to find any that fail to give carbon–carbon bond cleavage products.

Phosphines (such as PMe_3 or PPh_3) and CO cause facile ligand-promoted reductive elimination of **6–8** back to the starting ketones.[21] This fact explains why $RhCl(PPh_3)_3$ does not react with **1–3** and has obvious implications for the selection and design of other transition-metal reagents for carbon–carbon bond activation.

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Supplementary Material Available: Atom coordinates, temperature factors, and bond lengths and angles for compound **6** (5 pages). Ordering information is given on any current masthead page.

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(21) A mechanistic study of this ligand-promoted reductive elimination reaction shows, in the case of PPh_3, reductive elimination occurs from a five-coordinate complex in which pyridine is replaced by PPh_3.[20]

Photochemistry and Photophysics of Phenylmethyl Radicals[†]

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The photophysics of arylalkyl radicals, notably that of the prototype benzyl radical ($PhCH_2\cdot$), have been extensively studied. Fluorescence lifetimes and quantum yields have been experimentally measured in solid matrices at low temperatures and theoretical calculations have estimated the energy levels and the various decay modes of a variety of substituted benzyl radicals.[1-7] Fluorescence from the closely related diphenylketyl radical has also been observed in a glassy matrix[8] as well as at room temperature.[9-11] For the ketyl radical the fluorescence lifetime has decreased from ~20 to ~2 ns on increasing the temperature from 77 K to room temperatue, indicating a possible photochemical reaction of the excited state of the radical at the higher temperature.[8] While the fluorescence lifetime of the benzyl and its analogue radicals at 77 K is in the range of 1.0 ± 0.5 μs, no information is available in the literature on their fluorescence lifetime at higher temperatures. In fact, information on the photochemistry and photophysics of radicals in liquid solutions is very scarce. To bridge this gap, we have initiated a systematic study of such systems. In the present communication we report on the room temperature lifetime, excited-state doublet–doublet and fluorescence spectra of the diphenylmethyl radical as well as on the photochemistry of its triphenylmethyl homologue.

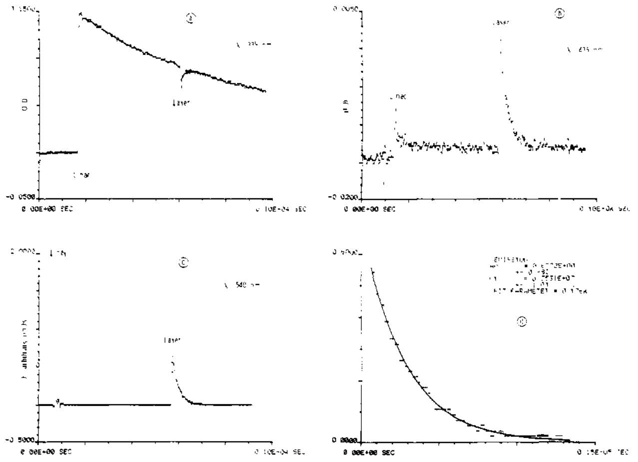

Figure 1. Excitation of diphenylmethyl radicals detected at different regions of the spectrum: (a) λ = 335 nm, bleaching of the ground state; (b) λ = 435 nm, doublet–doublet absorption by the excited state of the radical; (c) λ = 540 nm, fluorescence of the excited radical. Argon-saturated solution of 1 mM Ph_2CHCl in CH_3CN; (d) expansion of (c) to show least-squares best fit to exponential decay of the fluorescence.

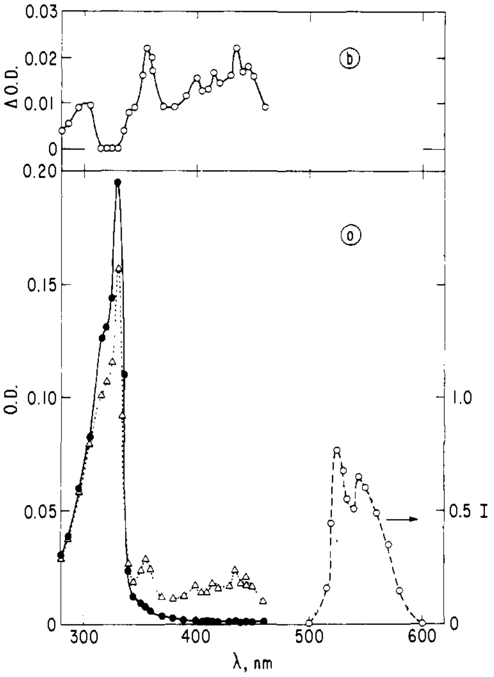

Figure 2. Fluorescence and absorption spectra of the $Ph_2CH\cdot$ radical; (a) absorption spectrum of the ground state before the laser flash (solid curve and solid points); absorption at the end of the laser flash (dotted curve and open triangles); fluorescence spectrum of the first excited doublet state (dashed line). (b) Doublet–doublet absorption spectrum of the first excited state of the radical; calculated assuming ΔOD = 0 at 330 nm. Errors for ΔOD are <±10%. Spectra obtained following pulse radiolysis of 10^{-3} M Ph_2CHCl in CH_3CN.

The diphenylmethyl and triphenylmethyl radicals were produced pulse radiolytically by 40-ns electron pulses (~5 μM of radicals

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(12) In the presence of alcohols, the appropriate carbinol was used instead of the halide in order to avoid problems associated with alcoholysis of the halide. Substrate concentrations were in the range 1–5 mM. Solutions were deaerated by bubbling Ar through the solutions. In CH_3CN solutions bubbling N_2O or SF_6 completely eliminated the absorption due to the radical. In cyclohexane solutions ~1 mM of ethanol was added as positive hole scavenger. That these systems produce the diphenylmethyl or triphenylmethyl radicals is well documented.[13]

per pulse) through reaction 1.[13] A frequency-doubled ruby laser

$$\mathrm{Ph_2CHCl + e^- \rightarrow Ph_2CH\cdot + Cl^-} \qquad (1)$$

(λ_{exc} = 347 nm, ~15 ns, ~30 mJ/pulse) synchronized with the radical-producing linac pulse (typically 4-μs delay) was used to excite the radicals. The electron beam, the laser beam, and the analyzing light were all focused onto a 1-cm cell and were all perpendicular to one another. A similar setup has been previously utilized in the study of the ketyl radicals.[10] Blanks were checked to ensure that all the observations described below originate from the radicals and not from the parent molecules.

The sequence of events, starting with the production of diphenylmethyl radicals in acetonitrile, is shown in Figure 1 for three different wavelengths. The lifetimes for the recovery of the ground state (Figure 1a), the decay rate of the absorption of the excited states (Figure 1b), and the fluorescence lifetime (Figure 1c) are all the same within experimental error, τ_f = 280 ± 30 ns. All three modes display single exponential behavior. The fluorescence lifetime of the diphenylmethyl radical is slightly longer lived at 77 K (440 ns in EtOH matrix[6a]) than found in this study. The long lifetime of the excited state of the benzyl-type radicals has been attributed to the low oscillator strength of the symmetry-allowed $^2A_2 \leftarrow {}^2B_2$ transition. It should be noted that no new absorption band could be observed at the end of the decay of the excited state of the radical in CH_3CN.

The fluorescence spectrum of the excited $Ph_2CH\cdot$ radical is shown in Figure 2a (dashed curve). This could be compared with the fluorescence spectra obtained at 77 K.[14] Although the spectrum at room temperature is not as richly structured as in the glassy matrix,[14b] vibrational structure is clearly observable. The higher energy peak, which probably corresponds to the O–O transition of the first excited doublet,[14b] is at 19048 cm^{-1} (2.38 eV) above the ground state. The vibrational frequency of 610 cm^{-1} is probably a C–C bending mode. Using $Ru(bpy)_3^{2+*}$ as a fluorescence actinometer (ϕ_{em} = 0.042)[15] we estimate the quantum yield for fluorescence of the radical as ϕ_{em} ~ 0.3, and thus the radiative lifetime is 1.1 μs.[17] This estimate also implies that the quantum yield for fluorescence at 77 K is ~0.5.

Assuming that the excited state of the radical absorbs negligibly at λ_{max} = 330 ± 3 nm of its ground state,[18] we can, for the first time, obtain the doublet–doublet absorption spectrum of the excited state. This spectrum is shown in Figure 2b. With the above mentioned assumption, one can estimate the extinction coefficients for the absorption of the first excited state of the radical. Taking for the ground state $\epsilon_{330} = 4.0 \times 10^4$ M^{-1} cm^{-1}, one obtaines $\epsilon^*_{355} = 3.0 \times 10^4$, obviously allowed transitions of large oscillator strength. The structure obtained in the 400–440-nm region (λ_{max} = 403, 417, 435 nm) consistently appears in repetitive spectra measurements. We cannot at present offer a decisive result to indicate whether this is vibrational structure or actually different electronic excitations. The lowest band presently observed for these excitations is situated at 5.25 eV above the ground state and thus would correspond to electronic excitations to the eighth or higher levels above the ground state.[6e]

Excitation of the triphenylmethyl radical yields dramatically different results. No emission from an excited state of this radical could be observed in EtOH, CH_3CN, or cyclohexane solutions at room temperature (compare to fluorescence lifetime of 280 ns in EtOH at 77 K[6a]). On the other hand, high quantum yields (Φ ~ 1.0) of permanent (within the lifetime of the radical) bleaching of the parent radical and rather strongly absorbing transient species ($\lambda_{max} \simeq$ 490 nm, ϵ ~ 12 500 M^{-1} cm^{-1}) could be observed. Positive identification of this product still awaits further experiments, but several conceivable routes for the photochemical reaction could be eliminated. No long-lived (on the time scale of tens of milliseconds) excited state is expected for this radical. Photoionization of the radical is rejected since an ejected electron would immediately produce back the parent radical in the systems studied. The fact that products similar to those produced in cyclohexane and CH_3CN are produced in EtOH (and their lifetime is independent of the concentration of alcohol in the other solvents) eliminates the possibility of homolytic bond scission to form a phenyl radical and a diphenylmethylene carbene. Also the similarity of the results in the different solvents makes participation of the solvent in the initial photochemical step rather unlikely. We, therefore, tentatively favor an internal geometric isomerization as the major photochemical route for the triphenylmethyl radical. Inter-ring photocyclization similar to the one observed in related systems[16] is one such pathway. Further identification of the photochemical product and the reasons for such pronounced differences between the two seemingly similar radicals are currently under investigation.

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Registry No. Diphenylmethyl, 4471-17-4; triphenylmethyl, 2216-49-1.

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[17] The determination of the fluorescence quantum yield should be considered only as a rough estimate since all fluorescence spectra measured in this study are uncorrected for changes in detector sensitivity as a function of wavelength.

[18] This assumption seems reasonable in view of the correspondence of the spectrum after the laser flash with that of the narrow band of the ground-state radical in the region 310–335 nm. Furthermore with this assumption we obtain the expected quantum yield of excitation of the radical Φ_{exc} = 1.05 ± 0.1 from the bleaching of the ground state at 330 nm.

Reactions at Phase Boundaries Using Immobilized Hydrophobic Monolayers[1]

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Biphase reactions involving hydrophobic substrates and water-soluble reagents are generally slow, if there exist solubility problems of the reactants. Such reactions can be facilitated by the use of phase-transfer catalysts[2] or surface-active agents,[3] although not many reactions proceed at appreciable rates at the liquid–liquid interface in spite of the attentions.[4] We report here

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