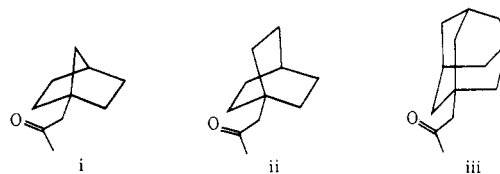


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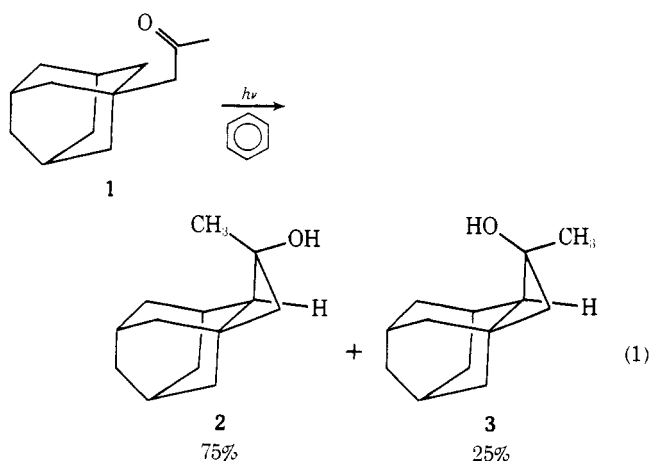
Mechanistic Photochemistry of 1-Adamantylacetone

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Contribution from the Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, the Department of Chemistry, University of Rochester, Rochester, New York 14627, and the Department of Chemistry, Columbia University, New York, New York 10027. Received December 4, 1974

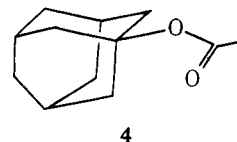
Abstract: Irradiation of 1-adamantylacetone (**1**) results in essentially a quantitative yield of two cyclobutanols, **2** and **3**. Quantum yields for the formation of **2** and **3** from the S_1 and T_1 states of **1** in benzene and methanol are reported. Formation of cyclobutanols from the excited triplet state of **1** is much more efficient in methanol than in benzene. The cyclobutanol product ratio, **2**:**3**, is 1.0–1.8 for the T_1 reaction and approximately 5 for the S_1 reaction. The observed stereoselectivity from the excited singlet state reaction is consistent with the intermediacy of a short-lived 1,4 biradical which undergoes rehybridization, resulting in a preference for rotation and closure to yield **2** rather than **3**. The reactivity of the S_1 and T_1 states of **1** toward intramolecular γ -hydrogen abstraction is determined by fluorescence measurements and Stern–Volmer treatments of 1,3-pentadiene quenching of cyclobutanol formation, respectively.

We² and others³ have recently reported that irradiation of 1-adamantylacetone (**1**) results in nearly quantitative formation of two cyclobutanols, **2** and **3** (eq 1). Neither of



the Norrish type II photoelimination products, acetone and adamantene, was observed on photolysis of **1**, although

Gano has subsequently reported trapping adamantene in low yields from irradiation of ester **4**.⁴ The absence of ada-



mantene among the photoproducts of 1-adamantylacetone^{2–4} and the structure assignments for **2** and **3**^{2,3} have been discussed in some detail elsewhere. We report here our studies of solvent and multiplicity effects on the efficiency and stereochemistry of cyclobutanol formation from **1**.⁵

Results and Discussion

The quantum yields for formation of **2** and **3** in benzene and methanol given in eq 2 were determined using benzo-

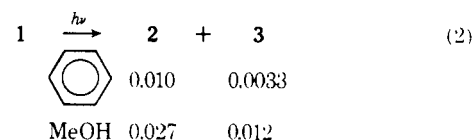


Table I. Quantum Yields for Cyclobutanol Formation

Solvent	Excited state	Φ_2	Φ_3	Φ_2/Φ_3
Benzene	Both	0.010	0.0033	3.3
Benzene	S_1	0.0083	0.0017	4.9
Benzene	T_1	0.0017	0.0016	1.0
Methanol	Both	0.027	0.012	2.3
Methanol	S_1	0.0084	0.0016	5.1
Methanol	T_1	0.0186	0.0104	1.8

phenone-benzhydrol actinometry.⁶ The ratio of 2/3 is somewhat lower in methanol (2.3) than in benzene (3.3), while the efficiency of cyclobutanol formation is about a factor of 3 greater in methanol. Similar effects have been observed by Sauers for photolysis of **1** in benzene vs. *tert*-butyl alcohol.^{3a}

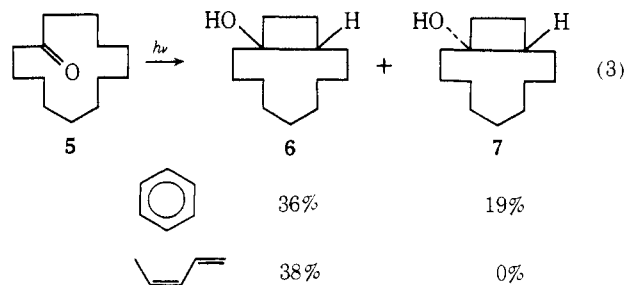
In order to establish the contributions of reaction from both $^1n,\pi^*$ (S_1) and $^3n,\pi^*$ (T_1) states to the overall efficiency for cyclobutanol formation, **1** was irradiated in benzene and methanol with sufficient 1,3-pentadiene added to quench all the T_1 reaction (*vide infra*). The nonquenchable and quenchable fractions of cyclobutanol formation were assigned to the S_1 and T_1 reactions, respectively.⁷ Quantum yields determined for formation of **2** and **3** from the excited singlet and triplet states of **1** in benzene and methanol are given in Table I.

Concentrating first on solvent effects, we see from Table I that Φ_2 and Φ_3 for cyclobutanol formation from the first excited singlet state of **1** are nearly identical in benzene ($\Phi_2 = 0.0083$; $\Phi_3 = 0.0017$) and methanol ($\Phi_2 = 0.0084$, $\Phi_3 = 0.0016$). On the other hand, the efficiency of cyclobutanol formation from the lowest triplet state is much higher in methanol ($\Phi_2 = 0.0186$, $\Phi_3 = 0.0104$) than in benzene ($\Phi_2 = 0.0017$, $\Phi_3 = 0.0016$). Increased efficiency for alkane triplet state, but not singlet state, intramolecular γ -hydrogen abstraction photoprocesses in polar solvents, has been observed previously.⁸ This effect is attributed to diminished return of the abstracted hydrogen to the γ carbon, caused by hydrogen bonding of the solvent to the hydroxyl hydrogen of the 1,4-biradical intermediate known to be formed in T_1 intramolecular γ -hydrogen abstractions.^{8,9} Recent evidence suggests that intramolecular γ -hydrogen abstraction photoprocesses from ketone excited singlet states also involve the intermediacy of a 1,4 biradical,^{9a,b,10} albeit short-lived.^{8d,9a,b} The lack of solvent effect on the S_1 reaction requires that, if a 1,4-biradical intermediate is formed by intramolecular γ -hydrogen abstraction in the S_1 state of **1**, then such a biradical must have too short a lifetime for appreciable hydrogen bonding to the solvent to occur.⁸

The increase in the Φ_2/Φ_3 T_1 product ratio in going from benzene (1.0) to methanol (1.8) is presumably a steric effect related to the larger "effective" size of the hydroxyl group when it is hydrogen bonded to solvent.¹¹ Increasing the bulk of the hydroxyl group destabilizes **3** relative to **2** since, in **3**, the OH is endo, in a sterically more hindered environment.

Perhaps the most interesting result in Table I is the effect of excited state multiplicity on the cyclobutanol product ratio, Φ_2/Φ_3 , which is 1.0–1.8 for T_1 reaction, but approximately 5 for S_1 reaction. A similar effect of multiplicity on cyclobutanol product ratios has been recently reported for the photolyses of large-ring cycloalkanones.¹² For example, irradiation of cyclotridecanone (**5**) in benzene yields cyclobutanols **6** and **7** in a ratio of 2:1, while irradiation in 1,3-pentadiene gives only *cis*-cyclobutanol **6** (eq 3), indicating that the S_1 state of **5** forms **6** stereoselectively, while the T_1 state reaction yields a mixture of **6** and **7**.¹²

Since the triplet state intramolecular γ -hydrogen abstraction involves a long-lived 1,4-biradical intermediate,^{8,9}

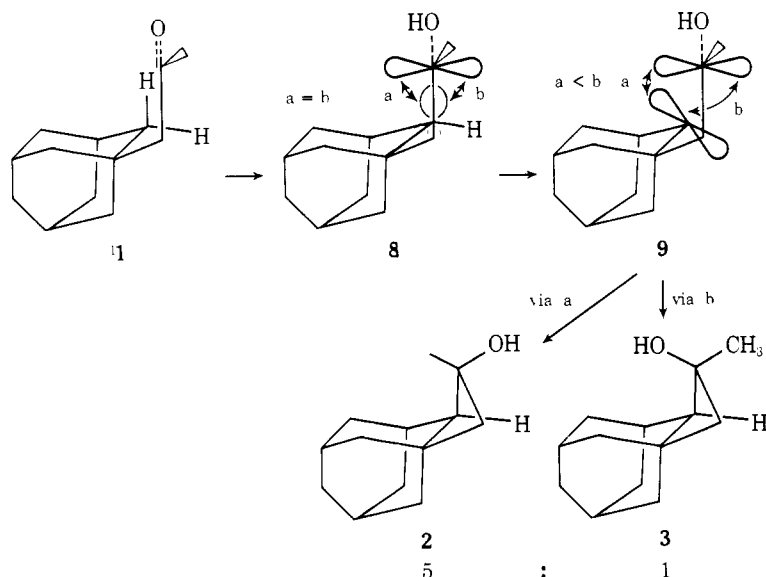


the Φ_2/Φ_3 value for **31** should reflect the cyclobutanol product ratio when the biradical has a sufficient lifetime to seek out many possible conformations. On the other hand, the stereoselectivity observed in the S_1 reaction indicates that the short-lived 1,4 biradical formed from the 1-adamantylacetone S_1 state must have a preference for formation of cyclobutanol **2**.

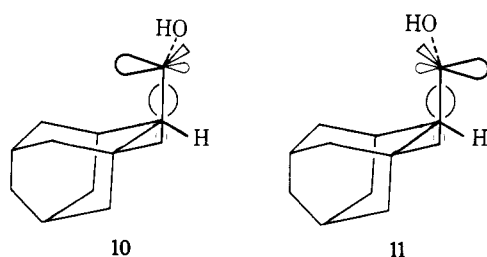
Inspection of models suggests possible explanations for why the 1,4 biradical from S_1 preferentially closes by rotating the OH exo and the CH₃ endo. Intramolecular γ -hydrogen abstraction in **1** will take place from the conformation shown in eq 4. The rigidity of the tricyclic ring system requires that the abstraction occur through such a "non-planar transition state".¹³ If hydrogen abstraction occurs without rehybridization at the γ carbon, then, in the initially formed 1,4 biradical **8**, the γ -carbon sp^3 orbital and the carbonyl carbon p orbital are orthogonal. The γ -carbon sp^3 orbital is equidistant from both lobes of the carbonyl carbon p orbital in **8**, i.e., $a = b$, and there will be no preferred direction of rotation about the carbonyl α -carbon bond. Thus we would expect both **2** and **3** to be formed with equal probability. On the other hand if intramolecular γ -hydrogen abstraction in **1** is accompanied or followed by rehybridization of the γ carbon from sp^3 to sp^2 , then the rehybridized γ carbon will have to have the two adjacent carbons and the remaining γ hydrogen in a plane. Since both bridgehead carbons adjacent to the γ carbon are constrained from moving by the rigid tricyclic ring system, the required sp^2 planar configuration will have to be achieved by moving the remaining γ hydrogen into the plane determined by the γ carbon and the two adjacent bridgehead carbons, generating 1,4 biradical **9** (eq 4). This biradical has a preference for closure to yield cyclobutanol **2**, rather than **3**, since $a < b$, and therefore a much smaller rotation is required to give the cyclobutanol with the methyl endo (**2**) as opposed to the cyclobutanol with the hydroxyl endo (**3**). Since the singlet 1,4 biradical is very short-lived, i.e., $\tau_{BR} < \tau_{bond\ rotation}$, the initial preference for closure to **2** results in a 5:1 ratio for Φ_2 to Φ_3 . Any initial preference would be washed out of the 1,4 biradical formed from the T_1 state of **1** since that biradical would be expected to undergo many bond rotations before closure.

The stereoselectivity in cyclobutanol formation from the $^1n,\pi^*$ state of **1** can also be rationalized by assuming that the rehybridization of the carbonyl carbon from sp^2 to sp^3 , which must occur in cyclobutanol formation, occurs simultaneously with, or immediately following, the intramolecular γ -hydrogen abstraction to yield **8**.¹⁴ Since the sp^2 to sp^3 conversion is likely to involve movement of the lighter CH₃ and OH groups rather than the bulkier adamantyl-CH₂ group, rehybridization of the carbonyl carbon could result in formation of either **10**, which has a preference for closure to **2**, or **11**, which has a preference for closure to **3**. Because there is clearly less steric crowding in **10**, its formation should be favored, explaining why the short-lived 1,4 biradical formed from the S_1 state of 1-adamantylacetone yields mainly **2**.

Thus the preference for formation of **2** from intramolecu-



(4)



lar γ -hydrogen abstraction from the S_1 state of 1-adamantylacetone can be rationalized by examining the effects of rehybridization in the short-lived 1,4 biradical. Lewis, Johnson, and Kory^{13a} have recently reported secondary deuterium isotope effects which suggest that rehybridization at the γ carbon accompanies intramolecular γ -hydrogen abstraction from the T_1 state of some bicyclic alkyl aryl ketones. Rehybridization arguments can also be utilized to rationalize the interesting observation of Matsui, Mori, and Nozaki¹² that cyclodecanone, cycloundecanone, and cyclododecanone undergo transannular intramolecular γ -hydrogen abstraction from the S_1 state to stereospecifically generate *cis*-cyclobutanols (eq 3). For example, if it is assumed that sp^3 to sp^2 rehybridization of the γ carbon is accompanied by motion of a lighter γ hydrogen rather than a heavier ring carbon, then the rehybridized 1,4 biradical has built-in preference for closure to *cis*-cyclobutanols.

It is also of interest to determine the reactivity of the n, π^* excited singlet (k_r^s) and triplet (k_r^t) state of 1-adamantylacetone toward intramolecular γ -hydrogen abstraction. Stern-Volmer plots for 1,3-pentadiene quenching of formation of **2** in benzene and methanol are nonlinear, reaching limiting Φ_2^0/Φ_2 values of 1.2 and 3.2, respectively, at rather low diene concentrations. The initial slope of the Φ_2^0/Φ_2 vs. [1,3-pentadiene] plot in methanol is 28.¹⁵ From the initial slope and the limiting Φ_2^0/Φ_2 value, an estimate of 41 can be obtained for $k_q\tau_1$, the product of k_q , the bimolecular rate constant for diene quenching of alkanone triplets, and τ_1 , the lifetime of 1-adamantylacetone triplets.¹⁶ Assuming that k_q is the diffusion-controlled rate constant, equal to $7.5 \times 10^9 M^{-1} \text{sec}^{-1}$ in methanol,¹⁷ a τ_1 value of $5.5 \times 10^{-9} \text{sec}$ is obtained. Since $T_1 \rightarrow S_0$ intersystem crossing for alkanones occurs with a rate constant of about 10^5sec^{-1} ,¹⁸ τ_1^{-1} can be equated to k_r^t , yielding a k_r^t value of $1.8 \times 10^8 \text{sec}^{-1}$ for intramolecular γ -hydrogen abstraction from the $^3n, \pi^*$ state of **1**. This rate constant is in the general range expected for intramolecular abstraction

of a secondary γ hydrogen by alkanone triplets,¹⁹ although somewhat lower than the k_r^t value recently reported for 1-adamantylacetone in benzene.^{13a}

The reactivity of the $^1n, \pi^*$ state of 1-adamantylacetone toward intramolecular γ -hydrogen abstraction, k_r^s , can be estimated by comparing the fluorescence lifetimes, τ_f , of **1** and 2-butanone.²⁰ Since (a) k_{st} , the rate of intersystem crossing in alkanones, is known to be insensitive to remote alkyl substitution²¹ and (b) k_f , the rate constant for fluorescence from S_1 , is much less than $1/\tau_f$,²² the increase in τ_f^{-1} , the S_1 decay rate in going from 2-butanone to **1**, can be reasonably attributed to intramolecular γ -hydrogen abstraction. A τ_f value of 0.24 nsec for **1** in *n*-hexane can be estimated from a comparison of the relative fluorescence quantum yields ($\Phi_{f,1}(\text{rel}) = 0.18$, $\Phi_{f,2\text{-butanone}}(\text{rel}) = 1.00$) and extinction coefficients ($\epsilon_1 = 26.4$, $\epsilon_{2\text{-butanone}} = 16.6$) of **1** and 2-butanone and the 2-butanone fluorescence lifetime ($\tau_f = 2.1 \text{nsec}$).^{20,23} This yields a k_r^s value of $4 \times 10^9 \text{sec}^{-1}$ for the $^1n, \pi^*$ state of **1**, somewhat greater than the S_1 reactivity of acyclic alkanones toward intramolecular γ -hydrogen abstraction (k_r^s , 2-hexanone, $1 \times 10^9 \text{sec}^{-1}$).^{20,21} This greater reactivity is consistent with the greater number of reactive γ hydrogens in **1**, as well as the reduced entropy requirements for attaining the proper transition state for γ -hydrogen abstraction in **1** relative to acyclic alkanones.^{13a}

The nearly order of magnitude greater reactivity of the S_1 state of **1** vs. the T_1 state is in line with the recent trend of results of the effects of multiplicity on intramolecular γ -hydrogen abstraction reactions.²⁴ Finally, the high k_r values for S_1 and T_1 states of **1** make it clear that the low efficiencies for formation of cyclobutanols **2** and **3** are due not to inefficient formation of 1,4 biradicals but rather to closure of the 1,4 biradicals being much less probable than return of the γ hydrogen to generate ground state **1**.

Experimental Section

Quantum Yields. Solutions of 1-adamantylacetone (0.2 *M*) in purified methanol or benzene with hexadecane as an internal standard were degassed on a vacuum line and sealed in 10-mm o.d. Pyrex tubes. The solutions were then photolyzed on a merry-go-round apparatus using a 450-W Hanovia medium-pressure mercury lamp with a potassium chromate filter solution to isolate the 313-nm wavelength. Photolyses were carried to less than 5% conversion, and the resulting solutions were analyzed by GLC, using an Aerograph Model 1200 chromatograph with a 10 ft \times $\frac{1}{8}$ in. 15% Carbowax 20M on Chromosorb P column. Quantum yields for formation of **2** (Φ_2) were measured using benzophenone-benzhydrol actinometry.⁶ The quantum yields for formation of **3** were

calculated from the Φ_2 values and the ratio of 2:3 determined from NMR spectroscopy. This was necessary because of overlap of 1 and 3 in the GLC. The 2:3 ratio was shown by NMR to be constant as a function of percent conversion and equal to the ratio determined by GLC at 100% conversion.

Quenching Studies. Sample preparations, photolysis, and analysis were as for the quantum yield determinations except that varying amounts of 1,3-pentadiene (0.0–4.0 M) were added to the solutions. Product ratios in the presence of 1,3-pentadiene were determined by NMR. Initial slopes of the Stern–Volmer plots were determined at low 1,3-pentadiene concentration (0.0–0.02 M).

Spectra. Relative fluorescence quantum yields were determined using a Hitachi Perkin-Elmer MPF-2A spectrofluorometer. UV spectra were recorded on a Cary 14 or a Cary 118C spectrophotometer. The ϵ_{\max} values were measured from Beer's law plots.

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- minimal quenching of the S_1 state of 1 at the diene concentrations used. The essentially zero slope of the Φ_2^0/Φ_2 plot at high diene concentrations (vide infra) indicates that this is the case. (b) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Am. Chem. Soc.*, **92**, 1793 (1970); N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971); R. R. Hautala and N. J. Turro, *ibid.*, **93**, 5595 (1971).
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Quenching of Alkyl Ketone Fluorescence by Alkylamines

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Abstract: The solution phase fluorescence of 11 acyclic, cyclic, and bicyclic alkanones is quenched by diethylamine (DEA) and triethylamine (TEA). Observed bimolecular quenching rate constants (k_q) are obtained from fluorescence lifetimes (τ_f^0) and Stern–Volmer treatments of fluorescence quenching as a function of amine concentration. The effects of ketone structure, amine oxidation potential, and the nature of the solvent on k_q values are described. The results suggest that singlet quenching occurs by interaction of the electrophilic half-vacant oxygen n orbital of the alkanone n, π^* state and the amine lone pair electrons to generate a charge-transfer complex. The rate of formation of the charge-transfer complex is very sensitive to steric effects. Acetone $^1n, \pi^*$ states are shown to be about an order of magnitude more reactive toward amine quenching than acetone $^3n, \pi^*$ states.

There has been considerable recent interest in the reactions of n, π^* excited electronic states of ketones with aliphatic and aromatic amines.^{1–5} These reactions usually result in formation of ketone photoreduction products, e.g., pinacols and alcohols, and are commonly postulated to occur via the mechanism shown in Scheme I.¹ Initially a charge-transfer complex (1) is formed in which the electrophilic half-vacant oxygen n orbital of the ketone is the electron acceptor, and the amine nonbonding (lone pair) orbital

is the electron donor. The charge-transfer complex then partitions between decay back to ground state ketone and amine (path A) and transfer of an α proton from the amine to the carbonyl oxygen (path B), forming a radical pair and leading to photoreduction products. This mechanism predicts that the reactivity of ketone n, π^* states toward amines should be a function of the amine oxidation or ionization potential (measures of the energy required to remove an electron from the amine) and the n, π^* ketone reduction po-