Photochemistry of *exo*- and *endo*-5-Benzoylbicyclo[2.1.1]hexane[1]

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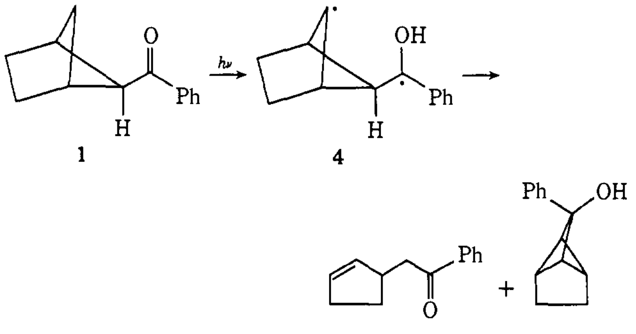
Abstract: The photolysis in benzene of *endo*-5-benzoylbicyclo[2.1.1]hexane (**5**) has been found to afford Δ^3-cyclopentenylacetophenone (**7**) and 2-phenyltricyclo[3.2.0.0^{3,7}]heptan-2-ol (**8**). Tricyclic alcohol **8** was found to rearrange thermally to Δ^3-cyclopentenylacetophenone. In the presence of 90% acetic acid, tricyclic alcohol **8** rearranged to give 2-phenyl-2-norbornen-*exo*-6-ol (**11**), 2-phenyl-6-*exo*-acetoxy-2-norbornene (**12**), 2-phenyltricyclo[2.2.1.0^{2,6}]heptan-3-ol (**13**), and 2-phenyl-3-acetoxytricyclo[2.2.1.0^{2,6}]heptane (**14**). The photochemical transformations encountered in this work appear to be best described by a transannular hydrogen abstraction followed by subsequent reactions of the diradical thus formed. The photoreactions were shown to proceed by way of a triplet n–π^* state. In striking contrast to the extraordinarily slow cyclobutylphenyl ketone system, both *exo*- and *endo*-5-benzoylbicyclo[2.1.1]hexanes were found to rearrange at a faster rate than valerophenone. The inefficiency of these reactions (Φ exo = 0.06, Φ endo = 0.20) can be attributed to an unusually rapid triplet degradation.

In the preceding paper, it was shown that the irradiation of *exo*-5-benzoylbicyclo[2.1.1]hexane (**1**) in benzene afforded Δ^2-cyclopentenylacetophenone (**2**) and 7-phenyltricyclo[3.2.0.0^{2,6}]heptan-7-ol (**3**) as major products. The isolation of these products seemed most consistent with the intermediacy of the diradical **4**, which proceeds to products by ring closure or bond fragmentation. The formation of the diradical is brought about by a novel transannular hydrogen abstraction by the electronically excited benzoyl group. At the time this study was initiated, there were few examples of the utilization of the Norrish type-II reaction to synthesize highly strained cyclobutanols.[3,4] Since that time, the photochemical synthesis of novel bridged polycyclic cyclobutanols has attracted considerable interest.[5-8]

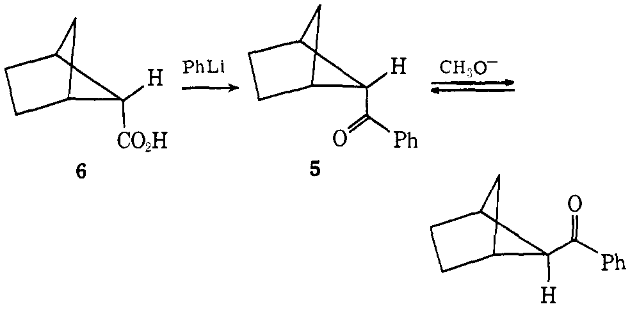


1 **4** **2** **3**

As part of a broad program on the photochemical transformations of small ring carbonyl compounds,[9] an investigation was initiated and directed toward enlarging our understanding of the scope of the transannular hydrogen abstraction reaction. Specifically, we sought to determine the structural factors which affect the relative efficiencies of the product-forming steps. To this end we chose to examine the photochemical behavior of the *endo*-5-benzoylbicyclo[2.1.1]hexane system (**5**) and compare it with the corresponding exo bicyclic ketone **1**. It was hoped that the transannular hydrogen abstractions in these two carbocyclic systems could be put on a firm quantitative basis by examining both the quantum efficiencies and rates of reaction.

Results

endo-5-Benzoylbicyclo[2.1.1]hexane (**5**) was prepared in good yield by treatment of bicyclo[2.1.1]hexane-*endo*-5-carboxylic acid (**6**)[10,11a] with phenyllithium. The configuration of the phenyl ketone follows from its preparation from an acid of known stereochemistry and the absence of a long-range W coupling between the distant exo C-5 and anti C-6 protons.[11b] The spectral data and elemental analysis were consistent with this structure and are summarized in the Experimental Section. Equilibration of **5** with the thermodynamically less stable exo form **1** may be readily effected with methanolic sodium methoxide. Irradiation of **5** in benzene with a Pyrex filter for 2 hr gave a mixture of products which were separated by preparative vapor-phase chromatography. In addition to unreacted starting material, two new compounds were obtained



6 **5** **1**

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[1] Photochemical Transformations of Small Ring Carbonyl Compounds. XL. For part XXXIX see A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.*, **94**, 5852 (1972).

[2] Fellow of the Alfred P. Sloan Foundation, 1968–1972.

[3] A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969).

[4] A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *ibid.*, **89**, 4435 (1967).

[5] R. R. Sauers, M. Gorodetsky, J. A. Whittle, and C. K. Hu, *ibid.*, **93**, 5520 (1971).

[6] R. B. Gagosian, J. C. Dalton, and N. J. Turro, *ibid.*, **92**, 4752 (1970).

[7] S. L. Murov, *14th Annu. Rep. Res. (Petrol. Res. Fund)*, **14**, 110 (1970).

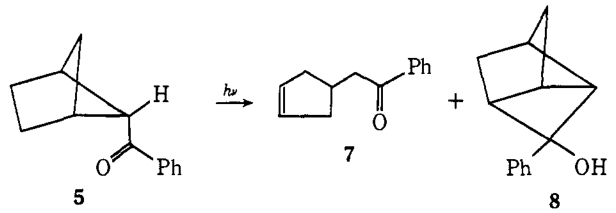
[8] F. D. Lewis and R. A. Ruden, *Tetrahedron Lett.*, 715 (1971).

[9] For a review see A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).

[10] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, **83**, 2769 (1961).

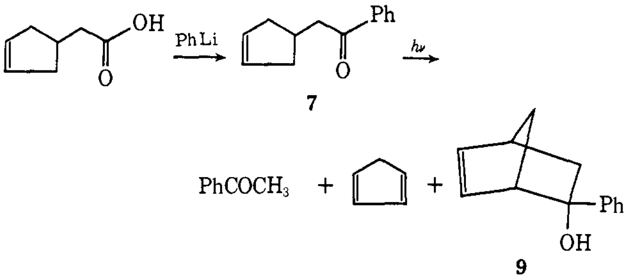
[11] (a) J. Meinwald, C. Blomquist, A. Lewis, and C. Swinthenbank, *J. Org. Chem.*, **29**, 3469 (1964); (b) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961).

and subsequently identified as Δ^3-cyclopentenylacetophenone (**7**, 80%) and 2-phenyltricyclo[3.2.0.$0^{3,7}$]heptan-2-ol (**8**, 8%). The structure of the major product



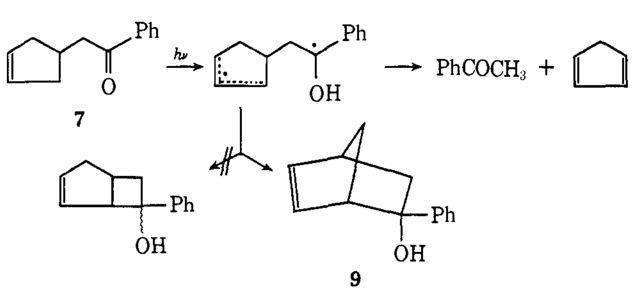
(**7**) was elucidated from its chemical analysis and spectral data (see Experimental Section). Structure **7** was further confirmed by its unequivocal synthesis from Δ^3-cyclopentenylacetic acid and phenyllithium.

With short exposures **7** and **8** account for nearly all the products produced from **5**. At longer exposures, owing to secondary reactions, the yield of **7** gradually decreases and acetophenone, cyclopentadiene (and its dimers), and *exo*-2-phenyl-5-norbornen-2-ol (**9**) are formed. By studying the reaction as a function of time it became clear that **7** is an intermediate in the formation of the remaining products. This was further confirmed by irradiating a pure sample of **7** in benzene under conditions comparable with those used for **5**. Photolysis of **7** afforded acetophenone (42%), cyclopentadiene, and **9** (50%) in about the same distribution as found in runs beginning with *endo*-5-benzoylbicyclo[2.1.1]hexane. The structure of **9** was unambiguously

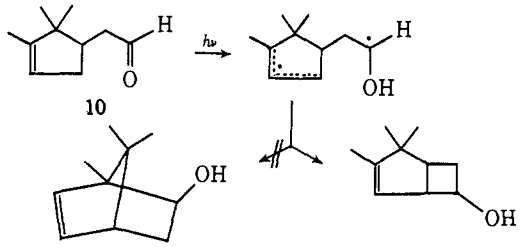


established by comparison with an authentic sample prepared by treating 5-norbornen-2-one with phenyllithium.

The formation of **9** is readily rationalized by cyclization of a 1,4-diradical intermediate which is formed upon γ-hydrogen abstraction by the carbonyl n–π* excited state. The formation of only one of two pos-

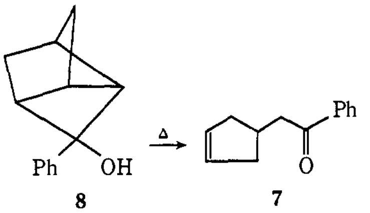


sible alcohols indicates the existence of a small activation energy barrier for cyclization of the 1,4 diradical, in agreement with previous results reported in the literature.[8,12] It is interesting to note that the alcohol produced from **7** (**9**) is different from that obtained from the irradiation of the structurally related campholenic aldehyde (**10**) system.[13] One possible explana-



tion to account for this difference may be related to the unfavorable steric factors associated with the *gem*-dimethyl group present in the bicyclo[2.2.1]heptanol. This would imply that the cyclization of the 1,4 biradical is sensitive to the relative stabilities of the products formed.

The structure of the tricyclic alcohol **8**, mp 85–86°, obtained from irradiation of **5** was elucidated on the basis of the physical and chemical data cited.[14] The infrared spectrum shows hydroxyl bands at 2.86 and 3.04 μ and a carbon–oxygen stretching band at 9.60 μ. The ultraviolet spectrum (95% ethanol) with maxima at 264, 258, 252, and 247 mμ (ϵ 160, 220, 200, and 150) is characteristic of an isolated benzene ring. The mass spectrum of **8** included peaks with *m/e* 186(M^+), 158, 120, 105 (base), 91, and 77. The 100-MHz nmr spectrum showed multiplets at τ 9.15 (1 H), 8.68 (2 H), 8.05 (1 H), 7.56 (1 H), 7.30 (2 H), 6.92 (1 H), and 3.02 (5 H), and the hydroxyl proton at τ 8.24 (1 H) which disappeared on addition of deuterium oxide. Chemical confirmation was obtained by pyrolysis of **8** at 200°. The product obtained in high yield (85%) was identical with an authentic sample of Δ^3-cyclopentenylacetophenone (**7**). No detectable quantities of *endo*-2-



benzoyl- or *endo*-5-benzoylbicyclo[2.1.1]hexane were found in the crude pyrolysis mixture. Evidently cleavage of the initially formed 1,4-biradical intermediate is faster than 1,5-H transfer. It is noteworthy that opening of the four-membered ring proceeded regiospecifically to afford a single biradical intermediate. This undoubtedly is related to the stability of the radicals attached to the bicyclo[2.1.1]hexyl framework.

Tricyclic alcohol **8** was stable to basic conditions but was found to rapidly rearrange in the presence of 90% acetic acid. Four products were isolated and subsequently identified as 2-phenyl-2-norbornen-*exo*-6-ol (**11**, 22%), 2-phenyl-6-*exo*-acetoxy-2-norbornene (**12**, 23%), 2-phenyltricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**13**, 27%), and 2-phenyl-3-acetoxytricyclo[2.2.1.$0^{2,6}$]heptane (**14**, 28%). The assignment of structures **11** and **12** follow from their spectral characteristics. The nmr spectrum (100 MHz) of **12** is composed of a multiplet centered at τ 8.38 (4 H), a singlet at τ 8.06 (3 H),

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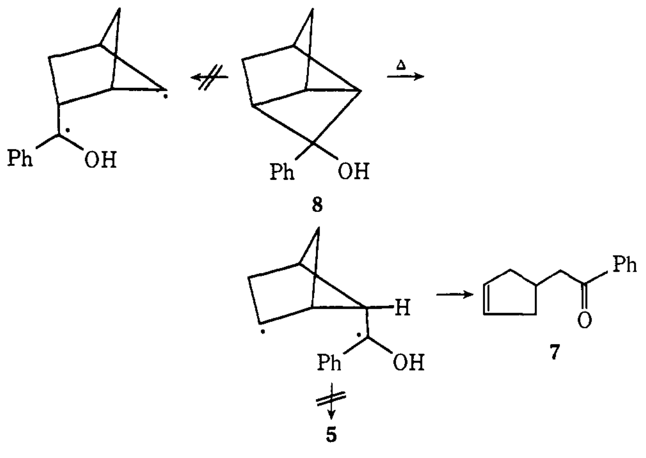
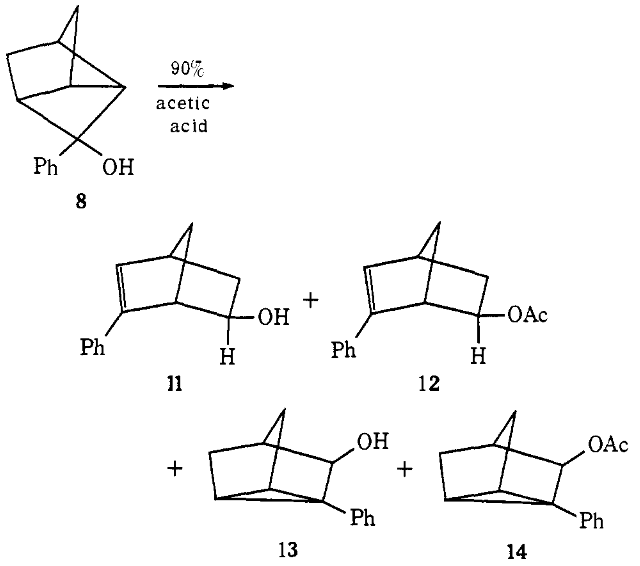
(12) J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, **90**, 6584 (1968).

(13) J. Meinwald and R. A. Chapman, *ibid.*, **90**, 3218 (1968).

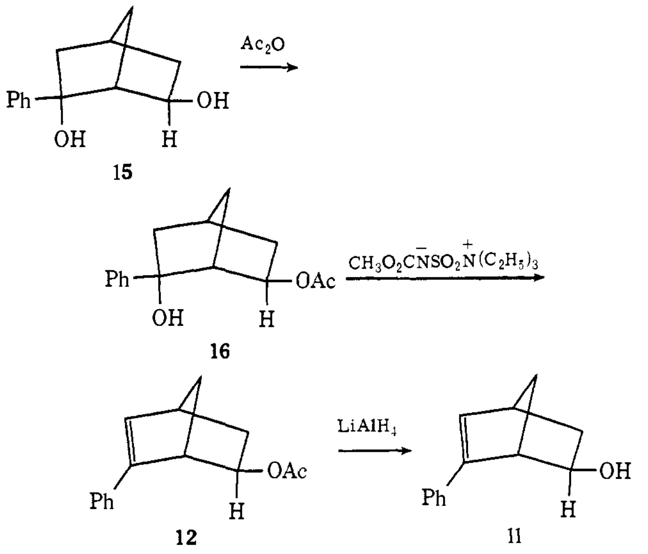
(14) The stereochemistry about the tertiary center of **8** is unknown.



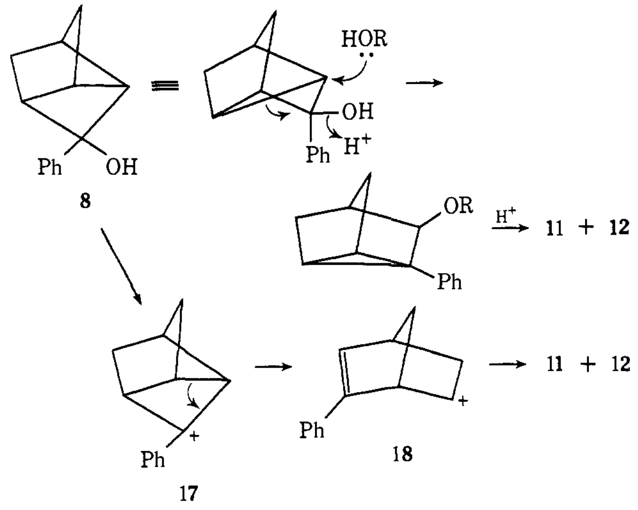
broad singlets at τ 7.16 (1 H) and 6.76 (1 H), a doublet of doublets at τ 5.36 (1 H, J = 7.0 and 3.0 Hz), a doublet at τ 3.76 (1 H, J = 3.0 Hz), and a multiplet at τ 2.80 (5 H). The structure of acetate **12** was unambiguously established by an independent synthesis. A sample of 2-*exo*-phenylnorbornene-2-*endo*,6-*exo*-diol[15] (**15**) was converted to the corresponding 6-exo acetate (**16**) by reaction with acetic anhydride. Acetate **16** was dehydrated with methyl(carboxysulfamoyl)-triethylammonium hydroxide inner salt according to the procedure of Burgess, Penton, and Taylor.[16] The sample of **12** produced by this route was identical with acetate **12** obtained from the reaction of **8** with 90% acetic acid. The structure of alcohol **11** was established by the lithium aluminum hydride reduction of **12**. All attempts to dehydrate diol **15** to **11** failed; the only product that was formed was identified with 3-phenyl-Δ^3-cyclopentenylacetaldehyde (see Experimental Section for a description of its properties).



The structure assigned to the other alcohol (**13**) isolated from the reaction of **8** with 90% acetic acid was based on its method of formation and on several pieces of spectroscopic and chemical data. The infrared spectrum of **13** shows hydroxyl bands at 2.78 and 3.01 μ and a carbon–oxygen stretching band at 9.20 μ. The mass spectrum has peaks at m/e 186 (M^+, base), 168, 142, 115, and 91 mass units. The nmr spectrum shows multiplets at τ 8.60 (6 H) and 8.01 (2 H), a singlet at τ 6.06 (1 H), and a multiplet at τ 2.90 (5 H). In addition, reaction of **13** with aqueous acid afforded **11**. All attempts to prepare **13** by treating **11** with acid were unsuccessful. The structure of acetate **14** was established by the reaction of **13** with acetic anhydride.



The formation of **13** (and/or **14**) from **8** can best be rationalized by a 1,2 shift of the strained C–C bond to the developing electron-deficient center followed by addition of nucleophilic solvent. Products **11** and/or **12** may be attributed to either the acid-catalyzed rearrangement of the initially formed tricyclo[2.2.1.0^{2,6}]-heptanol system or to the opening of tricyclic cation **17** to the 2-norbornenyl cation (**18**) followed by solvent capture.



Photochemical Discussion

The Norrish type-II photoelimination and cyclobutanol formation is undoubtedly the most common photoreaction of aliphatic and aromatic ketones that possess a hydrogen bearing γ carbon.[17] The available evidence suggests that abstraction of the γ hydrogen is reversible and can occur from either the first excited

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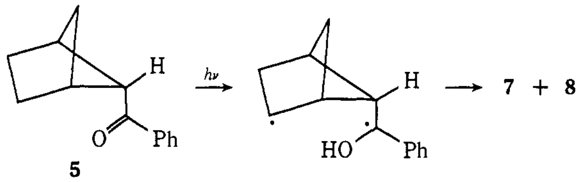
[15] C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 1652 (1967).

[16] E. M. Burgess, H. R. Penton, and E. A. Taylor, *ibid.*, **92**, 5224 (1970).

[17] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 377–427.

singlet[18] or triplet state.[19] The intermediate diradical formed in this process can either ring close or fragment. Scheme I illustrates an adaption of this mechanism to describe the results of the present study. A similar mechanism can be written for the corresponding exo ketone system.

Scheme I



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The reactions of aliphatic ketones involve both singlet and triplet excited states of the parent ketones,[20] but photoelimination of phenyl ketones involves only the triplet state.[19,21] On the basis of the spectral data available for ketones **1** and **5**, the photoreactions may be formulated as occurring by means of $n-\pi^*$ excitation (*i.e.*, 3130 Å excitation). The phosphorescence emission spectrum of **1** in an EPA glass was determined at 77°K. From the location of the 0–0 band, the energy of the lowest triplet is found to be 73.3 kcal/mol. The triplet excitation level of ketone **5** is similar and is located at 72.9 kcal. The emission spectra for these compounds show very distinct vibrational fine structure (δE around 1600 cm^{-1}), and the energy gap between the 0–0 and 0–1 bands is approximately 1700 cm^{-1}. These results provide strong evidence for the emission coming from an $n-\pi^*$ triplet. The absorption data suggest that the conclusions reached about the nature of the lowest triplet state in a glass at 77°K may still be valid in liquid solution at room temperature, since only those ketones which are thought to have a lowest $n-\pi^{*3}$ state in a glass show a low-intensity (ϵ <100) absorption maximum (shifted to shorter wavelengths in a more polar solvent) at wavelengths longer than those at which the intense $\pi-\pi^*$ absorption occurs.

The elimination and cyclization reactions of ketones **1** and **5** could be quenched completely by piperylene. Naphthalene and biacetyl were also effective in quenching the reactions. The observation of retardation of the reaction of **1** (or **5**) with piperylene supports a $n-\pi^*$ triplet as the reactive electronic state involved. In order to determine whether the cyclization and fragmentation reactions have a common intermediate, *endo*- (and/or *exo*-) 5-benzoylbicyclo[2.1.1]hexane was irradiated with piperylene in amounts insufficient to quench the reaction completely. The products were analyzed and found to contain the same ratio of cyclopentenylacetophenone and tricyclic alcohol as for the unquenched reaction. This strongly supports the concept that the $n-\pi^{*3}$ state is a common intermediate for both reactions.

The quantum yields were determined at 3130 Å on degassed solutions irradiated in parallel with benzophenone–benzhydrol actinometer solutions.[22] Quantum yields were determined at 25° and product formation was analyzed by glpc after 5–15% conversion and was found to be independent of per cent reaction. The quantum yield for disappearance of **1** with direct irradiation was found to be 0.058 in benzene. The quantum yield for appearance of Δ^2-cyclopentenylacetophenone (**2**) is 0.052 and for tricyclic alcohol is 0.006. These reactions thus contrast with the photochemistry of the related valerophenone system where virtually every quantum of light is utilized in product formation.[19] The quantum efficiencies for the *endo*-5-benzoylbicyclo[2.1.1]hexane system are summarized in Table I.

Table I. Quantum Yield Data for Product Formation of *exo*- and *endo*-5-Benzoylbicyclo[2.1.1]hexanes[a]

Ketone[b]	Solvent	Φ total[c]	Φ olefin	Φ cyclobutanol
1	Benzene	0.058	0.052	0.006
1	Acetonitrile	0.071	0.063	0.008
1	1-Propanol	0.104	0.079	0.025
5	Benzene	0.202	0.189	0.013
5	Acetonitrile	0.235	0.174	0.061
5	1-Propanol	0.298	0.234	0.064

[a] All runs at 25°; irradiation conditions described in the Experimental Section. [b] Ketone concentration was 0.086 *M*. [c] Quantum yield for disappearance of ketone, average for three runs.

The quantum yield for disappearance of ketone **1** is considerably smaller than that of related acyclic ketones[23] and its value is not significantly enhanced with added acetonitrile or alcohol (see Table I). Wagner has demonstrated that the quantum efficiency for the Norrish type-II reaction of phenyl ketones is considerably enhanced when the irradiation is carried out in alcohol rather than benzene.[19] He attributed the increase in quantum efficiency to solvation of the hydroxyl hydrogen in the biradical, which impeded back transfer to regenerate starting ketone, thus reducing k_{-r}. Solvent polarity was argued to have little effect on the rate of cleavage of the biradical; hence, the efficiency of the type-II elimination was greatly increased in polar solvents. Since the quantum yield of **1** (and/or **5**) is not significantly altered by solvent, the low efficiency cannot be attributed exclusively to disproportionation of the 1,4 diradical; unless the alcohol effect does not compete with reverse transfer.

One possibility to account for the low efficiency of ketone **1** may be related to some molecular feature of **1** which retards formation of the diradical and allows direct radiationless decay to compete with chemical reaction of the triplet. In order to ascertain whether the inefficiency of the photoprocess is due to an unfavorable geometry in the internal hydrogen abstraction step,[24] we have studied the variation of quantum yield *vs.* quencher concentration. Figure 1 is a plot of the reciprocal of the quantum yield of disappearance of **1** against piperylene concentration. The Stern–Volmer formulation for quenching a unimolecular reaction of an

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(18) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969).

(19) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(20) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(21) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966).

(22) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).

(23) P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5383 (1969).

(24) The preferred transition state for internal hydrogen transfer has been suggested to be one in which the carbon, hydrogen, and nonbonding electron on oxygen can approximate a linear configuration.[25] These stereoelectronic requirements cannot readily be met with ketone 1.

(25) N. J. Turro and D. W. Weiss, *J. Amer. Chem. Soc.*, **90**, 2185 (1968).

excited state (rate constant = k_r) results in the following expression (eq 1),

$$\frac{1}{\Phi} = \frac{1}{\Phi_p}\left(\frac{k_r + k_d}{k_r} + \frac{k_q[Q]}{k_r}\right) \qquad (1)$$

where Φ_p is the probability that the biradical will proceed on to product. The slope of the plot gives $(1/\Phi_p)(k_q/k_r)$ and the intercept gives $(1/\Phi_p)(k_r + k_d/k_r)$. The value of Φ_p can be estimated by dividing the measured Φ values for disappearance of **1** in benzene by that found in neat 2-propanol (*i.e.*, Φ_p 0.56 = Φ_1 (benzene)/Φ_1(2-propanol)). This should be the maximum value of Φ_p, since in many cases quantum yields are still increasing with alcohol concentration at very high (neat) alcohol concentration.[23] Quenching by piperylene will be diffusion controlled since the triplet state of **1** is 73.3 kcal/mol. From the observed slope of 2.27×10^1 for the Stern-Volmer plot, and using $k_q = 5 \times 10^9$ l. mol^{-1} sec^{-1},[19] the value for the unimolecular rate constant for disappearance of **1**, k_r, is found to be 3.9×10^8 sec^{-1}. Knowing k_r and the intercept we obtain k_d (unimolecular rate of triplet decay to ground state) as 4.0×10^9 sec^{-1}. The constant, k_d for decay of **1** is much larger than that observed with benzophenone.[26] Thus, the inefficiency of the photoreaction can be attributed to an unusually rapid triplet degradation. The unimolecular rate of reaction, k_r, is three times larger than that of valerophenone[19] (*i.e.*, $k_r = 1.3 \times 10^8$ sec^{-1}). The high rate of reaction of **1** implies that the inefficiency encountered in the photoreaction of **1** cannot be attributed to a low reaction rate as was previously observed with cyclobutyl phenyl ketone.[3]

It is interesting, at this point, to compare the photochemistry of **1** with that of cyclobutyl phenyl ketone (**19**) ($\Phi = 0.03$, $k_r = 5.5 \times 10^3$ sec^{-1}).[3] The cyclobutane ring is quite flexible and exhibits a dynamic ring-bending equilibrium which allows for conformation equilibration of monosubstituted cyclobutanes.[27] It was previously argued that one possible source of inefficiency in the cyclobutyl phenyl ketone system was the low concentration of the conformer having the benzoyl group in the pseudoaxial position.[3] As was indicated earlier,[1] bicycloketone **1** is an appropriate model for the reactive conformer of **19**, since the benzoyl group is now locked into the axial position. If the inefficiency of **19** was totally due to the low population of the reactive conformer, then we would expect that **1** would be similar to valerophenone in terms of its triplet state reactivity. This appears to be the case and suggests that the inefficiency of internal hydrogen abstraction in cyclobutyl phenyl ketone, both in terms of quantum yield and reaction rate, may be attributed to the low concentration of the reactive conformer of **19**.[28]

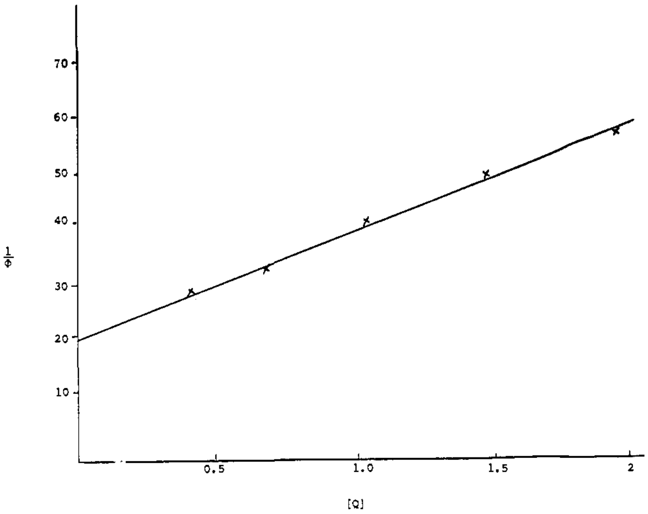

Figure 1. Reciprocal of quantum yield *vs.* quencher concentration.

The low quantum efficiency observed for the photoreaction of **1** and the absence of a significant alcohol effect may be an indication that other pathways for radiationless decay are operative. Heller's suggestion that the quantum efficiencies of photochemical hydrogen abstraction reactions may be controlled by the rates of relaxation of vibrationally excited stretching modes formed *via* conversion of electronic energy into vibrational energy may be important in this system.[30] This mode of deactivation does not require back transfer of hydrogen atoms, and would, therefore, not lead to a significant alcohol effect. Alternatively, the triplet state of **1**, in which the α hydrogen is held near the carbonyl group may lead to a diradical which disproportionates at an extremely fast rate, and consequently precludes much of a solvent effect. Predominant back transfer of a hydrogen in the biradical is not unexpected in view of the energetic constraints on cyclization and elimination. The available evidence does not decisively distinguish among the preceding possibilities. In fact, it is quite probable that both explanations account for the observed inefficiency. There is, of course, a point where the difference between efficient back transfer and Heller's mechanism becomes one of semantics.

The diradicals produced by transannular hydrogen abstraction with ketones **1** and **5** prefer fragmentation to ring closure. This is in marked contrast to the results obtained in the cyclobutyl phenyl ketone system, where ring closure predominates.[3] As stated earlier,[1] the preferred conformation for fragmentation requires that the four carbon atoms be coplanar for maximum overlap between the developing π orbitals and the π orbitals at the radical centers. Such overlap seems to be geometrically more feasible in the bicyclic system and may account for the preponderance of ring scission over ring closure with ketones **1** and **5**. Additionally, the lower barrier to cleavage in the bicyclic system may be a manifestation of the relief of ring strain in these systems.

The reciprocal of the quantum yield for disappearance of *endo*-5-benzoylbicyclo[2.1.1]hexane was also found to vary linearly with quencher concentration (piperylene) in accordance with the normal Stern–

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(26) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

(27) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2483 (1947).

(28) In our earlier communication[29] we suggested that the inefficiency was related to the poor stereoelectronic features of these ketones (*i.e.*, **1** and **19**). This argument was based on the fact that ketones **1** and **19** show no significant solvent effects and consequently it was assumed that quantum efficiency and triplet reactivity of these ketones were closely related. The determination of the rate of reaction of **1** and the large difference obtained (*vs.* **19**) now allows us to reject this prior assumption.

(29) A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 2590 (1970).

(30) A. Heller, *Mol. Photochem.*, **1**, 257 (1969).

Volmer expression (see eq 1). From the observed slope of 0.18×10^1 for the Stern–Volmer plot, and using $k_q = 5 \times 10^9$ l. mol^{-1} sec^{-1} [31] and $\Phi_p = 0.68$, the value for the unimolecular rate constant for abstraction from the triplet state, k_r, is found to be 4.1×10^9 sec^{-1}. This result indicates that k_r for the endo ketone is ten times larger than the corresponding rate for the *exo* ketone.[32] The rate constant for triplet decay ($k_d = 10 \times 10^9$ sec^{-1}) however, is only two and a half times larger than the decay rate in the corresponding exo system. This would account for the increase in quantum yield of **5** relative to **1**, since the rate of internal transfer has now increased more than the rate of decay. The absence of any significant solvent effect can still be attributed to the extremely fast rate of decay. It is well known that the rate constant for internal hydrogen transfer increases as the bond strength decreases.[33] It would appear therefore, that a radical located at the 2 position of the bicyclo[2.1.1]hexyl framework is more stable than one located at the 6 position. This seems to be consistent with the results previously encountered in the pyrolysis of tricyclic alcohol **8** and satisfactorily accounts for the larger reaction rate observed with ketone **5**. The effect of geometry on the stability of bicyclic radicals is considerable and is related to the fact that carbon free radicals prefer a planar geometry, as do carbonium ions.[34,35] The extent of geometrical destabilization is expected to be greater at the 6 position of the bicyclo[2.1.1]hexyl system than at the 2 position. This is not surprising since the C–H bond dissociation energy of cyclopentane is 1 kcal less than that of cyclobutane.[36] The correlation between bond angle strain and expected radical stability nicely rationalizes the difference in rates of abstraction of the triplet states of ketones **1** and **5**. The difference in rates can also be attributed to the proximity of the α hydrogen to the carbonyl group. Molecular models show that the distance is shorter for the endo ketone than the exo ketone.

Conclusions on Reaction Efficiency and Rate

The values found for the quantum yield and triplet reaction rates for the benzoylcycloalkanes studied are summarized in Table II. From Table II, it can be concluded that the ability of the n–π^{*3} state to undergo transannular hydrogen abstraction is markedly dependent on conformational factors. The higher reaction rate of *endo*-5-benzoylbicyclo[2.1.1]hexane, when compared to the other benzoylcycloalkanes, can be attributed to the proximity of the γ hydrogen to the carbonyl group. As was pointed out earlier,[33] quantum yields do not necessarily have any relation to triplet-state reactivity.

Table II. Quantum Yields and Reaction Rates of Benzoylcycloalkanes in Benzene

Ketone	Φ	k_r, sec^{-1}
Cyclobutyl phenyl ketone	0.03	5.5×10^3
Cyclopentyl phenyl ketone	0.40	6.7×10^6
endo-2-Benzoyl-2-methylnorbornane[8]	0.49	8.3×10^7
Valerophenone[33]	0.44	1.3×10^8
exo-5-Benzoylbicyclo[2.2.1]hexane	0.06	3.9×10^8
endo-5-Benzoylbicyclo[2.2.1]hexane	0.20	4.1×10^9

Experimental Section[37]

Bicyclo[2.1.1]hexane-*endo*-5-carboxylic Acid (6). Lithium metal (2.0 g), cut in small pieces, was added to a solution of *exo*-5-chlorobicyclo[2.1.1]hexane-*endo*-6-carboxylic acid (**6**)[11] (mp 95–96°) (2.0 g) in anhydrous *tert*-butyl alcohol (18 ml) and tetrahydrofuran (80 ml). After the initial exothermic reaction had subsided, the reaction mixture was heated under reflux for an additional 1 hr, then was cooled and poured into ice water (100 ml) to decompose the excess lithium. The tetrahydrofuran was removed on a flash evaporator and the cold aqueous solution was carefully acidified with concentrated hydrochloric acid and extracted thoroughly with ether. The combined extracts were washed with water and dried, and the solvent was removed to give a crude solid: mp 87–93° (1.2 g, 65%). Two sublimations at 60° (0.5 mm) gave an analytical sample: mp 94–95°.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.37; H, 7.97.

The infrared spectrum showed a broad carboxylic acid band at 3.0–4.2 μ, and bands at 5.85, 7.08, 8.10, 8.95, 10.64, 11.51, 13.50 μ. The nmr spectrum (CCl$_4$) shows a doublet at τ 9.18 (1 H, J = 8.0 Hz), a broad multiplet from τ 7.70–9.0 (5 H), a broad singlet at τ 7.51 (1 H), a broad singlet at τ 7.24 (2 H), and a singlet at τ −0.7 (1 H).

***endo*-5-Benzoylbicyclo[2.1.1]hexane (5).** To an ice-cooled solution of bicyclo[2.1.1]hexane-*endo*-5-carboxylic acid (1.0 g) in 50 ml of anhydrous ether was added 9.0 ml of a 2.2 *M* phenyllithium solution. The mixture was warmed to room temperature and stirred for an additional 1 hr. The excess phenyllithium was destroyed with 2 ml of ethyl formate. The resulting mixture was hydrolyzed with 50 ml of a saturated ammonium chloride solution. The aqueous layer was extracted with ether and the ethereal extracts were dried over sodium sulfate. The solvent was removed under reduced pressure to give an oil which was distilled to give 0.5 g (45%) of a clear liquid: bp 60–61° (0.1 mm).

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol to give an analytical sample: mp 104–105°.

Anal. Calcd for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95. Found: C, 61.91; H, 5.10.

The infrared spectrum of **5** showed absorption bands at 3.45, 5.98, 6.91, 8.15, 10.51, 11.32, 11.83, 13.31, and 14.45 μ. The mass spectrum showed the parent ion at *m/e* 186 and had major peaks at 158, 120, 105 (base), 91, and 77. The 100-MHz nmr spectrum (CCl$_4$) consists of a doublet at τ 9.20 (1 H, J = 7.0 Hz), a multiplet between τ 8.24–8.68 (6 H), a singlet at τ 7.19 (2 H), and multiplets at τ 2.80 (3 H) and 2.30 (2 H).

Irradiation of *endo*-5-Benzoylbicyclo[2.1.1]hexane in Benzene. A solution of 0.5 g of *endo*-5-benzoylbicyclo[2.1.1]hexane in 400 ml of benzene was irradiated at room temperature in a nitrogen atmosphere with a Hanovia 450-W mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. The progress of the reaction was followed by vapor-phase chromatography with a 8 ft × 0.25 in. aluminum column packed with 5% Degs on Chromosorb W at a flow rate of 60 cc/min and at a temperature of 150°; after 2 hr the reaction was 95% complete. The solvent was removed on a rotatory evaporator, and the remaining oil was subjected to preparative vpc. The chromatogram showed three peaks with retention time of 8.5, 9.8, and 11.5 min. The first material

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(31) W. D. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969); G. Porter and M. R. Topp, *Proc. Roy. Soc., Sect. A*, **315**, 163 (1970).

(32) The high rate of internal hydrogen abstraction for both ketones **1** and **5** account for their inability to undergo photoreduction in 1-propanol at a concentration of 10^{-3}.

(33) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

(34) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *J. Amer. Chem. Soc.*, **90**, 5266 (1968).

(35) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968).

(36) A. F. Trotman-Dickenson, "Advances in Free-Radical Chemistry," Vol. 1, G. H. Williams, Ed., Academic Press, New York, N. Y., 1965, p 21.

(37) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associates high-resolution spectrometer and at 100 MHz using a Jeolco-MH-100 spectrometer.

to be eluted was identified as recovered starting material. The major peak (80%) was identified as Δ^3-cyclopentenylacetophenone (**7**): bp 60–62° (0.1 mm); infrared spectrum, 3.45, 5.97, 6.02, 8.25, and 10.18 μ; mass spectrum (*m/e*) 186 (M^+), 120, 105, 91, and 77; nmr (60 MHz, CCl_4) multiplets at τ 7.50–8.0 (5 H) and 7.10–7.25 (2 H), broad doublet centered at τ 4.50 (2 H), multiplets at τ 2 80 (3 H) and 2.30 (2 H).

A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol to give an analytical sample: mp 138–140°.

Anal. Calcd for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95. Found: C, 61.89; H, 4.99.

The structure of Δ^3-cyclopentenylacetophenone (**7**) was further confirmed by its unequivocal synthesis from Δ^3-cyclopentenylacetic acid[38] and phenyllithium. The conversion of 2 g of Δ^3-cyclopentenylacetic acid, bp 77–80° (0.5 mm), to the phenyl ketone using phenyllithium (10 ml of a 2.2 *M* solution) in 100 ml of anhydrous ether was carried out exactly as described above for *endo*-5-benzoylbicyclo[2.1.1]hexane. The product was obtained as a colorless liquid: bp 60–62° (0.1 mm). The infrared and nmr spectra of Δ^3-cyclopentenylacetophenone prepared in this fashion were identical in every detail with those of the material isolated from the photolysis of *endo*-5-benzoylbicyclo[2.1.1]hexane.

2-Phenyltricyclo[3.2.0.0^{3,7}]heptan-2-ol (8). The third product collected from preparative vpc was a crystalline solid, mp 85–86°, whose structure is assigned as 2-phenyltricyclo[3.2.0.0^{3,7}]heptan-2-ol (**8**) on the basis of the following data.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.56; H, 7.55.

The infrared spectrum shows hydroxyl bands at 2.86 and 3.04 μ, a carbon–oxygen stretching band at 8.96 μ, as well as bands at 8.45, 9.60, 9.81, and 11.02 μ. The ultraviolet spectrum (95% ethanol) with maxima at 264, 258, 252, and 247 mμ (ϵ 160, 220, 195, and 155) is characteristic of an isolated benzene ring. The mass spectrum of this material included peaks with *m/e* 186 (M^+), 158, 120, 105 (base), 91, and 77. The 100-MHz nmr spectrum (CCl_4) showed multiplets at τ 9.15 (1 H), 8.68 (2 H), 8.05 (1 H), 7.56 (1 H), 7.30 (2 H), 6.92 (1 H), and 3.0 (5 H), and the hydroxyl proton at τ 8.24 (1 H), which disappeared on addition of D_2O.

Irradiation of Δ^3-Cyclopentenylacetophenone in Benzene. A solution of 0.5 g of Δ^3-cyclopentenylacetophenone (**7**) in 400 ml of benzene was photolyzed for 2 hr in the same manner as described above for *endo*-5-benzoylbicyclo[2.1.1]hexane. Gas chromatographic analysis of the product mixture revealed the presence of acetophenone (42%), cyclopentadiene, starting material, and a fourth component. The authenticity of the first three materials was derived by comparison with authentic samples. The fourth component isolated (50%) was identified as *exo*-2-phenyl-5-norbornen-2-ol (**9**) on the basis of its spectroscopic properties and by comparison with an authentic sample. The infrared spectrum (neat) had bands at 2.98, 3.41, 6.21, 7.51, 8.59, 8.88, 9.56, 10.07, and 10.99 μ. The mass spectrum of this material included peaks with *m/e* 186 (M^+), 120 (base), 91, and 77. The 100-MHz nmr spectrum (CCl_4) shows a doublet at τ 8.75 (1 H, J = 8.0 Hz), a singlet τ 8.52 (2 H), the hydroxyl proton at τ 8.04 (disappears on addition of D_2O), a doublet of doublets at τ 7.75 (1 H, J = 12.0 and 3.5 Hz), broad singlets at τ 7.23 (1 H) and 7.02 (1 H), a doublet of doublets at τ 3.92 (1 H, J = 5.1 and 2.8 Hz), a doublet of doublets at τ 3.71 (1 H, J = 5.1 and 2.8 Hz), and a multiplet centered at τ 2.70 (5 H). A *p*-nitrobenzoate derivative was prepared and recrystallized from ethanol to give an analytical sample: mp 105–106°.

Anal. Calcd for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11. Found: C, 71.40; H, 5.27.

The structure of the alcohol was unambiguously established by comparison with an authentic sample prepared by treating 5-norbornen-2-one[39] with phenyllithium.

Thermolysis of 2-Phenyltricyclo[3.2.0.0^{3,7}]heptan-2-ol (8). A 0.01-g sample of the tricyclic alcohol **8** in 10 ml of benzene was heated in a sealed tube at 200° for 5 hr. The solvent was removed under reduced pressure and the residual oil was analyzed by vapor-phase chromatography using an 8 ft × 0.25 in. 5% Degs on Chromosorb W column at a temperature of 150°. The chromatogram showed that Δ^3-cyclopentenylacetophenone was the only major product (85%). No detectable quantities of *endo*-5-benzoylbicyclo[2.1.1]hexane were found.

Treatment of 2-Phenyltricyclo[3.2.0.0^{3,7}]heptan-2-ol (8) with 90% Acetic Acid. A 0.02-g sample of **8** was added to 15 ml of 90% acetic acid and the resulting solution was heated at reflux for 6 hr. The acetic acid was removed at 25° under reduced pressure and the remaining oil was subjected to preparative vpc using a 5% Degs on Chromosorb W column at 150°. The chromatogram showed four peaks with retention times of 12.5, 19.0, 20.1, and 20.9 min. The fourth peak to be eluted was identified as 2-phenyl-2-norbornene-*exo*-6-ol (**11**) (22%): bp 70° (0.1 mm); infrared spectrum, 2.79, 3.02, 3.45, and 9.30 μ; mass spectrum (*m/e*) 186 (M^+), 142 (base), 128, and 115; nmr (100 MHz, $CDCl_3$) multiplet at τ 8.0–8.6 (4 H), singlet at τ 7.90 (1 H, disappears on D_2O addition), broad singlets at τ 7.14 (1 H) and 6.96 (1 H), doublets at τ 6.08 (1 H, J = 6.0 Hz) and 3.76 (1 H, J = 3.5 Hz), and a multiplet at τ 2.80 (5 H).

The third product collected from preparative vpc was identified as 2-phenyl-6-*exo*-acetoxy-2-norbornene (**12**) (23%) on the basis of the following evidence: bp 70° (0.1 mm).

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.93; H, 7.14.

The infrared spectrum shows a strong carbonyl band at 5.73 μ and has other bands at 3.40, 6.20, 8.00, and 9.51 μ. The ultraviolet spectrum (95% ethanol) has a λ_{max} at 262 nm (ϵ 11,600). The mass spectrum of **12** exhibited peaks *m/e* 228 (M^+), 186, 168, 142 (base), and 115. The nmr (100 MHz) showed a multiplet from τ 8.16–8.60 (4 H), a singlet at τ 8.06 (3 H), broad singlets at τ 7.16 (1 H) and 6.76 (1 H), a doublet of doublets at τ 5.36 (J = 7.0 and 3.0 Hz, 1 H), a doublet at τ 3.76 (1 H, J = 3.0 Hz), and a multiplet at τ 2.80 (5 H).

2-Phenyl-6-*exo*-acetoxy-2-norbornene (**12**) could be converted to 2-phenyl-2-norbornene-*exo*-6-ol (**11**) by reduction with lithium aluminum hydride. To a sample of 0.1 g of acetate **12** in 5 ml of anhydrous ether was added an excess of lithium aluminum hydride. The resulting suspension was stirred for 2 hr at room temperature and then quenched by the slow addition of 1 ml of water. The ethereal layer was dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave 0.075 g (92%) of 2-phenyl-2-norbornen-*exo*-6-ol. The structure of both the alcohol and acetate were unambiguously identified by comparison with authentic samples synthesized in the manner described below.

The second peak to be eluted from the column was identified as 2-phenyltricyclo[2.2.1.0^{2,6}]heptan-3-ol (**13**) (27%) on the basis of its spectral data: infrared spectrum, 2.78, 3.00, 3.49, and 9.20 μ; mass spectrum (*m/e*) 186 (M^+, base), 168, 142 115 and 91; nmr (100 MHz $CDCl_3$) multiplets at τ 8.60 (6 H) and 8.0 (2 H), a singlet at τ 6.06 (1 H), and a multiplet at τ 2.90 (5 H).

The first peak to be eluted from the preparative vpc column was assigned as 2-phenyl-3-acetoxytricyclo[2.2.1.0^{2,6}]heptane **14** (28%): infrared spectrum, 3.34, 5.76, 8.01, and 9.50 μ; mass spectrum (*m/e*) 228 (M^+), 186, 168, 142 (base), 129, 120, 105, and 91. Treatment of 2-phenyltricyclo[2.2.1.0^{2,6}]heptan-3-ol with acetic anhydride in pyridine in the standard fashion gave **14** as the sole acetate.

Establishment of Structure of 2-Phenyl-6-*exo*-acetoxy-2-norbornene. To a 1.0-g sample of 2-*exo*-phenylnorbornane-2-*endo*,-6-*exo*-diol[38] (**15**) in 10 ml of pyridine was added 1 ml of acetic anhydride. After standing for 12 hr the solution was diluted with 40 ml of water and extracted with ether. The ethereal extracts were washed with 10% hydrochloric acid followed by water. Evaporation of the solvent after drying gave 1.2 g of 2-*exo*-phenyl-6-*exo*-acetoxynorbornan-2-ol (**16**): bp 70° (0.1 mm); infrared spectrum 2.80, 2.95, 3.40, 5.78, 8.03, and 9.72 μ; nmr (100 MHz, $CDCl_3$) broad singlet at τ 8.5 (4 H), singlet at τ 8.16 (3 H), multiplet at τ 8.08 (2 H) and 7.80 (1 H), singlets at τ 7.36, (1 H) and 6.52 (1 H disappears on addition of D_2O), doublet at τ 4.72 (1 H, J = 7.0 Hz), multiplet at τ 2.80 (5 H).

A mixture of 2.0 g of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt and 2.0 g of 2-*exo*-phenyl-6-*exo*-acetoxynorbornan-2-ol (**16**) in 25 ml of benzene was heated at reflux for 6 hr. The reaction mixture was diluted with 25 ml of water and the two-phase system was extracted with benzene. The combined benzene layer was dried and the solvent was removed under reduced pressure. The crude oil was purified by a molecular distillation, bp 70° (0.1 mm), and gave 1.4 g of 2-phenyl-6-acetoxy-2-norbornene (**12**). The spectral properties of this compound were identical in every way with the acetate isolated from the reaction of 2-phenyltricyclo[3.2.0.0^{3,7}]heptan-2-ol (**8**) with acetic acid.

3-Phenyl-Δ^3-cyclopentenylacetaldehyde. To a 0.5-g sample of 2-*exo*-phenylnorbornane-2-*endo*,6-*exo*-diol (**15**) in 25 ml of 95% ethanol at 0° was added 10 drops of concentrated hydrochloric acid. The solution was allowed to stir at 0° for 1 hr and was then

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[38] Synthesized according to the procedure of P. G. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, **89**, 946 (1967).

[39] C. J. Collins and B. M. Benjamin, *ibid.*, **89**, 1652 (1967).

diluted with 50 ml of water. The aqueous solution was washed with 10% sodium bicarbonate and water and dried over magnesium sulfate. Evaporation of the solvent gave 3-phenyl-Δ^3-cyclopentenylacetaldehyde as a colorless liquid. A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol to give an analytical sample: mp 132–133°.

Anal. Calcd for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95. Found: C, 62.54; H, 4.89.

The infrared spectrum has absorption bands at 3.45, 3.70, 5.78, 6.10, 13.31, and 14.40 μ. The mass spectrum shows the parent ion at *m/e* 186 and has the base peak at *m/e* 142. The 100-MHz nmr spectrum shows multiplets centered at τ 7.80 (4 H) and 7.30 (3 H), a triplet at τ 4.12 (1 H, J = 2.0 Hz), a multiplet at τ 2.90 (5 H), and a triplet at τ 0.48 (1 H, J = 1.5 Hz).

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450-W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly approximately 6 cm from the immersion well. The light was filtered by circulation of solution containing 46 g of nickel sulfate hexahydrate and 14 g of cobaltous sulfate heptahydrate in 100 ml of water through the inner jacket.[20] This solution permitted the following wavelength distribution to pass through: 6% 2967 Å, 20% 3025 Å, 62% 3130 Å, 10% 3340 Å. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations.[22] Reliably reproducible output rates of 4.86×10^{16} quanta sec^{-1} were recorded. After the irradiation the degree of reaction was determined by quantitative vapor-phase chromatography. The conversions in the irradiations were run to 15% or less. The mass balance in these runs were generally better than 95%.

Quenching Studies. Benzoylbicyclo[2.1.1]hexane (90 mg) was dissolved in 5 ml of benzene. To each of five Pyrex tubes was added 1 ml of the above solution. To four of the tubes was added respectively 2 ml of a 0.05, 0.10, 0.15, and 0.20 *M* solution of piperylene in benzene. One tube without any piperylene was set aside as a control, and the four degassed, sealed tubes were placed in a turntable surrounding a 450-W Hanovia medium-pressure Hg lamp in a quartz immersion well. The turntable was rotated slowly and the tubes were irradiated for 10% conversion of starting material. At the end of this time, an internal standard (biphenyl) was added to each of the tubes, and the solvent was removed at reduced pressure at room temperature until the residual volume was about 0.1 ml. The mixture was analyzed by glpc on a 5 ft × 0.25 in. 5% Degs on 60–80 mesh Chromosorb W column at an oven temperature of 150° and a helium flow rate of 60 cc/min. The area under the peaks due to the standard (biphenyl) and products were measured using a planimeter after triangulation. Each set of chromatograms was measured twice in this way, and the results were converted to per cent reaction based on starting ketone.

Phosphorescence Emission Studies. The emission spectra were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high-pressure xenon lamp, as supplied by the manufacturer. All emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. All compounds having relatively long radiative lifetimes were recorded on a *x-y* plotter. Samples having short radiative lifetimes (<100 sec) were measured by photographing the decay curve on an oscillograph. The chopper was rotated manually to obtain the decay curve. The logarithmic intensities of the decay curve were plotted *vs.* time and the slope of the line at a logarithmic value of 2.303 gave the mean lifetime (τ_0).

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Nature of the Reactive Species in the Photohydration of Uracil and Cytosine Derivatives

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Abstract: The photohydration rates as functions of pH of 3-methyluracil, 5-fluorouracil, cytidine, deoxycytidine, uridine 2′-phosphate, and uridine 5′-phosphate are presented and discussed; the functions are sigmoidal and the inflection points of the curves are interpreted to reflect the pK values of the singlet excited molecules. From these curves, it is suggested that in general for uracil and cytosine derivatives, the neutral excited molecule is the species which reacts fastest with water; cationic and anionic species react more slowly. The curves for uracils substituted in the 3 position or unsubstituted in the 1 and 3 position reflect the pK for loss of the 1 proton (pK = 4–5); those for 1-substituted uracils reflect the pK for loss of the 3 proton (pK = 6–7). These values agree fairly well with the pK^* values calculated for the singlet excited states of uracil and thymine, and suggest strongly that the reactive state for photohydration does not resemble the ground state electronically, but does resemble a singlet excited state. This evidence is supported by the observation of negative temperature coefficients for photohydration, analogous to the negative temperature coefficients observed for fluorescence.

Photolysis of uracil (I) and uracils substituted in the 1 and 3 positions converts them into mixtures of cyclobutane type photodimers and 5,6-dihydro-6-hydroxyuracil derivatives (II) "photohydrates."[2] The ratio of photohydrate to dimer obtained depends upon the nature of the uracil derivative and the photolysis conditions.[2] Cytosine and thymine and their derivatives form analogous photoproducts. These types of photoproducts are known to have important roles in the inactivation and mutation of living organisms and viruses by ultraviolet light.[2] Information about the charge on the reactive species and about the pK of the excited species may be gained by examining the

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(2) (a) J. G. Burr, *Advan. Photochem.* 6, 193 (1968), and general references cited therein; (b) K. C. Smith and P. C. Hanawalt, "Molecular Photobiology," Academic Press, New York, N. Y., 1969.