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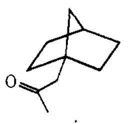

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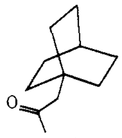

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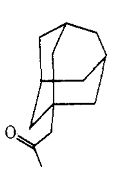

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Mechanistic Photochemistry of 1-Adamantylacetone

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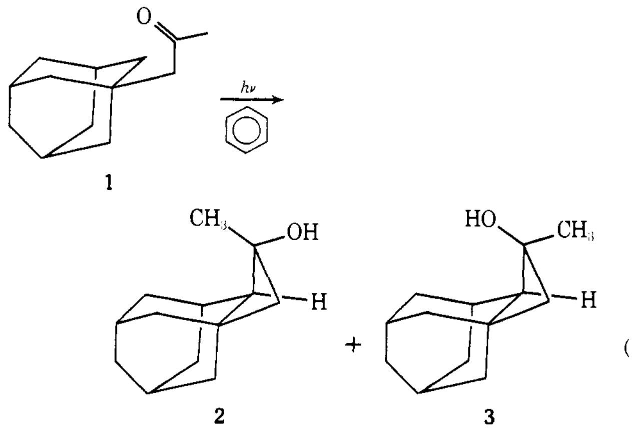
Abstract: Irradiation of 1-adamantylacetone (**1**) results in essentially a quantitative yield of two cyclobutanols, **2** and **3**. Quantum yields for the formation of **2** and **3** from the S_1 and T_1 states of **1** in benzene and methanol are reported. Formation of cyclobutanols from the excited 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.

We[2] and others[3] 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 adamantene 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]

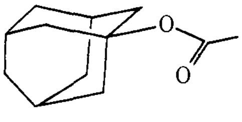


1

2
75%

3
25%

(1)



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Results and Discussion

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

$$1 \xrightarrow{h\nu} 2 + 3 \qquad (2)$$

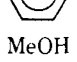
	2	3
	0.010	0.0033
MeOH	0.027	0.012

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

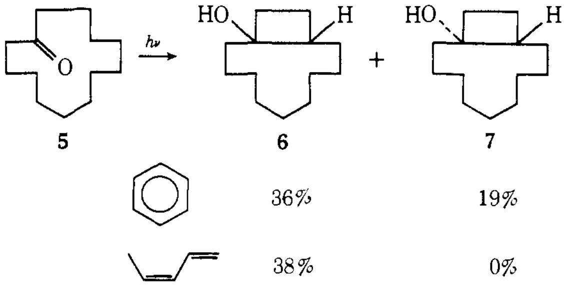
phenone-benzhydrol actinometry.[6] The ratio of **2**/**3** is somewhat lower in methanol (2.3) than in benzene (3.3), while the efficiency of cyclobutanol formation is about a factor of 3 greater in methanol. Similar effects have been observed by Sauers for photolysis of **1** in benzene vs. *tert*-butyl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



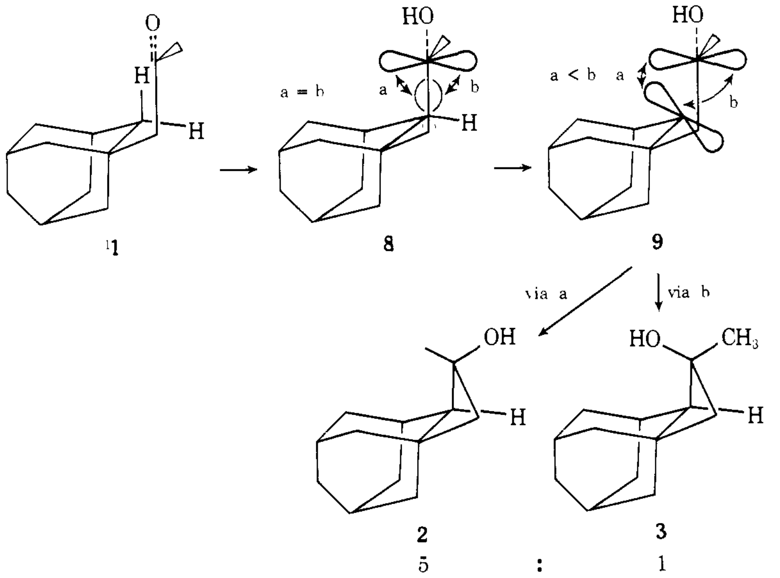
5 **6** **7** (3)

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 ^{3}**1** 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**.

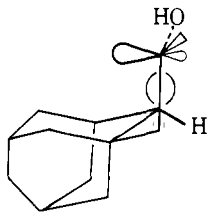
Inspection of models suggests possible explanations for why the 1,4 biradical from S_1 preferentially closes by rotating the OH exo and the CH_3 endo. Intramolecular γ-hydrogen abstraction in **1** will take place from the conformation shown in eq 4. The rigidity of the tricyclic ring system requires 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., $\tau_{BR} < \tau_{\text{bond rotation}}$, 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 CH_3 and OH groups rather than the bulkier adamantyl-CH_2 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)



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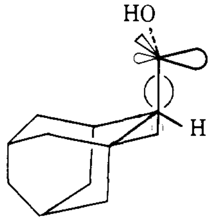

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lar γ-hydrogen abstraction from the S_1 state of 1-adamantylacetone can be rationalized by examining the effects of rehybridization in the short-lived 1,4 biradical. Lewis, Johnson, and Kory[13a] have recently reported secondary deuterium isotope effects 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 Nozaki[12] 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 $\Phi_2{}^0/\Phi_2$ values of 1.2 and 3.2, respectively, at rather low diene concentrations. The initial slope of the $\Phi_2{}^0/\Phi_2$ vs. [1,3-pentadiene] plot in methanol is 28.[15] From the initial slope and the limiting $\Phi_2{}^0/\Phi_2$ value, an estimate of 41 can be obtained for $k_q\tau_t$, the product of k_q, the bimolecular rate constant for diene quenching of alkanone triplets, and τ_t, 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_t value of 5.5×10^{-9} sec is obtained. Since $T_1 \rightarrow S_0$ intersystem crossing for alkanones occurs with a rate constant of about $10^5\ \text{sec}^{-1}$,[18] τ_t^{-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-adamantylacetophenone 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 substitution[21] 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 ($\tau_f = 2.1$ 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 × ⅛ 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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(15) The total amount of quenching in benzene is sufficiently small that determination of the initial slope of the Stern–Volmer plot in benzene is difficult.

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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 ($\tau_f{}^0$) 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 ^{1}n,π^* states are shown to be about an order of magnitude more reactive toward amine quenching than acetone ^{3}n,π^* 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-