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Photochemistry of Singlet and Upper Triplet States of Dibenzocycloheptadienone[1]

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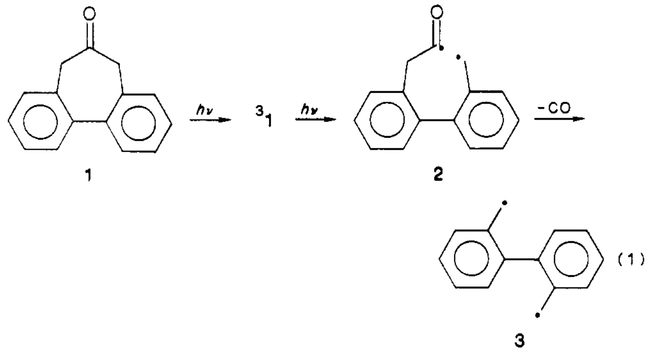
Dibenzocycloheptadienone (1) undergoes Norrish type I α-cleavage from both its first excited singlet state and an upper triplet state with quantum yields of 0.02 and 0.04, respectively. The major product in both cases is dihydrophenanthrene formed by loss of carbon monoxide from the initial biradical, followed by ring closure. The triplet state of ketone 1 has been characterized by laser flash photolysis. Photolysis of the triplet leads to irreversible bleaching and the generation of a short-lived (~350 ns) transient at 325 nm, which is tentatively assigned to biradical 3.

Several recent reports have identified ketones with triplets that are unreactive toward the usual Norrish type I α-cleavage but that undergo reaction from an upper excited triplet level.[4,5] For example, cleavage of an upper triplet state of 1,3-di(1-naphthyl)-2-propanone was demonstrated by both transient absorption measurements and product studies under two-photon excitation.[4] In contrast, the first excited triplet was completely unreactive due to localization of the excitation energy on the lower energy naphthalene chromophore rather than on the carbonyl. Some inefficient ($\Phi = 0.002$) cleavage was observed from the singlet state.

On the basis of the above results, it was anticipated that dibenzocycloheptadienone (1) would be unreactive with respect to α-cleavage from its lowest triplet state since the excitation would again be localized on the (presumably) unreactive biphenyl moiety rather than the carbonyl. This would be in sharp contrast to the structurally similar dibenzyl ketone, which has a quantum yield of 0.7 for α-cleavage.[6,7] However, ketone 1 might also undergo reaction from an upper triplet to generate biradical 2, which would lose carbon monoxide to generate biradical 3. The latter reaction should occur with a rate constant at least as fast as that for decarbonylation of the phenylacetyl radical ($k_{-CO} = 9.1 \times 10^6$ M^{-1} s^{-1}).[8,9] Thus, ketone 1 was expected to provide a two-photon source of biradical 3.



Ketone 1 has been examined by a combination of product studies and transient absorption measurements under conditions of both one- and two-photon excitation. The results confirm the above hypothesis and are reported herein.

Results

Transient Absorption Experiments. Laser excitation at 308 nm of deaerated solutions of ketone 1 in either benzene or cyclohexane ($\leq$0.001 M) generated a strongly absorbing transient with $\lambda_{max} = 400$ nm (Figure 1). The transient had a lifetime of $\geq$5 μs although the decays were not cleanly first order but showed some second-order contributions due to triplet–triplet annihilation, particularly at high laser doses. This species was readily assigned to triplet 1 on the basis of the following observations.

The spectrum from 1 was very similar to that of triplet 2,2′-dimethylbiphenyl (4, Figure 1), which was produced by energy transfer from acetone triplet in benzene. The triplet of biphenyl is shifted by approximately 40 nm ($\lambda_{max} = 360$ nm in benzene, Figure 1) from that of 1 and 4, presumably as a result of conformational changes which are prevented by the two ortho substituents.[10] The spectrum shown for 1 in Figure 1 could also be produced by energy transfer from xanthone. In this experiment xanthone in benzene was excited at 337 nm and the quenching of its triplet at 640 nm by the addition of 1 was measured. A rate constant of $(4.0 \pm 0.4) \times 10^9$ M^{-1} s^{-1} was obtained. Direct excitation of 1 was negligible, even at the highest concentration used.

Triplet 1 was readily quenched by both oxygen and 1,3-cyclohexadiene; a quenching rate constant of $(8.8 \pm 0.6) \times 10^9$ M^{-1} s^{-1} was measured for the latter. These results further confirm the triplet assignment.

Lamp Product Studies. Although the transient measurements described above gave no evidence for reaction of ketone 1, irradiation of deaerated solutions of 1 (1–5 mM) in benzene or cyclohexane with RPR-3000 lamps did produce low yields of products. In benzene these were identified as 9,10-dihydrophenanthrene (5, 90%), phenanthrene (6, 2–3%), and trace amounts of 2,2′-dimethylbiphenyl (4), reaction 2. Formation of 5 as the major product was confirmed by its isolation from a preparative-scale photolysis and comparison of its NMR and GC/MS spectra with those of an authentic sample. Phenanthrene is presumed to result from secondary re-

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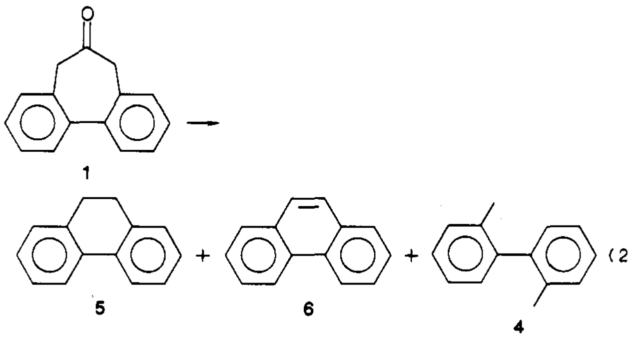
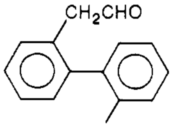


action of 5 since irradiation of 0.5 mM 5 under the same conditions did yield ~5% of 6.

In cyclohexane the major product was again 5 although, in addition to small amounts of 6 and 4, there were two other minor products (1–2%). These were tentatively identified (on the basis of GC/MS data) as 7 and 8 derived from biradical 2 before loss of CO. Surprisingly, there was little increase in the amount of 4 produced in the hydrogen-donating solvent.



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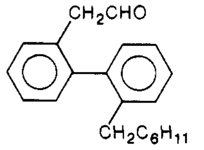

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In order to ascertain whether singlet or triplet 1 was responsible for the observed chemistry, we irradiated a solution of 1 plus 0.004 M 1,3-cyclohexadiene in benzene at 300 nm. Despite the fact that this is sufficient diene to quench >99% of the triplets, the amount of ketone consumed was identical (~25% conversion) to that in an irradiated blank which contained no diene. Furthermore, sensitization with triplet xanthone (350-nm excitation to prevent direct irradiation of 1 but with a similar dose to that used for direct excitation) gave <1% product formation. These two results demonstrate that α-cleavage of ketone 1 occurs from the first excited singlet as is also the case for 1,3-di(1-naphthyl)-2-propanone.[4]

The quantum yield for reaction 2 in benzene was measured relative to the production of acetophenone from valerophenone ($\Phi = 0.30$).[14] A value of 0.02 ± 0.01 for loss of ketone was obtained, indicating that the reaction is inefficient compared to the α-cleavage from many other triplet ketones.

The above results are consistent with the fact that ketone 1 shows a typical ketone-like fluorescence with λ_{max} at ca. 400 nm in cyclohexane as compared to λ_{max} at ca. 310 nm for 2,2′-dimethylbiphenyl. The lowest singlet of the ketone is, thus, localized on the carbonyl rather than the biphenyl chromophore.

Ketone 1 was also photolyzed at 350 nm in the presence of 0.1 M benzenethiol in an attempt to trap biradicals 2 and/or 3. However, no biradical trapping products were detected. This is not too surprising in view of the known rate constants[11] for reaction of benzyl radicals with benzenethiol and the expected short lifetime for a singlet biradical. The stable free radical tetramethyl-1-piperidinyloxy (TEMPO) is known to react more rapidly with benzyl radicals.[12,13] However, irradiation of 1 at 350 nm in benzene containing 0.1 M TEMPO did not yield any biradical trapping products, on the basis of GC analysis.

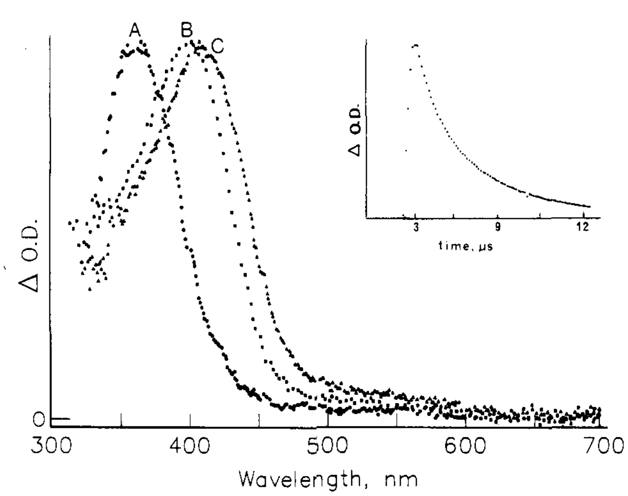

Figure 1. Normalized transient absorption spectra produced by 308-nm excitation of 1 in benzene (B), of biphenyl plus acetone as sensitizer in benzene (A), and of 2,2′-dimethylbiphenyl plus acetone sensitizer in benzene (C). All spectra were recorded 1 μs after the laser pulse. Insert: decay at 390 nm of the transient absorption of 1.

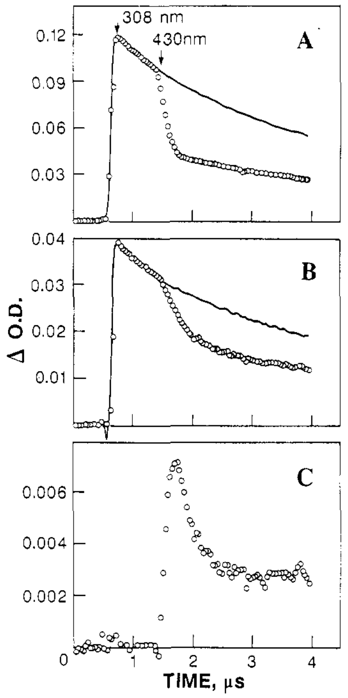

Figure 2. Transient decay for 1 in cyclohexane in matched one (—, 308 nm) and two (○, 308 + 430 nm) laser experiments at 390 nm (A) and 325 nm (B). Trace C was obtained by a normalized subtraction of the two-laser traces shown in A and B.

Photochemistry of Triplet 1. Excitation of triplet 1 using the pulses from a dye laser (λ ~ 430 nm) gave efficient and irreversible bleaching at 390 nm, as shown in Figure 2A.[15] In these experiments the triplet ketone was generated by using 308-nm excitation and then reexcited after ca. 1 μs by the 430-nm pulse. Similar results were observed in a variety of solvents (e.g., cyclohexane, benz-

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[11] A rate constant of 3.1×10^5 M^{-1} s^{-1} in hexane at 25 °C has been reported: Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19.

[12] Trapping of benzyl radical with TEMPO occurs with a rate constant of 4.9×10^8 M^{-1} s^{-1}: Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.*, in press.

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[15] The approach used in two-laser experiments has recently been described.[16]

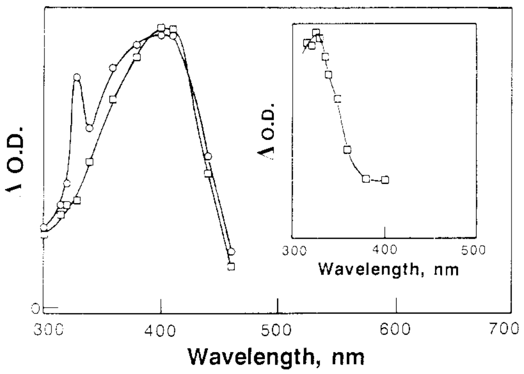

Figure 3. Normalized transient absorption spectra obtained by 308 + 430 nm excitation of 1 in benzene and measured 0.3 μs before (□) and toward the end of (○) the 430-nm pulse. Insert: transient absorption spectrum of the benzyl radical produced by *tert*-butoxyl radical abstraction from 2,2′-dimethylbiphenyl in benzene.

ene, methanol). Excitation of the triplet at 337 nm also gave similar results although the lower laser power at this wavelength led to considerably less efficient bleaching.

Somewhat different results were obtained when the above two-laser experiment was monitored at shorter wavelengths (e.g., 320–325 nm). Bleaching of the triplet was still observed (Figure 2B), but there was some indication for the formation of a relatively short-lived species within the 430-nm laser pulse. Note that in Figure 2A the bleaching kinetics are determined by the laser pulse width of ca. 250 ns whereas in 2B there is obviously an additional transient with a longer lifetime. However, there was no convenient wavelength at which this new species could be monitored without interference from the residual triplet ketone signal. A normalized subtraction of the two-laser traces at 390 and 325 nm gives the trace shown in Figure 2C. From this a lifetime of 300–350 ns may be estimated. Furthermore, similar results were obtained in either isooctane or methanol at −50 °C, which indicates that the lifetime of the new species is not particularly solvent or temperature dependent.

The spectra obtained before and during the 430-nm pulse in the above two-laser experiment are shown in Figure 3. There is an increase in absorption at short wavelengths in the two-laser spectrum. It should be noted that no additional absorptions were observed at wavelengths between 500 and 700 nm in the two-laser spectrum. The additional short-wavelength absorption is quite similar to that of the benzylic radical produced by *tert*-butoxyl radical abstraction from 2,2′-dimethylbiphenyl (λ_{max} = 325 nm in benzene; Figure 3, insert). Excitation at 430 nm of triplet 9,10-dihydrophenanthrene in cyclohexane did not result in triplet bleaching or the production of any additional transients.[17]

The quantum yield for triplet bleaching was estimated by using Aberchrome-540 actinometry, a technique that requires the triplet extinction coefficient of 1.[18] A value of 14 300 M^{-1} cm^{-1} at 390 nm in cyclohexane was obtained for $\Phi_{ISC}\epsilon_1$ by using Aberchrome-540 actinometry.[19] This leads to an extinction coefficient of 14 300 M^{-1} cm^{-1} assuming a value for 1 for Φ_{ISC} for 1.[20] A value of 0.045 was then measured for the quantum yield of bleaching.

Product studies under two-laser excitation conditions were carried out to determine whether or not the observed bleaching resulted in the formation of new or increased yields of products. Three identical samples of 1 in cyclohexane were photolyzed by using (a) 308-nm excitation, (b) 308-nm followed ~0.5 μs later by 430-nm excitation, and (c) 430-nm followed by 308-nm excitation. Product analysis indicated that photolysis of triplet 1 produces the same product as does the lamp irradiation. However, comparison of the yields showed a threefold increase in the amount of 5 produced in the 308 + 430 nm experiment over one-laser or the reversed two-laser irradiation. This result confirms that at least part of the bleaching observed is due to α-cleavage from an upper triplet to yield the expected biradical-derived products.

Discussion

The above results indicate that ketone 1 undergoes inefficient α-cleavage from both its first excited singlet state and an upper triplet. The products in both cases are those expected from α-cleavage followed by loss of CO to yield biradical 3. The failure to trap significant amounts of biradical 3 in the presence of either benzenethiol or TEMPO in the direct singlet reaction is not unexpected since singlet biradicals are typically very short-lived.

Although the product studies provide strong support for the presence of biradical 3, the transient experiments are somewhat less conclusive. The additional transient produced at short wavelengths by excitation of triplet 1 has a spectrum that is consistent with either biradical 2 or 3 since the chromophore in either case is the benzylic radical center. It should be noted that although 3 is a conjugated biradical, this has not been shown to cause a large shift in absorption spectra in other cases. For example, the photoenol biradical from 2-methylbenzophenone has a similar absorption spectrum to that of the diphenylketyl radical.[21]

The observed lifetime of 300–350 ns for the two-laser transient is somewhat longer than would be expected for 2 on the basis of the known lifetime for the phenylacetyl radical (110 ns in isooctane at room temperature)[8,9] or the acyl–benzyl 1,6-biradical derived from 2,6-diphenylcyclohexanone (121 ns in methanol at room temperature).[22] However, it is not unreasonable for a biradical such as 3 since relatively long lifetimes have been observed for some similar biradicals (e.g., $Ph_2\dot{C}(CH_2)_2\dot{C}Ph_2$, 500 ns;[23] $Ph_2\dot{C}(CH_2)_3\dot{C}Ph_2$, 900 ns;[23] $Ph\dot{C}H(CH_2)_4\dot{C}HPh$, 1080 ns[22]). The apparent insensitivity of the transient lifetime to temperature is also reasonable since activation energies for intramolecular biradical decay are typically quite low.[23,24] Additional experiments aimed at finding a suitable one-photon precursor to biradical 3 for use in transient experiments are planned to confirm the above assignments.

Experimental Section

Materials. Ketone 1 was prepared according to a literature procedure by coupling of (2-methylphenyl)magnesium bromide in the presence of cobalt chloride to give 2,2′-dimethylbiphenyl,[25]

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[17] We thank a referee for suggesting this experiment.

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[19] This measurement was done at 390 nm rather than the λ_{max} for triplet 1 since the former was more convenient for the bleaching experiments. The quoted value is the average of two determinations.

[20] Intersystem crossing efficiencies of 1 are typical for similar ketones: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 49.

[21] Haag, R.; Wirz, J.; Wagner, P. J. *Helv. Chim. Acta* **1977**, *60*, 2595.

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[24] Scaiano, J. C., Biradicals, *Landolt-Börnstein*, New Series; Fischer, H., Ed.; Springer-Verlag: Berlin, 1985; Vol. 13e, Chapter 11.

which was dibrominated by using *N*-bromosuccinimide/benzoyl peroxide.[26] The dibromide was treated with KCN, and the resulting 6-amino-5-cyanodibenzocycloheptatriene was treated with concentrated sulfuric acid to give **1**, which was further purified by crystallization from ethanol;[27] mp 77 °C (lit.[27] mp 76–78). 2,2′-Dimethylbiphenyl was available from the first step of the above synthesis and was purified by distillation followed by chromatography. Biphenyl and xanthone were recrystallized before use, and 1,3-cyclohexadiene was distilled. Aberchrome-540 was used as received from Aberchromics Ltd., Cardiff, U.K. Solvents were Aldrich gold label or spectrograde and were used as received.

General. Fluorescence and phosphorescence spectra were measured on a Perkin-Elmer LS-5 spectrofluorimeter. GC analyses were done on a Perkin-Elmer 8320 instrument equipped with a 12-m BP1 capillary column. GC/MS spectra were recorded on a Hewlett-Packard 5995 instrument equipped with a 10-m Ultra I (OV-101) capillary column.

Laser Flash Photolysis. The basic laser flash photolysis equipment as well as the modifications required for two-laser experiments has been described.[28,29] A Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm, 5-ns pulses, ≤20 mJ/pulse), a Molectron UV-24 nitrogen laser (337 nm, ~8-ns pulses, ≤15 mJ/pulse), and a Candela flash pumped dye laser (Stilbene 420 dye in 50% aqueous methanol; 100–200 mJ/pulse; ~250-ns pulses) were used for sample excitation. Samples were contained in 7 × 7 mm^2 quartz cells and were deaerated by nitrogen purging.

Preparative Photolysis of 1. A solution of 100 mg of **1** in 50 mL of benzene was deaerated and then irradiated for 80 h by using RPR-3000 lamps. GC analysis showed 85% conversion to a single product in >90% yield. The product was separated by low-pressure chromatography on silica gel using hexane as eluent. It was confirmed to be dihydrophenanthrene by comparison of its GC/MS and NMR spectra with those of an authentic material.

Quantum Yields. Quantum yields for the disappearance of **1** in benzene were measured by using the formation of acetophenone from valerophenone in benzene as an actinometer ($\Phi = 0.30$).[14] Samples of **1** and valerophenone with matched optical densities at 310 nm were deaerated and irradiated with RPR-3000 lamps to ~10% conversion. Quantitative analyses were done by GC using appropriate internal standards and calibration solutions.

Two-Laser Photolyses. Three separate aliquots of a 1.1 mM benzene solution of **1** were irradiated with (a) 500 308-nm pulses, (b) 500 pairs of 308-nm plus 430-nm pulses with a 0.5-μs delay between the two lasers, and (c) 500 pairs of pulses with the reverse sequence of b. Product analysis by GC against an internal standard showed 2.5, 8.0, and 2.6% dihydrophenanthrene for a, b, and c, respectively.

Acknowledgment. We thank S. E. Sugamori for technical assistance and Dr. J. C. Scaiano for helpful discussions.

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Alkylenation with Geminal Dialuminoalkane Reagents: The Synthesis of Olefins from Ketones[1]

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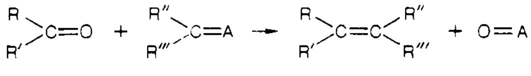
Bis(dichloroalumino)methane (BDAM, **1**) has been synthesized in high yield from aluminum powder and methylene chloride by a published procedure carefully modified for safety. By the screening away of aluminum metal fine particles and the gradual addition of methylene bromide promoter over the course of reaction, a safe procedure was attained. Although **1** itself was a poor methylenating agent for ketones, its dietherate complex was distinctly more reactive. By exchanging half the halogens of **1** with Me_3Al, MeMgBr, or Et_3Al, two very effective methylenating agents for ketones, namely $CH_2(AlClMe)_2$ (**2**) and $CH_2(AlClEt)_2$ (**3**), were obtained. As dietherates with Et_2O or THF, **2** and **3** smoothly converted a broad variety of ketones (aliphatic, alicyclic, and aromatic) into their corresponding methylene derivatives, with little or no competitive alkylation or reduction. A titanium-modified reagent, $Cl_2AlCH_2TiCl_3$ (**4**), was also effective toward ketones, but gave only low conversions of esters to vinyl ethers. Finally, as an example of a multicarbon, alkylenating agent, the reagents **5–7** ($(R_2Al)_2CH(CH_2)_4CH_3$, **5**, R = Et; **6**, R = Cl; and **7**, R = Cl or Et) were examined. Good to fair yields of alkylenation were obtained with aromatic ketones, but aliphatic ketones underwent alkylation, hydride reduction, and/or aldol condensation. The great influence of alkyl groups and donor solvent on the reactivity of **1–3** is briefly discussed.

The alkylenation of carbonyl compounds, the so-called carbonyl olefination reaction (eq 1),[2] became a feasible transformation with the discovery of the methylenating action of methylenetriphenylphosphorane by Wittig and Geissler in 1953 (eq 1, A = Ph_3P).[3] In the succeeding 35 years such Wittig reactions have been widely applied in organic synthesis, in general,[4,5] and in natural product or pharmaceutical synthesis, in particular.[6] Although the Wittig reaction is general for aldehydes and ketones and



$$RR'C{=}O + R''R'''C{=}A \rightarrow RR'C{=}CR''R''' + O{=}A \quad (1)$$

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