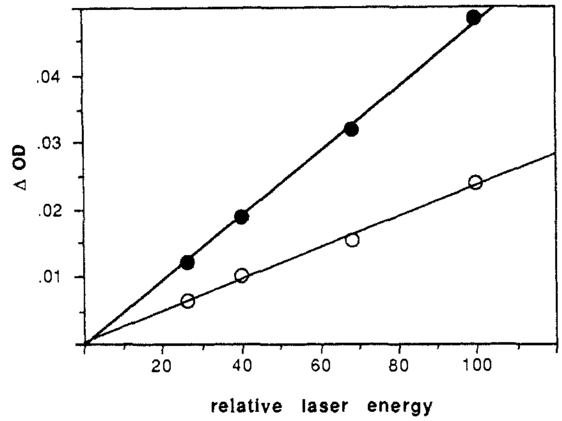

Figure 4. Dependence of the transient absorption (ΔOD) observed following 308-nm photolysis of 5 mM benzophenone (●) in acetonitrile containing 10^{-2} M 1,4-cyclohexadiene (detected at 550 nm) and Aberchrome-540 (○) in toluene (detected at 494 nm) on the incident laser energy.

II are then excited with the second laser, and the relative amount of bleaching of each is measured under conditions where <50% of the absorption is bleached for each one. The quantum yield for bleaching (Φ_{bl}) of the transient is then readily evaluated according to the procedure outlined in the Experimental Section.

Application of the above technique to the benzophenone ketyl system requires the extinction coefficient of the ketyl radical in acetonitrile. A value of 3500 M^{-1} cm^{-1} in acetonitrile was measured using Aberchrome-540 as the actinometer from the ratio of slopes in Figure 4 and assuming a value of 0.94 for the quantum yield for radical formation.[19] This number is in good agreement with the previously measured value of 3300 M^{-1} cm^{-1} for the ketyl radical at 550 nm in cyclohexane.[12] The bleaching quantum yield was then measured using the 515-nm pulses from the dye laser to excite the ketyl radical and II and monitoring the bleaching at 550 and 494 nm, respectively (Figure 5). A value of 0.10 ± 0.03 was obtained for the quantum yield for bleaching of the ketyl radical in acetonitrile.

In order to verify the reduced efficiency of photobleaching of the benzophenone ketyl radical in acetonitrile compared to that seen in cyclohexane ($\Phi_{bl} = 0.27$), a bleaching experiment was carried out with exactly the same conditions for optically matched samples of benzophenone in both acetonitrile and cyclohexane containing 1,4-cyclohexadiene. The photobleaching of the ketyl radical in cyclohexane was observed to indeed be 3–4 times more efficient that in acetonitrile. A similar approach was used to study the photobleaching in methanol and dioxane (benzophenone + 1,4-cyclohexadiene in these solvents); in dioxane the photobleaching efficiency was identical with that seen in acetonitrile while in methanol the bleaching was ~75% of that in acetonitrile.

A comparison of the relative amounts of bleaching of the ketyl radical at 550 nm and of production of the 720 nm transient allows the estimation of the fraction of bleaching that gives a new transient if the extinction coefficients of both species are known. Assuming that the 720-nm transient is in fact the radical anion (as discussed below) and using the reported extinction coefficient of 7000 M^{-1} cm^{-1},[22] we estimate that approximately 20% of the radicals that are bleached lead to the formation of radical anion. It should be noted that in these experiments it is not necessary to correct for spectral overlap between the ketyl radical and the benzophenone radical anion. For example, in an experiment where the bleaching ΔOD at 550 nm was 0.034, the positive ΔOD at 720 nm was 0.012. Taking into account the spectrum of $Ph_2CO^{\bullet-}$, we estimate that the change at 550 nm due to $Ph_2CO^{\bullet-}$ generation would be 0.0025, i.e., sufficiently small as not to warrant a correction of the bleaching data.

Discussion

It had originally been suggested that the two most likely candidates for the new species produced by bleaching of diphenylketyl radicals in acetonitrile were the solvated electron and the benzophenone radical anion.[12] On the basis of the above data the latter possibility appears to best account for the observed results. The spectrum of the new transient agrees very well with that of the benzophenone radical anion generated by an independent method. Furthermore, the observed spectral shifts for the dichloro ketone are also consistent with an anion and would not be expected if the transient was the solvated electron. In this regard it should also be noted that although the hydrated electron is known to absorb in the 700-nm region,[25] in acetonitrile the solvated electron has been suggested to exist as an equilibrium mixture of monomeric and dimeric radical anions that absorb from 500 to 1500 nm.[26] The monomeric species reacts readily with oxygen and nitrous oxide and also with benzophenone for which a rate constant of 5.5×10^{10} M^{-1} s^{-1} has been measured.[26] This would result in a lifetime of only ~4 ns in the presence of 5 mM benzophenone.

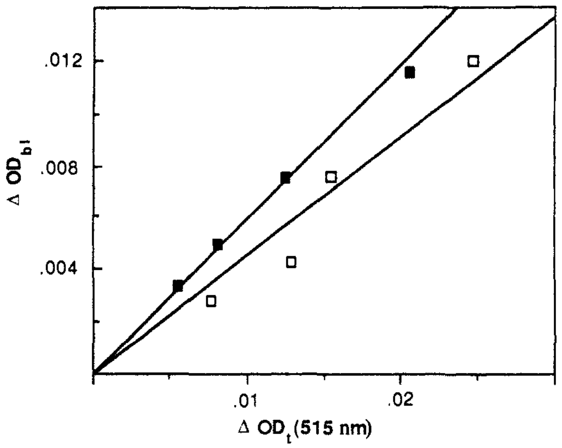

Figure 5. Dependence of the bleached absorption (ΔOD_{bl}) on the transient absorbance at the dye laser wavelength (ΔOD_t) following 308 + 515 nm photolysis of 5 mM benzophenone (■) in acetonitrile containing 10^{-2} M 1,4-cyclohexadiene (detected at 550 nm) and Aberchrome-540 (□) in toluene (detected at 494 nm).

There are two possible routes for formation of the benzophenone radical anions. The first is deprotonation of the excited radical to yield the anion plus a proton (reaction 7). The second involves ejection of an electron from the excited radical to produce the diphenylhydroxymethyl carbocation (i.e., protonated benzophenone that later deprotonates), followed by trapping of the solvated electron with ground-state benzophenone (reactions 8 and 9).

$$Ph_2\dot{C}OH^* \rightarrow Ph_2CO^{\bullet-} + H^+ \tag{7}$$

$$Ph_2\dot{C}OH^* \rightarrow Ph_2\overset{+}{C}OH + e(solv)^- \tag{8}$$

$$Ph_2CO + e(solv)^- \rightarrow Ph_2CO^{\bullet-} \tag{9}$$

There is considerable evidence that favors the latter possibility. Firstly, the red absorption is not observed upon excitation of the diphenylketyl radical produced from benzhydrol and di-*tert*-butyl peroxide, which suggests that benzophenone is necessary for its formation. Secondly, the 720-nm transient is eliminated by bubbling N_2O through the solution even though the radical anion has been shown not to react with N_2O. This suggests that a precursor to the radical anion is being efficiently quenched, consistent with the reported rate constant for trapping of the hydrated electron by N_2O ($k_q = 8.7 \times 10^9$ M^{-1} s^{-1})[27] and with the observed reactivity of the solvated electron in acetonitrile with N_2O.[26]

The proposed mechanism for formation requires that the growth of the radical anion be dependent upon the benzophenone concentration. However, at the concentrations required in our ex-

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periments for 308-nm excitation of the ketone (~5 mM), this growth would occur in <10 ns, which is approximately 2 orders of magnitude shorter than the dye laser pulse used to generate the anion. We have not obtained any evidence for the formation of the protonated benzophenone produced by ejection of an electron from the excited radical. This is not too surprising since its acid–base properties suggest that it should deprotonate rapidly. Protonated benzophenone fluoresces in the 420–490-nm region and would be expected to absorb at shorter wavelengths.[28-30]

Although production of the radical anion via reaction 7 does not agree with our experimental observations, it should be noted that the reaction is not unreasonable on the basis of the expectation that the excited ketyl radical should be a stronger acid than the ground state. This is in turn suggested by the larger difference between the ground- and excited-state surfaces for the radical as compared to the radical anion (the radical anion being red shifted with respect to the ketyl radical) and the higher energy of the radical anion/proton pair as compared to the neutral radical in acetonitrile.

The efficiency of bleaching of the diphenylketyl radical in acetonitrile is significantly lower than in cyclohexane. The slightly longer fluorescence lifetime is also consistent with this reduced reactivity and suggests that the dominant reaction path (loss of H atom) is 3–4 times slower in acetonitrile than in hydrocarbon solvents. Earlier work indicated that both the loss of H atom and radiationless decay had a considerable H/D isotope effect and that therefore both processes involved considerable stretching of the O–H bond. It is possible that both processes have, at least in part, a common pathway on the reaction surface and that polar solvents through hydrogen-bonding interactions modify the partition between reactive and unreactive paths. Although the photochemistry in acetonitrile involves a new reaction pathway (ejection of an electron that is trapped by ketone), this accounts for only ≈20% of the total bleaching of the radical. It is likely that the majority of the radicals undergo the same reaction as that observed in nonpolar solvents; i.e., loss of a hydrogen atom to regenerate benzophenone.

In conclusion, we have demonstrated that the bleaching of diphenylketyl radicals in polar solvents results in photoejection of an electron that is then recaptured by benzophenone to yield the ketone radical anion. Although the bleaching quantum yield is 0.10 for the benzophenone ketyl radical in acetonitrile, only ≈20% of the bleached radicals yields the radical anion.

Experimental Section

Materials and General Techniques. The benzophenones (Aldrich) were recrystallized before use, and 1,4-cyclohexadiene was vacuum distilled to remove polymeric impurities. DABCO (Aldrich), acetone (Fisher), acetonitrile (BDH, omnisolv), methanol (Aldrich, Gold Label), and dioxane (Fisher) were used as received.

Laser Flash Photolysis. The laser flash photolysis facility[31] and the modifications necessary for two-laser experiments[5] have been described. A Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm; ~5-ns pulses; ≤20 mJ/pulse) was used as the synthesis laser for the ketyl radicals. A Candela flash-pumped dye laser (Coumarin 503 dye in 50% aqueous methanol; ~250-ns pulses; ≤40 mJ/pulse) was used for bleaching of the radicals. For fluorescence lifetime studies the radicals were excited with a PRA LN-1000 nitrogen laser (337 nm; ~600-ps pulses; ≤1 mJ/pulse). Samples were contained in 7 × 7 mm^2 quartz cells and were deaerated by nitrogen purging unless otherwise indicated. A flow cell was used for two-laser spectra and the bleaching quantum yield measurements.

Extinction Coefficient of the Benzophenone Ketyl Radical. The determination of the extinction coefficient for the benzophenone ketyl radical in acetonitrile was carried out with reference to the actinometer system of Aberchrome-540. On 308-nm photolysis, the colored form is produced with a quantum yield ($\Phi_{\mathrm{I-II}}$) of 0.20 in toluene and has an extinction coefficient (ϵ_{II}) of 8200 M^{-1} cm^{-1} at its λ_{max} of 494 nm. The quantum yield of formation of the benzophenone ketyl radical (Φ_{BpK}) under our conditions is 0.94. The extinction coefficient of the benzophenone ketyl radical (ϵ_{BpK}) at 550 nm is given by the expression

$$\epsilon(\mathrm{BpK}) = \frac{\Delta \mathrm{OD}(\mathrm{BpK})}{\Delta \mathrm{OD}(\mathrm{II})} \frac{\Phi(\mathrm{I} \rightarrow \mathrm{II})}{\Phi(\mathrm{BpK})} \epsilon(\mathrm{II}) \tag{10}$$

where ΔOD(BpK) and ΔOD(II) are transient absorbances following 308-nm photolysis of optically matched samples of benzophenonc in acetonitrile containing 0.01 M 1,4-cyclohexadiene and Aberchrome-540 in toluene at the laser wavelength of 308 nm, respectively. Better accuracy was achieved by measuring transient absorbances as a function of laser dose (Figure 4). This resulted in straight-line plots of ΔOD vs laser dose, and the ratio of the measured slopes was substituted for the first term on the right-hand side of the equation, along with other known values to allow the determination of the extinction coefficient of the benzophenone ketyl radical at 550 nm.

Bleaching Quantum Yields. The quantum yield of photobleaching of the benzophenone ketyl radical in acetonitrile was measured with Aberchrome-540 in toluene as the two-laser actinometer. The experiment was done in the following manner:

(i) Kinetic traces arising from 308-nm excitation of solutions of both benzophenone in acetonitrile containing 0.01 M 1,4-cyclohexadiene and Aberchrome-540 in toluene were recorded at the dye laser emission maximum of 515 nm. This was repeated for different 308-nm laser energies, varied by using a series of calibrated neutral-density filters. These measurements allow for the measurement of transient absorbance at the dye laser wavelength at the exact time of the dye laser pulse ($\Delta \mathrm{OD}_t$).

(ii) Kinetic traces arising from 308 + 515 nm excitation of the above systems were recorded at 550 and 494 nm for benzophenone ketyl radical and the colored form of Aberchrome-540, respectively. Again this was done for each 308-nm laser dose. The dye laser energy was constant in each case. From these traces the bleached transient absorbances ($\Delta \mathrm{OD}_{\mathrm{bl}}$) were measured, where

$$\Delta \mathrm{OD}_{\mathrm{bt}} = \Delta \mathrm{OD}_1 - \Delta \mathrm{OD}_2 \tag{11}$$

and $\Delta \mathrm{OD}_1$ and $\Delta \mathrm{OD}_2$ are transient absorbances immediately before and after the dye laser pulse.

(iii) The quantum yield of photobleaching (Φ_{bl}) of the benzophenone ketyl radical, under conditions of optical matching of radical and Aberchrome-540 at the time of the dye laser pulse, is given by eq 12,

$$\Phi_{\mathrm{bl}}(\mathrm{BpK}) = \frac{\Delta \mathrm{OD}_{\mathrm{bl}}(\mathrm{BpK})}{\Delta \mathrm{OD}_{\mathrm{bl}}(\mathrm{II})} \frac{\epsilon(\mathrm{II})}{\epsilon(\mathrm{BpK})} \Phi_{\mathrm{bl}}(\mathrm{II}) \tag{12}$$

where ε(BpK) and ε(II) are extinction coefficients of both species at the respective detection wavelengths (ε(BpK) = 3500 M^{-1} cm^{-1} at 550 nm and ε(II) = 8200 M^{-1} cm^{-1} at 494 nm). $\Phi_{\mathrm{bl}}(\mathrm{II})$ is the quantum yield of photobleaching of the colored form of Aberchrome-540 that has the value of 0.054 at the excitation wavelength of 515 nm.

A somewhat more accurate approach is to replace the first term on the right-hand side of the equation with the ratio of the slopes obtained from plots of $\Delta \mathrm{OD}_{\mathrm{bl}}$ vs $\Delta \mathrm{OD}_t$ for both sample and reference. This ratio should be statistically more accurate than that based on a single matched absorbance. Substitution of this value in the equation along with the other known parameters allows the evaluation of the quantum yield of photobleaching of the benzophenone ketyl radical in acetonitrile.

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Registry No. N$_2$O, 10024-97-2; acetone, 67-64-1; benzophenone, 119-61-9; diphenylketyl radical, 4971-41-9; diphenylketyl radical anion, 16592-08-8.

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