the proton-coupled mode). UV–vis, λ_{max} 408 nm (ϵ 142 000), 506 (13 700), 540 (10 500), 576 (6200), 630 (4400), 654 (700).

Acknowledgment. This research was supported by grants from the National Institutes of Health (HL 22252) and the National Science Foundation (CHE-81-20891). We are pleased to acknowledge financial assistance (to H.D.T.) from Yarmouk University, Jordan.

Registry No. **2**, 104834-69-7; **3**, 104834-70-0; **4**, 104834-71-1; **5**, 104834-72-2; **6**, 104848-65-9; **7**, 104834-62-0; **8**, 104834-63-1; **9**, 104834-65-3; **10**, 104848-64-8; **11**, 104834-60-8; **12**, 104834-61-9; **13**, 104834-64-2; **14**, 104834-50-6; **15**, 104834-54-0; **16**, 104834-58-4; **17**, 89909-45-5; **18**, 62562-74-7; **19**, 89909-44-4; **20**, 87462-15-5; **21**, 87462-14-4; **22**, 104834-47-1; **23**, 104834-49-3; **24**, 60024-79-5; **25**, 50622-71-4; **26**, 50622-73-6; **27**, 104834-51-7; **28**, 104834-52-8; **29**, 89909-50-2; **30**, 104834-55-1; **31**, 104834-56-2; **32**, 104834-57-3; **33**, 32725-82-9; **34**, 104834-59-5; **36**, 30089-44-2; **37**, 31896-88-5; **38**, 88055-46-3; **39**, 104848-66-0; **39** (Cu(II) complex), 104834-73-3; **40**, 87434-71-7; **41**, 104834-66-4; **41** (Cu(II) complex), 104834-74-4; **42**, 92735-21-2; **43**, 104834-45-9; **44**, 18818-25-2; **45**, 104834-67-5; **45** (Cu(II) complex), 104848-67-1; **46**, 104834-68-6; **46** (Cu(II) complex), 104834-75-5; benzyl acetoacetate, 5396-89-4; acetoacetaldehyde dimethyl acetal, 5436-21-5; dimethyl 1,3-acetonedicarboxylate, 1830-54-2; dimethyl 1,3-acetonedicarboxylate (oxime), 73870-13-0; *tert*-butyl acetoacetate, 1694-31-1; benzyl 3-(2-chloroethyl)-5-iodo-4-methylpyrrole-2-carboxylate, 104834-44-8; 2-[(benzyloxy)carbonyl]-3-(2-chloroethyl)-4-methylpyrrole-5-carboxylic acid, 104834-46-0; *tert*-butyl 2-[(benzyloxy)carbonyl]-3-(2-chloroethyl)-4-methylpyrrole-5-carboxylate, 89909-57-9; benzyl 4-(2-hydroxyethyl)-3,5-[3-^{13}C]dimethylpyrrole-2-carboxylate, 104834-48-2; benzyl 3-(2-chloroethyl)-4,5-[4-^{13}C]dimethylpyrrole-2-carboxylate, 104834-53-9; methyl hydrogen malonate, 16695-14-0.

Photochemistry of Polyfunctional Molecules. Intramolecular Aryl to Ketone Singlet Energy Transfer in the *trans*- and *cis*-Decalins, 7-Keto-13β-methyl-5,6,7,8,9,10,13β,14α-octahydrophenanthrene, and Its 14β Isomer[1a]

Harry Morrison,* Michael Pallmer,[1b] Robert Loeschen,[1c] Bipin Pandey, Kayambu Muthuramu, and Brad Maxwell

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received June 23, 1986

The photochemistry and photophysics of the title compounds are reported. The trans fused aryldecalone (TAK), upon excitation with 254-nm light in methanol, undergoes typical ketone photochemistry to give products of reduction (1) and α cleavage (2–4) with $\phi_{loss} = 0.27$. The cis fused aryldecalone (CAK) also gives ketone photochemistry upon 254-nm excitation; $\phi_{loss} = 0.17$. Both isomers show greatly reduced aryl fluorescence and appreciable ketone emission upon excitation of the aryl functionality, and it is proposed that their photochemistry derives from intramolecular (exchange) singlet energy transfer from the aryl to the keto chromophore. Rate constants for this energy transfer in CAK and TAK, in isopropyl alcohol, are estimated at $\geq 5 \times 10^9$ and 2.7×10^9 s^{-1}, respectively, in good agreement with literature estimates for such rates in other aryl ketones.

The photochemistry and photophysics associated with polyfunctional organic molecules has evolved into an area of broad interest to synthetic and physical organic chemists concerned with the consequences of intramolecular interactions in the excited states of complex substrates.[2] Despite the extensive activity in this field, nonconjugated aryl ketones have been relatively neglected when one considers that (1) the coexistence of these moieties is quite common, as for example among the steroids, (2) this functional group pair has the potential for several significant interactions including exothermic singlet and triplet aryl to ketone energy transfer, as well as exciplex quenching of the ketone excited state by the aryl group,[3,4] and (3) intramolecular energy transfer could by synthetically useful if one could selectively sensitize (i.e., "activate") a particular keto group in an aryl polyketone (by capitalizing on a ketone's propitious location relative to the sensitizing chromophore). It was within the latter context that we decided to study the 254-nm initiated photochemistry of two prototypical aryl ketones, the trans and cis fused decalins, 7-keto-13β-methyl-5,6,7,8,9,10,13β,14α-octahydrophenanthrene (TAK) and its 14β isomer CAK.

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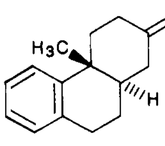
(1) (a) Organic Photochemistry. 68. Part 67: Morrison, H.; Muthuramu, K.; Severance, D. *J. Org. Chem.*, in press. (b) Abstracted, in part, from the Doctoral Dissertation of M.P., Purdue University, 1978. (c) While on leave from California State College, Long Beach, CA.

(2) Reviews and leading references for some functional group pairs include: (a) Aryl olefins. Morrison, H. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1979; Vol. 4. (b) Keto olefins. Schuster, D. I. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic: New York, 1980; Vol. 3. (c) Aryl chlorides. Cristol, S. J.; Bindel, T. H. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1984; Vol. 6.

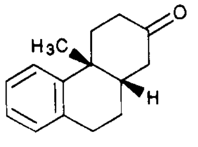
(3) For previous spectroscopic studies of aryl to ketone intramolecular singlet energy transfer, see: (a) Weinreb, A.; Werner, A. *Photochem. Photobiol.* **1974**, *20*, 313 (a study of estrogens). (b) Zimmerman, H. E.; Goldman, T. D.; Hirzel, T. K.; Schmidt, S. P. *J. Org. Chem.* **1980**, *45*, 3933 (naphthyl to ketone energy transfer to bicyclo[2.2.2]octane derivatives (rods). (c) Hassoon, S.; Lustig, H.; Rubin, M. B.; Speiser, S. *J. Phys. Chem.* **1984**, *88*, 6367 (phenyl to α-diketone energy transfer).

(4) For studies of intramolecular quenching of the *ketone* singlet and triplet states by an aromatic ring, see: (a) Carlson, G. L. B.; Quina, F. H.; Zarnegar, B. M.; Whitten, D. B. *J. Am. Chem. Soc.* **1975**, *97*, 347 and references therein. (b) Sauers, R. R.; De Paolis, A. M. *J. Org. Chem.* **1973**, *38*, 639. (c) Moon, J.; Roussi, G. *Ibid.* **1978**, *43*, 4215. (d) Schaffner, K.; Amrein, W.; Larsson, I.-M. *Isr. J. Chem.* **1975**, *14*, 48. (e) Netto-Ferreira, J. C.; Leigh, W. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 2617. Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W.; Platz, M. S.; Barcus, R. L. *J. Photochem.* **1983**, *21*, 137.

0022-3263/86/1951-4676$01.50/0



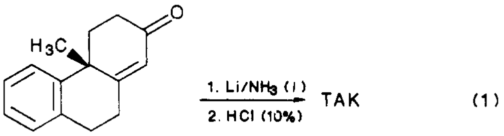
TAK



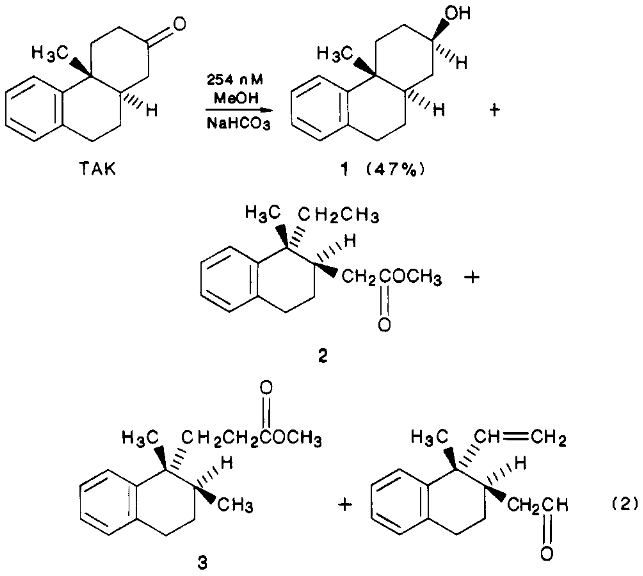
CAK

Results

A. Photochemistry of TAK. Synthesis. TAK[5] was readily prepared by a Li/NH_3 reduction of the conjugated ketone as previously described (cf. eq 1).[6,7] About 10% of the saturated ketone is CAK, and the pure trans isomer is obtained by recrystallization from methanol.



Photochemistry of TAK in Methanol at 254 nm. Irradiation of TAK (3.3×10^{-2} M) with 254-nm light in argon-degassed, sodium bicarbonate saturated[8] methanol resulted in the isolation of four primary photoproducts (eq 2). The major product is the alcohol 1;[7,10] in a preparative experiment (94% loss of TAK), 1 was isolated in 47% yield. This diastereomer is also formed by the reduction of TAK with $LiBH_4$ whereas reduction with $NaBH_4$ provided 1 plus a lesser amount of the α (axial) alcohol 5. As one would anticipate,[11] the axial methine proton (C*H*OH) in 1 (δ 3.65) is upfield of the equatorial proton in 5 (δ 4.11). Though none of 5 is observed upon photolysis of TAK in methanol, it is formed on photolysis in cyclohexane (see below).



TAK 1 (47%) 2 3 4

The esters 2 and 3 are formed in a 7:3 ratio. The assignment of structures rests upon the spectral data (see the Experimental Section). For 2, the most characteristic features are a methyl triplet at δ 0.65 and a base peak at m/e 143 corresponding to a $C_{11}H_{11}$ ion formed by a McLafferty rearrangement followed by loss of $C_2H_5\cdot$. Compound 3 shows a doublet at δ 0.95 and a base peak at m/e 159 due to benzylic cleavage of $\cdot CH_2CH_2CO_2CH_3$. The aldehyde 4 was isolated in small amounts; mass spectrometry indicates it is isomeric with TAK, and NMR shows an aldehyde resonance at δ 9.78 with vinyl signals at δ 5.03–5.44 and 5.82 in the expected AMX pattern. Both NMR and GC/mass spectral analysis of the reaction mixture indicate the presence of a second aldehyde 6, presumably that which would be formed via the same α cleavage that leads to 2. The oxetane corresponding to the secondary photolysis of 6 has also been observed in some cases.

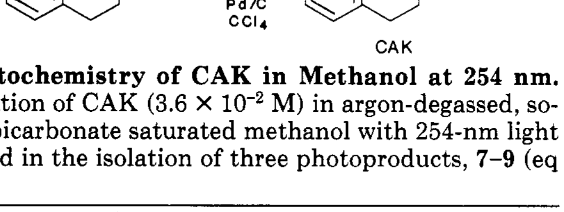
Quantum Efficiencies for TAK/Methanol Photolysis at 254 nm. The quantum efficiency for loss of TAK (1.0×10^{-2} M) was found to be 0.27 at a 20% loss of the starting material. For product formation, conversions were limited to ~13%, with $\phi_1 = 0.11$ and $\phi_{2,3,4,6} = 0.13$.

Photochemistry of TAK in Other Solvents at 254 nm. Photolysis of TAK (7.42×10^{-3} M) in degassed cyclohexane gave three isolable products: cyclohexylcyclohexane and the two alcohols 1 and 5. Photolysis in isopropyl alcohol (1×10^{-2} M TAK) also gave 1 and 5 but no other isolable products. A comparative photolysis of TAK in methanol and isopropyl alcohol indicated a 60% increase in the formation of alcohol 1 + 5 in isopropyl alcohol.

Effect of Cyclohexanone on TAK Photochemistry. Solutions of TAK (1.0×10^{-2} M) in isopropyl alcohol were photolyzed with 254-nm light with and without added 1.0×10^{-2} M cyclohexanone. The disappearance of TAK was slightly *increased* (2–7%) by the added ketone, and extensive (71%) loss of cyclohexanone was observed. In a second experiment, 300-nm light was used, with a large excess of cyclohexanone relative to TAK (1.0×10^{-1} vs. 1.0×10^{-2} M, respectively), so that >90% of the incident light was absorbed by the added ketone. A second tube containing only 1.0×10^{-2} M TAK was irradiated simultaneously (at this concentration, the TAK solution absorbed ca. 48% of the incident light). The tube containing cyclohexanone showed a loss of TAK some 10% *greater* than that observed for pure TAK.

Effect of *cis*-Piperylene on TAK Photochemistry. A solution of TAK in methanol containing 0.1 M diene was photolyzed with 254-nm light; complete quenching of the loss of TAK was noted.

B. Photochemistry of 7-Keto-13β-methyl-5,6,7,8,9,10,13β,14β-octahydrophenanthrene (CAK). Synthesis. The title compound[12] was prepared by catalytic hydrogenation of the conjugated ketone using Pd/C in carbon tetrachloride (eq 3); a 9:1 ratio of CAK to TAK is thus obtained. Pure CAK was obtained by preparative VPC.



CAK

Photochemistry of CAK in Methanol at 254 nm. Irradiation of CAK (3.6×10^{-2} M) in argon-degassed, sodium bicarbonate saturated methanol with 254-nm light resulted in the isolation of three photoproducts, 7–9 (eq

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(5) Barton, D. H. R.; Robinson, C. H. *J. Chem. Soc.* **1954**, 3045.

(6) Pallmer, M.; Morrison, H. *J. Org. Chem.* **1980**, *45*, 798.

(7) See also, Campbell, A. L.; Leader, H. N.; Spencer, C. L.; McChesney, J. D. *J. Org. Chem.* **1979**, *44*, 2746.

(8) Photolysis in pure methanol is known[9] to generate traces of acid that, with these ketones, catalyzes the formation of enol ethers.

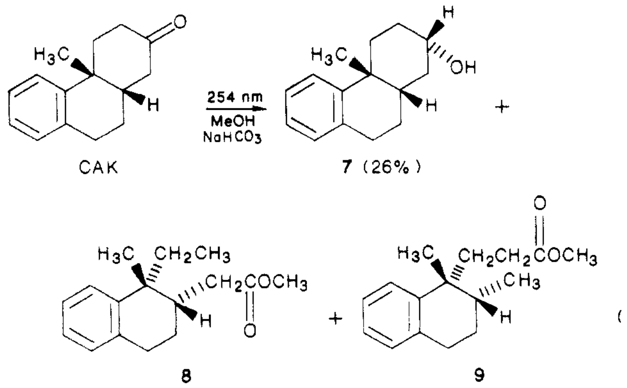
(9) Cristol, S. J.; Lee, G. A.; Noreen, A. L. *Tetrahedron Lett.* **1971**, 4175. Roussi, G.; Beugelmans, R. *Ibid.* **1972**, 1333.

(10) Howell, F.; Taylor, D. A. H. *J. Chem. Soc.* **1958**, 1248.

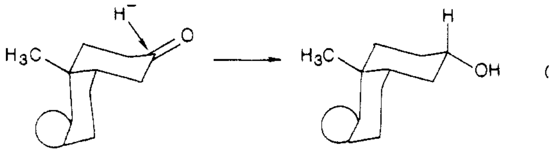
(11) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: Braunschweig, 1969; p 238.

(12) Wenkert, E.; Stevens, T. E. *J. Am. Chem. Soc.* **1956**, *78*, 2318.

4). The major products are the esters; in a preparative experiment, they and the alcohol were isolated in 30% and 26% yields, respectively. The alcohol 7[10] is identical with the reduction product formed by $NaBH_4$ reduction of CAK. Its assignment as the α isomer is based on the methine (C*H*OH) signal at δ 3.45–4.00, suggestive of an axial hydrogen (i.e., equatorial OH) (see the discussion of compound 1 above). We expect both the ketone and the alcohol to preferentially exist as the conformers having the β angular methyl group equatorial to ring C, in which case the alcohol 7 is the expected product of axial attack by hydride (eq 5).[13]



(4)



7

(5)

The esters 8 and 9 are formed in a ratio of 2:1 and could not be separated chromatographically. The assignments of structure are based on the NMR spectrum of the mixture, with the methyl triplet for 8 at δ 0.7 and the methyl doublet for 9 at δ 0.9 (see the Experimental Section).

Quantum Efficiencies for CAK/Methanol Photolysis at 254 nm. The quantum efficiency for loss of CAK (7.0×10^{-3} M) was found to be 0.17 at a 20% loss of the starting material. For product formation, conversions were 10–15% with $\phi_7 = 0.048$ and $\phi_{8+9} = 0.13$.

Effect of Cyclohexanone on CAK Photochemistry. Photolysis of CAK in isopropyl alcohol with 254-nm light gives the reduction product 7 as the only observable product. Addition of cyclohexanone (1×10^{-2} M) had no effect on the 254-nm induced loss of CAK, nor was there any evidence of cyclohexanone disappearance or cyclohexanol formation. When a large excess (0.1 M) of cyclohexanone was used with CAK (0.01 M) so that most (~90%) of the 300-nm light from a Rayonet reactor was absorbed by the cyclohexanone, an 8% loss of CAK was observed under conditions where the TAK loss was 14%.

Effect of CAK and TAK on Cyclohexanone Photochemistry. Three Pyrex tubes containing 0.1 M cyclohexanone, 0.1 M cyclohexanone + 0.01 M TAK, and 0.1 M cyclohexanone + 0.01 M CAK (all in isopropyl alcohol) were irradiated simultaneously with 300-nm light. The percentages of cyclohexanone loss were 32, 9, and 7%, respectively.

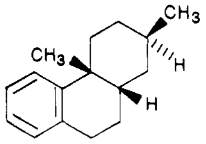
Effect of *cis*-Piperylene on CAK Photochemistry. Solutions of CAK in methanol were photolyzed with 254-nm light with and without 6×10^{-3} M diene; 53% quenching of CAK disappearance was observed. (At this concentration of diene, TAK loss is quenched by 25%.)

C. Spectroscopic Studies of CAK and TAK. Absorption Spectra. The absorption spectra for both isomers are as one would expect for essentially independent chromophores, with the aryl B_{2u} transition in cyclohexane, isopropyl alcohol, and methanol appearing as fine structure at ~266 and ~274 nm (ϵ ~395 and 400 M^{-1} cm^{-1}). The $n \rightarrow \pi^*$ transition appears as a broad, ill-defined shoulder in all three solvents with the short-wavelength onset at ca. 280 nm (ϵ ~26 M^{-1} cm^{-1}).

Fluorescence Spectra. CAK shows only broad carbonyl emission (λ_{max} ~395 nm) when excited at 254 nm (Hg lamp) or 300 nm (xenon arc/monochromator) in isopropyl alcohol. The quantum efficiency with 254-nm excitation, using toluene in hexane as the reference ($\phi_f = 0.12$),[14] is 2.8×10^{-3} (all ϕ_f values are for ca. 1×10^{-4} M substrate). Direct excitation with the 300-nm source was by reference to acetone in cyclohexane ($\phi_f = 9.3 \times 10^{-4}$)[15] and gave $\phi_f = 7.0 \times 10^{-3}$.[16] TAK shows dual fluorescence in isopropyl alcohol (λ_{max} ~290 and ~395 nm) when excited at 254 nm; the ϕ_f for aryl emission is 2.4×10^{-3} while ϕ_f for carbonyl emission is 1.3×10^{-3}. Direct excitation at 300 nm yielded a carbonyl $\phi_f = 1.1 \times 10^{-2}$. There was no concentration dependence noted for TAK emission from 5×10^{-4} to 5×10^{-3} M with the 254-nm source.

Both CAK and TAK show dual emission in methanol with 254-nm excitation. For CAK, $\phi_f^{aryl} = 9.8 \times 10^{-3}$ and $\phi_f^{keto} = 2.7 \times 10^{-3}$; for TAK, $\phi_f^{aryl} = 9.8 \times 10^{-3}$, but the carbonyl emission intensity was too low to measure accurately.

ϕ_f values of model compounds include 1.6×10^{-3} for cyclohexanone in isopropyl alcohol (300-nm excitation), 0.12 for the trans fused alcohol 1 in isopropyl alcohol, and 0.14 for a cis fused aryldecalin [7β,4bβ-dimethyl-4bβ,5,6,7,8,8aβ,9,10-octahydrophenanthrene (10)] in hexane (both with 254-nm excitation). The singlet lifetime for 1 is 17 ns.



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Discussion

A. Photoreactions of CAK and TAK. Qualitative Features. Though the 254-nm photons are initially absorbed by the aryl chromophores, the photochemistry of CAK and TAK (eq 2 and 4) centers about the carbonyl functionality. In methanol, both isomers give products resulting from hydrogen abstraction as well as from α cleavage (the Norrish type I reaction), with reduction to alcohol playing a more significant role for TAK than CAK (isolated yields, 48% vs. 28%; $\phi_{alcohol}$, 0.11 vs. 0.048; for TAK and CAK, respectively). As mentioned in the introduction, we are interested in the synthetic potential of selective photosensitization, and our preliminary observation of a 60% increase in TAK photoreduction in isopropyl alcohol suggests that high yields of alcohols should

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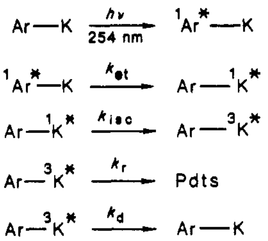
[13] The formation of 7 by reduction of CAK with sodium bis(2-methoxyethoxy)aluminum hydride has been reported. Cf. ref 7. These workers report the chemical shifts for the C*H*OH protons in 1 and 7 to both be δ 3.5.

[14] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

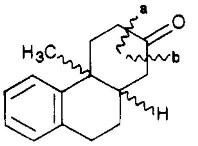
[15] Halpern, A. M.; Ware, W. R. *J. Chem. Phys.* **1971**, *54*, 1271.

[16] We discount the significance of the difference in these two CAK ϕ_f values; the instrument is not corrected for photomultiplier response, and the difference in standards used for the two measurements could cause the difference observed.

Scheme I. Mechanism for 254-nm-Induced Photolysis of CAK in *i*-PrOH



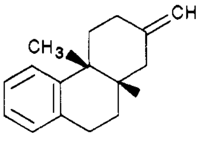
be attainable with more efficient photoreducing agents.[17] The preference in methanol for reduction to the equatorial alcohol (1, 7) is well precedented for trans-[18] and *cis*-[19a] decalin ring fusions. With respect to α cleavage,[20a] our observed ca. 2-fold greater cleavage at bond "a" vs. bond "b" (compare **2** vs. **3** in eq 2; **8** vs. **9** in eq 4) is consistent with the factor of 1.7 reported for *trans*-bicyclo[4.4.0]decan-3-one, though the ratio for *cis*-bicyclo[4.4.0]decan-3-one drops to 0.9.[21] Overall, TAK is somewhat more reactive than CAK (ϕ_{dis} = 0.27 vs. 0.17, respectively).



The photoreduction of cycloalkanones is generally triplet derived[18,19,22] as is usually,[20] but not always,[23] the case for α cleavage. Since our primary interest was in the aryl sensitization step (see below), we did not pursue the nature of the ketone reactive state in detail, but the piperylene quenching data indicate that the reactions of TAK and CAK are primarily derived from the ketone triplet state.

B. Aryl Sensitization Step. As noted in the introduction, the phenyl group is capable of both singlet[24-26] and triplet[27] exothermic radiationless energy transfer to a keto group.[28] The 50-fold diminution in aryl fluorescence for TAK and >100-fold diminution for CAK in isopropyl alcohol relative to the tricyclic alcohol 1 leaves little doubt that for these substrates singlet sensitization is the principle process.[29] This should be the case in methanol as well, though aryl emission in this solvent increases to 10% of the model.[30] The detailed mechanism for *inter*molecular aryl/ketone singlet energy transfer has been extensively explored and it appears that a short-range exchange mechanism[31] dominates, with a small contribution from the long-range dipole–dipole process.[24,25,32] As a consequence, rates of energy transfer have been shown to be subject to steric retardation[25,32] and to be diffusion controlled.[24] Apparently, the exchange mechanism is also operative in those cases where *intra*molecular aryl/ketone singlet energy transfer has been observed,[3,33] and it has been suggested that this might be generally so when the two groups are separated by less than 10 Å.[33]

In fact, the highly efficient singlet energy transfer in CAK is entirely intramolecular. This is evidenced by the lack of quenching of CAK photochemistry by cyclohexanone and the inability of CAK to sensitize a cyclohexanone photoreaction. Thus, Scheme I outlines the mechanism for CAK photolysis in isopropyl alcohol upon 254-nm excitation. This scheme treats the aryl (Ar) and ketone (K) chromophores as separate entities, a reasonable supposition in light of the relatively unperturbed aryl absorption spectrum and the normal aryl emission wavelength seen for the aryl fluorescence from CAK/methanol solutions. In other words, interaction is viewed as a "postexcitation" phenomenon.[2a] Using the ϕ_f (0.14) and $^1\tau$ (24 ns) measured[6] for the model *cis*-decalin (**10**), assuming the aryl k_f's for CAK and **10** are comparable (a reasonable assumption given the similarity in absorption spectra), and placing an upper limit of $\phi_f \leq 1 \times 10^{-3}$ for CAK, one calculates a *$^1\tau$ for $^1Ar^*$-K of CAK <0.2 ns.* Since $\phi_{et} \simeq 1.0$, $^1\tau = {}^1/k_{et}$ so that in *isopropyl alcohol $k_{et} \geq 5 \times 10^9$ s^{-1}*.[34] This rate constant is well in excess of the rate for conformational reorientation (ca. 5×10^6 s^{-1})[6] of the *cis*-decalin from an extended half-chair/chair to a half-chair/boat. The latter conformation is needed to bring the two functional groups into close proximity as, for example, is required for formation of an intramolecular singlet aryl/olefin exciplex in the olefin analogue **11**.[6,35]



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Thus, *intramolecular singlet energy transfer is efficient and rapid at the 3.5 Å distance that separates the aryl and ketone chromophores in the low-energy conformer of CAK.* Our calculated k_{et} for the *phenyl* to *ketone* single energy transfer may be compared to the value of 2.4×10^9 s^{-1} estimated for estrone (by a Forster-type mechanism)[3a] and 1.3×10^9 to 3.0×10^9 s^{-1} measured by Zimmerman et al.[3b] for naphthyl to ketone energy transfer in 1,4-disubstituted bicyclo[2.2.2]octanes. In the first case, the interchromophore distance is ca. 4.6 Å while, in the latter

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[17] Some of the increase in alcohol formation in isopropyl alcohol may also be due to more efficient energy transfer in this solvent.

[18] Micheau, J. C.; Paillous, N.; Lattes, A. *Tetrahedron* **1973**, *31*, 441.

[19] (a) Keller, P.; Eggert, G.; Wehrli, H.; Schaffner, K.; Jeger, O. *Helv. Chim. Acta* **1967**, *50*, 2259. (b) Simonaitis, R.; Cowell, G. W.; Pitts, J. N., Jr. *Tetrahedron Lett.* **1967**, 3751.

[20] (a) For a review, see: Weiss, D. S. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1981; Vol. 5. (b) Wagner, P. J.; Spoerke, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4437. (c) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *Ibid.* **1971**, *93*, 7213.

[21] Coyle, J. D. *J. Chem. Soc. B* **1971**, 1736.

[22] For a review, see: Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.

[23] For example, see: Yang, N. C.; Chen, R. H.-K. *J. Am. Chem. Soc.* **1971**, *93*, 530.

[24] Augustyniak, W.; Wiechowicz, E.; Wojtczak, J. *J. Photochem.* **1976/1977**, *6*, 229.

[25] Loper, G. L.; Lee, E. K. C. *J. Chem. Phys.* **1975**, *63*, 264 and references therein.

[26] For a recent example, see: Cristol, S. J.; Kaufman, R. L.; Opitz, S. M.; Szalecki, W.; Bindel, T. H. *J. Am. Chem. Soc.* **1983**, *105*, 3226.

[27] For example, see: Wettack, F. S.; Noyes, W. A., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 3901.

[28] There is also the potential for a radiative trivial energy transfer involving ketone absorption of the aryl fluorescence emission (note the spectral regions for absorption and emission in the Results). Contribution from this pathway should be minimal considering the extinction coefficient of the ketone chromophore.

[29] For related spectroscopic observations in the tetracyclic estrone series, see ref 3a.

[30] We attribute the increased aryl emission of both CAK and TAK in methanol to the expected blue shift of n $\rightarrow$ π^* transition in the more polar solvent. This would move the transition to the high-frequency side of the aryl fluorescence, thus somewhat diminishing the spectral overlap integral and the efficiency of energy transfer.

[31] Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

[32] Janda, K.; Wettack, F. S. *J. Am. Chem. Soc.* **1972**, *94*, 305.

[33] It has been suggested that through-bond interactions may contribute to the "energy transfer" reported in ref 3b, though there is no spectral evidence for mixing of the chromophores. Cf.: Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5575. Pasman, P.; Rob, F.; Verhoeven, J. W. *Ibid.* **1982**, *104*, 5127.

[34] A similar analysis of CAK emission in methanol indicates k_{et} in this solvent is 5.5×10^8 s^{-1}.

[35] Similar close contact appears to be required for *phenyl* quenching of *ketone* excited states. Cf. ref 4. See also: Wilson, T.; Frye, S. L.; Halpern, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 3600.

series, the rates are lowered by an increased interchromophore distance (ca. 7.5 Å) and less favorable emission/absorption spectral overlap.

The chemical and spectroscopic evidence indicates that TAK also undergoes efficient intramolecular singlet energy transfer in isopropyl alcohol, albeit at a slightly reduced rate relative to CAK. Thus, aryl emission is very low ($\phi_f = 2.4 \times 10^{-3}$), though by contrast with CAK it is now measurable. (A comparison with a nonketonic model, **1** ($\phi_f = 0.12$), indicates energy transfer to be 98% efficient.) Since aryl emission is now observable, one can look for a concentration effect on the aryl/ketone fluorescence ratio as an indicator of *inter*molecular energy transfer, and no such effect is seen (nor is one seen for the dual fluorescence from the more distal aryl/ketone chromophores in the tetracyclic estrone).[36] Also, as with CAK, there is no quenching of TAK 254-nm initiated photochemistry by cyclohexanone.[37] A calculation of ${}^1\tau$ for ${}^1\mathrm{Ar}^*\text{–K}$ in TAK in isopropyl alcohol, using the ϕ_f and ${}^1\tau$ of **1** (0.12 and 17 ns) as a model and again assuming comparable values of k_f for the two compounds, yields ${}^1\tau = 0.35$ ns. Assuming the other radiationless decay rate constants for TAK approximate those for **1**, *one calculates* $k_{et} = 2.7 \times 10^9\ s^{-1}$. (The interchromophore distance in this substrate is ca. 4.6 Å.)

Conclusions

Excitation of the aryl chromophore in both CAK and TAK leads to rapid, efficient, primarily intramolecular singlet energy transfer to the ketone functionality. This appears to be a practical mechanism for indirectly eliciting carbonyl photochemistry, and efforts directed toward the development of this technique for achieving selectivity in multifunctional molecules are now in progress.

Experimental Section

NMR spectra were obtained with a Perkin-Elmer R-32 (90-MHz) or a Nicolet NT-470 (470-MHz) spectrometer. Chemical shifts are reported (ppm) relative to Me_4Si. Mass spectra were obtained with a Finnigan automated gas chromatograph EI/CI mass spectrometer. Ultraviolet spectra were recorded with a Cary Model 17D spectrophotometer. Vapor-phase chromatography utilized Varian Models 90-P, A-90-P, and A-700 chromatographs for qualitative or preparative work and Varian Models 1200 or 1400 fid chromatographs with a Hewlett-Packard 3300 or 3380-A digital integrator for quantitative studies. Flow rates for preparative and fid VPC were 60 mL and 30 mL/min, respectively. VPC columns were as follows (all on AW-DMCS treated Chromosorb W): A, 20 ft × 0.25 in., 5% OV-210, 40/60 mesh; B, 20 ft × 0.25 in., 20% Carbowax 20 M, 40/60 mesh; C, 20 ft × 0.125 in., 5% SE-30, 100/120 mesh; D, 20 ft × 0.125 in., 3% OV-210, 100/120 mesh; E, 15 ft × 0.125 in., 10% XF-1150, 100/120 mesh; F, 10 ft × 0.125 in., 20% Carbowax 20 M, 100/120 mesh; G, 10 ft × 0.125 in., 5% XF-1150, 100/120 mesh; H, 20 ft × 0.25 in., 20% XF-1150, 40/60 mesh. The internal standard used to monitor the loss of TAK and CAK and to quantify the formation of **1–5** and **7–9** was 7-keto-13-methyl-5,6,7,9,10,13-hexahydrophenanthrene (response factor (RF) = weight x/weight s × area s/area x = 0.40 and 0.30 for TAK and **1**, respectively). The response factor for TAK was assumed for CAK, and that for **1** was assumed for **2–5** and **7–9**.

Photochemical studies mainly employed rotating turntables with Vycor, quartz or Pyrex tubes, and a Canrad-Hanovia Model 68814-15 low-pressure mercury arc lamp or a Rayonet photochemical reactor (New England Ultraviolet Corp.). Deoxygenation was performed by bubbling argon through the solution for at least 15 min. Actinometry was done with *trans*-1-phenyl-2-butene using matched tubes.[39] Fluorescence quantum efficiencies were measured by reference to toluene or acetone and were corrected for substrate absorbance but not photomultiplier response. High-concentration studies utilized a triangular cell.[40] Singlet lifetime measurements utilized an Optitron Model NF-100 nanosecond decay fluorimeter; the details have been previously described.[41] All emission spectral measurements were made at room temperature. *trans*-1-Phenyl-2-butene and cyclohexanone were purified on column B before use. Hydrocarbon solvents were Burdick and Jackson distilled in glass spectroquality; methanol was Fischer spectroscopic grade; isopropyl alcohol was Baker analytical reagent.

7-Keto-13β-methyl-5,6,7,8,9,10,13β,14α-octahydrophenanthrene (TAK). The preparation of this known[5] compound has been previously described:[6,7] IR (CCl_4) 3.35, 5.83, 6.72, 6.89 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.00–7.40 (m, aryl, 4 H), 1.50–3.10 (m, 11 H), 1.28 (s, CH_3, 3 H); mass spectrum (70 eV) *m/e* 214 ($M^{\bullet+}$), 199 (base ion).

7-Keto-13β-methyl-5,6,7,8,9,10,13β,14β-octahydrophenanthrene (CAK). The preparation of this known[12] compound has been previously described.[6] Our most recent procedure utilized carbon tetrachloride (in place of methanol) as the solvent for catalytic reduction of the precursor unsaturated ketone. Conversion was limited to 75% to prevent the formation of difficulty resolved byproducts (analysis on column C at 190 °C; CAK retention time 5.78 min at 40 mL/min flow). The Pd/C was removed by filtration through a Celite cake and the solvent removed by rotary evaporation. Pure CAK was isolated by preparative VPC on column A at 220 °C: IR (neat) 3.35, 5.81, 6.72, 6.84, 6.93, 7.05, 13.16, 13.75 μm; ^1H NMR ($CDCl_3$, 470 MHz) β 7.10–7.36 (m, aryl, 4 H), 1.62–2.93 (m, 11 H), 1.39 (s, CH_3, 3 H); mass spectrum (70 eV) *m/e* 214 ($M^{\bullet+}$), 129 (base ion).

Photolysis of TAK in Methanol. Typically, a solution of 884 nm (1.81×10^{-2} M) of TAK in 350 mL of methyl alcohol containing ca. 3 g of $NaHCO_3$ was photolyzed with 254-nm light in an immersion well for 1.25 h with continuous argon degassing. The solvent was evaporated in vacuo at 40–50 °C and the residue chromatographed on 100 g of acid-washed alumina. The course of the chromatography was monitored: column G, 169 °C, flow 70 mL/min, (TAK) RT ≃ 28 min.

Methyl 2-(1α-Ethyl-1β-methyl-1,2,3,4-tetrahydronaphthalen-2β-yl)ethanoate (2). This compound (40 mg, 5.0%) eluted between 130 and 230 mL of benzene: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.95–7.38 (m, aryl, 4 H), 3.69 (s, OCH_3, 3 H), 2.80 (m, benzylic H, 2 H), 1.45–2.65 (m, 7 H), 1.11 (s, CH_3, 3 H), 0.65 (t, CH_3CH_2, 3 H); mass spectrum (70 eV) *m/e* 246 ($M^{\bullet+}$) 143 (base peak); sample purified by preparative VPC on column A; mol wt for $C_{16}H_{22}O_2$ calcd 246.16198, found 246.16237.

Methyl 3-(1β,2β-Dimethyl-1,2,3,4-tetrahydronaphthalen-1α-yl)propanoate (3). This compound could only be obtained as a 3:7 mixture (96 mg) with compound **2**, eluting between 230 and 650 mL of benzene. ^1H NMR ($CDCl_3$, 90 MHz), in addition to the peaks from compound **2**, shows the CH_3O group for **3** at δ 3.58 and a doublet at δ 0.95 (J = 6 Hz). The ratio of the two methoxy signals at δ 3.58 and 3.69 is 3:7. A VPC mass spectral analysis of this mixture resolved the minor ester peak and showed, at 70 eV, *m/e* 246 ($M^{\bullet+}$) and 159 (base peak).

2-(1β-Methyl-1α-vinyl-1,2,3,4-tetrahydronaphth-2β-yl)acetaldehyde (4). This compound (27 mg) eluted with 360 mL of a 90:10 mixture of benzene/diethyl ether: IR (neat) 3.30, 3.60, 6.72, 6.92, 10.92, 13.12, 13.75 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 9.78 (s, $CH{=}O$, 1 H), 7.00–7.45 (m, aryl, 4 H) 5.82 (q, vinyl, 1 H), 5.03–5.44 (m, vinyl, 2 H), 0.6–2.70 (m, including CH_3 at δ 1.08,

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[36] Weinreb, A.; Werner, A. *Chem. Phys. Lett.* **1969**, *3*, 231.

[37] In fact, there is a slightly *increased* loss of TAK in the presence of cyclohexanone, and cyclohexanone photochemistry is observed. This suggests (1) that a small amount of excitation leakage to the cyclohexanone by intermolecular singlet transfer can occur (presumably the consequence of a reduced rate of *internal* energy transfer [see below]) and (2) that the cyclohexanone triplet can sensitize TAK (our studies of TAK and CAK/cyclohexanone mixtures at 300 nm confirm this). A diffusion-controlled rate ($4.5 \times 10^9\ M^{-1}\ s^{-1}$ in isopropyl alcohol)[38] of singlet energy transfer to 0.01 M cyclohexanone would lead to a ϕ_{et} to cyclohexanone of ca. 2% (using a competitive intramolecular k_{et} of $2.7 \times 10^9\ s^{-1}$, see below). Further studies of TAK with cyclohexanone using flash techniques are planned.

[38] Murov, S. L. *Handbook of Photochemistry*; Dekker: New York, 1973; p 55.

[39] Morrison, H.; Peiffer, R. *J. Am. Chem. Soc.* **1968**, *90*, 3428.

[40] Leismann, H.; Mattay, J. *Tetrahedron Lett.* **1978**, 4265.

[41] Morrison, H.; Pandey, G. *Chem. Phys. Lett.* **1983**, *96*, 26.

10 H); VPC mass spectrum (70 eV) *m/e* 214 ($M^{\bullet+}$), 157 (base peak).

7β-Hydroxy-13β-methyl-5,6,7,8,9,10,13β,14α-octahydrophenanthrene (1). Following further elution with 200 mL of the 90:10 mixture of benzene/diethyl ether (in which fraction eluted 57 mg of TAK), this compound (573 mg) was eluted with 600 mL of diethyl ether. This is a known compound[7,10] and was independently synthesized by $NaBH_4$ or $LiBH_4$ reduction of TAK: IR (neat) 3.00, 3.41, 6.75, 6.86, 6.95, 7.31, 7.52, 9.16, 9.47, 9.67, 13.20, 13.87 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.94–7.39 (m, aryl, 4 H), 3.65 (m, C*H*OH, 1 H), 2.81–3.05 (m, benzylic, 2 H), 1.45–2.40 (m, 10 H), 1.08 (s, CH_3, 3 H), 7α-hydroxy isomer has a characteristic C*H*OH signal at δ 4.1.

Photolysis of CAK in Methanol. Typically, a solution of 561 mg (2.62×10^{-2} M) of CAK in 100 mL of methyl alcohol containing ca. 1.0 g of $NaHCO_3$ was photolyzed with 254-nm light in an immersion well for 3 h with continuous argon degassing. The solvent was evaporated in vacuo at 40–50 °C and the residue chromatographed on 100 g of acid-washed alumina as described above for the TAK photolysis. Three major products were isolated:

Methyl 2-(1α-Ethyl-1β-methyl-1,2,3,4-tetrahydronaphthalen-2α-yl)ethanoate (8) and Methyl 3-(1β,2α-Dimethyl-1,2,3,4-tetrahydronaphthalen-1α-yl)propanoate (9). These esters could only be isolated as a mixture: 196 mg; IR (neat) 3.41, 5.76, 6.72, 6.95, 7.75, 7.97, 8.34, 8.65, 13.17, 13.69 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.90–7.40 (m, aryl, 4 H), 3.60 and 3.57 (both s, CH_3O, total of 3 H in a ratio of 2:1), 2.70–2.85 (m, benzylic, 2 H), 1.40–2.65 (m, 7 H), 1.15 (s, CH_3, 3 H), 0.90 (d), 0.70 (t) (total of 3 H in a ratio of 1:2). Anal. ($C_{16}H_{22}O_2$) C, H.

7α-Hydroxy-13β-methyl-5,6,7,8,9,10,13β,14β-octahydrophenanthrene (7). This compound[10] was isolated as 145 mg (26%) and proved to be identical with a sample independently synthesized by $NaBH_4$ reduction of CAK. It was readily purified by preparative VPC [column H at 180 °C, flow 60 mL/min, RT = 12 min]: IR (neat) 2.90, 3.40, 6.71, 6.90, 7.30, 13.10 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.94–7.32 (m, aryl, 4 H), 3.45–4.00 (m, C*H*OH, 1 H), 2.65–2.95 (m, benzylic, 2 H), 0.70–2.50 (m, including CH_3 at 1.10, 13 H). Anal. ($C_{15}H_{20}O$) C, H.

Quantum Efficiency Determinations. The actinometer for these experiments was *trans*-1-phenyl-2-butene, for which the quantum efficiency of formation of the cis isomer in cyclohexane is 0.20 ± 0.01.[39] Quartz tubes containing 4 mL of argon-degassed actinometer solutions, 1.0×10^{-2} M in substrate, were irradiated with the low-pressure lamp for 10 min. This produced 7.16% of *cis*-1-phenyl-2-butene, corresponding to 1.44×10^{16} photons/s (analysis by column E at 110 °C). An analogous determination at the end of the photolysis gave a value of 1.62×10^{16} photons/s, which two measurements were averaged to 1.53×10^{16} photons/s. Simultaneous photolysis of 1.0×10^{-2} M TAK in methanol and 7.0×10^{-3} M CAK in methanol, for 20 min, gave 20.6 and 19.7% loss, respectively (column D at 220 °C), corresponding to ϕ_{dis} = 0.27 and 0.17.

A more extended irradiation (40 min) gave $\phi_1 = 0.11 \pm 0.02$, $\phi_{2,3,4,6} = 0.13 \pm 0.01$, $\phi_7 = 0.048 \pm 0.002$, and $\phi_{8+9} = 0.13 \pm 0.005$.

Experiments with Cyclohexanone. These were carried out in the turntable with Vycor tubes, argon-degassed isopropyl alcohol solutions, and the low-pressure lamp. TAK was monitored on column D at 220 °C while cyclohexanone and cyclohexanol were monitored on column F at 100 °C. With equimolar (1.0×10^{-2} M) concentrations of TAK, CAK, and cyclohexanone and a 2-h photolysis, the loss of TAK, with and without added ketone, was 71 and 76%, respectively. The corresponding loss of CAK was 23 and 24%. Also a 71% loss of cyclohexanone was observed in the TAK solution (cyclohexanol formation accounted for ca. 39% of this loss); no loss of cyclohexanone nor evidence of cyclohexanol was found in the CAK solution.

In a second series of experiments, the tubes contained 1.0×10^{-2} M TAK or CAK plus cyclohexanone at 1.0×10^{-1} M. The irradiation was conducted for 2 h with the 300-nm lamps in a Rayonet reactor. The losses of TAK and CAK were 14 and 8%, respectively, while cyclohexanone losses were 32% (no TAK or CAK), 9% (with TAK), and 7% (with CAK). When a TAK (1.0×10^{-2} M) solution without cyclohexanone was irradiated (300 nm, 3 h) together with one containing 1.0×10^{-1} M cyclohexanone, the losses of TAK were 51 and 56%, respectively (we estimate only 8% of the incident light as absorbed by TAK in the second solution).

Acknowledgment. We thank the National Science Foundation (Grant CHE-8318825) for support of this research. The 470-MHz data were obtained through the Purdue University Biological Magnetic Resonance Laboratory (NIH Grant RR01077), and the VPC/mass spectral data were obtained on an instrument provided by NSF Grant CHE-8010832.

Registry No. 1, 70524-87-7; 2, 104946-72-7; 3, 104946-73-8; 4, 104946-74-9; 7, 70524-92-4; 8, 104946-75-0; 9, 104946-76-1; TAK, 1686-50-6; CAK, 70524-91-3.

Photolytic Cleavage of Remote Functional Groups in Polyfunctional Molecules. Activation of a γ C-Cl Bond in the *endo*- and *exo*-Benzobicyclo[3.2.1]octen-3-yl Chlorides[1]

Harry Morrison,* Kayambu Muthuramu, and Daniel Severance

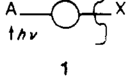
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received July 23, 1986

The aryl-induced photolytic cleavage of a distal C–Cl bond, earlier reported for a β-substituent in benzobicyclo[2.2.1] (eq 1) and -[2.2.2] (eq 2) substrates, has been extended to the γ position in the title compounds (*endo*-BBOC and *exo*-BBOC). Photolyses of these compounds in methanolic solution using 254-nm light primarily lead to products derived from carbocation intermediates (eq 4 and 5) with quantum efficiencies for loss of starting material $\phi_{dis} = 8.1 \times 10^{-2}$ and 7.6×10^{-3} (endo and exo, respectively). The greater reactivity of the endo isomer contrasts with that observed in the [2.2.1] and [2.2.2] series where large exo/endo rate ratios are the rule (Table III). This inverted reactivity pattern is attributed to the favorable aryl/chlorine relationship in the endo isomer (Figure 1), which compensates for the increased Ar–C_3 separation otherwise characteristic of these γ functionalities.

Introduction

The photolytic cleavage of a distal, relatively transparent nucleofuge upon excitation of a UV absorbing chromophore (cf. 1) has been a subject of continuing interest[2–5] as part of the more general concern with the photochemical



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