tert-Bu; retention time = 0.68 that of the diene): nmr (CCl_4) δ 0.7 (m, cyclopropyl, **13d**), 0.9–2.1 (m, methyl, methylene, and allyl), and 4.8 (m, vinyl, **14d**).

Irradiation of Triene 12a (R = H). A solution of 76.6 mg of a mixture of the triene **12a** and the bicyclo[3.1.0]hexene **13a** (71.6% triene, 16.7% bicyclo[3.1.0]hexene, 4% diene **12a**, and 8% isomer X) in 28 ml of pentane was placed in a 28-ml quartz irradiation flask fitted with a 100-W Hanovia lamp, a gas inlet, and a rubber serum stopper. The solution was degassed in the standard manner and irradiated for 170 min. The reaction was followed by glpc. The final mixture (65 mg, 85% yield), isolated by rotary evaporation of the pentane, contained 20% triene **12a**, 49% bicyclo[3.1.0]hexene **13a**, 1% diene **11a**, 10% vinyl cyclobutene **14a**, and 20% isomer X. Data for intermediate times are shown on Figure 1.

Irradiation of Triene 11c (R = *i*-Pr). A solution of 5.8 mg of the triene **12c** (83% triene, less than 1% diene **11c**, and 16% bicyclo[3.1.0]hexene **13c**, and vinyl cyclobutene **14c**) in 4 ml of pentane was placed in a 6-ml Vycor tube which was held in a merry-go-round apparatus. This solution was irradiated for 1630 min with a 254-nm mercury resonance lamp (Nester/Faust UV-300). The reaction was followed by glpc. The final solution contained 21% triene **13c**, 57% diene **11c**, and 22% bicyclo[3.1.0]hexene **13c** and vinyl cyclobutene **14c**. Data for intermediate times are shown in Figure 2.

Relative Quantum Yields of 11a and 11c. Three solutions, 6.9 mg of diene **11a** in 4 ml of pentane, 6.9 mg of diene **11c** in 4 ml of pentane, and 1.7 mg of both dienes in 4 ml of pentane (all solutions contained hexadecane as an internal standard), were placed in a 6-ml Vycor tubes and irradiated for 640 min with a 254-nm mercury resonance lamp in a merry-go-round apparatus. The disappearance of the dienes **11a** and **11c** was followed by glpc. The data up to 10% conversion were used to calculate the ratio of the quantum yields.

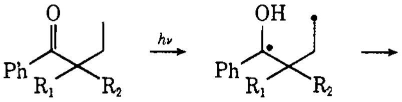
Photochemistry of Bicycloalkyl Phenyl Ketones[1a]

Frederick D. Lewis,* Richard W. Johnson, and Ronald A. Ruden[1b]

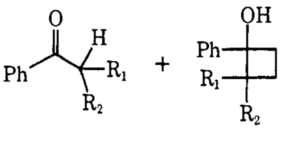
Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received September 13, 1971*

Abstract: The photochemistry of several bicycloalkyl and cyclopentyl phenyl ketones has been investigated. The quantitative and stereoselective photochemical syntheses of a tricyclo[3.2.1.$0^{3,6}$]octane and tricyclo[3.3.1.$0^{2,7}$]nonane are described. α-Methyl substituents are found to increase greatly the ratio of photocyclization to photoelimination products and to affect the reactivity of the carbonyl excited state toward γ-hydrogen abstraction. The large variation in the rate constants for secondary γ-hydrogen abstraction (2.5×10^6 to 1×10^{10} sec^{-1}) for the ketones studied is attributed primarily to conformational factors.

Recently we have described a marked enhancement of the ratio of photocyclization to photoelimination products from alkyl phenyl ketones upon α substitution.[2,3] For example, α-methyl (**2**) and α,α-dimethyl (**3**) substitution of butyrophenone (**1**) increases the percentage of cyclization from 10 to 29 and 89%, respectively (eq 1).[2] Both cyclization and elimination products are formed from a common 1,4-biradical intermediate, which can also undergo reversion to ground state ketone. The effects of substituents upon the behavior of the 1,4-biradical intermediates have been attributed to small nonbonded interactions in the conformations of the biradical necessary for cyclization and elimination.[2,4] These observations led to the prediction[2] that by proper choice of substituent some degree of control over product composition and stereochemistry might be obtained. The present investigation of the photochemistry of several bicycloalkyl and cyclopentyl phenyl ketones provides support for this supposition. High yield, stereoselective syntheses of several novel bridged polycyclic cyclobutanols are reported. In addition, excited state reactivity toward γ-hydrogen abstraction is found to be highly dependent upon conformational factors for both rigid (bicycloalkyl) and nonrigid (cyclopentyl and acyclic) phenyl ketones.



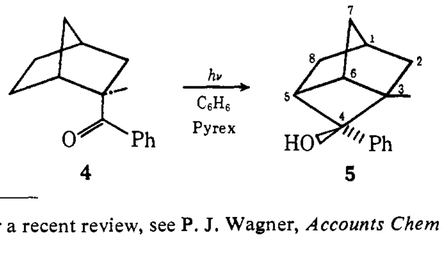
$1, R_1 = R_2 = H$
$2, R_1 = H; R_2 = CH_3$
$3, R_1 = R_2 = CH_3$



(1)

Results

Product Studies. The ketones studied were synthesized from the corresponding carboxylic acids by reaction with phenyllithium (see Experimental Section). Product studies were carried out on dilute ($\lesssim 1\%$) benzene solutions irradiated under nitrogen or argon with a 450-W, medium-pressure mercury lamp



(2)

4 **5**

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[1] (a) The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) National Institutes of Health Predoctoral Fellow, 1968–1971.

[2] (a) F. D. Lewis and T. H. Hillard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970). (b) F. D. Lewis and T. Hillard, *ibid.*, in press.

[3] For a preliminary communication of a portion of this work, see F. D. Lewis and R. A. Ruden, *Tetrahedron Lett.*, 715 (1971).

[4] For a recent review, see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

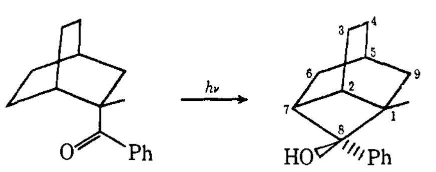
in a Pyrex immersion well. Irradiation of *endo*-2-benzoyl-2-methylnorbornane (**4**) results in quantitative conversion to a single photoproduct. No other products could be detected by analytical vpc or by nmr analysis. The photoproduct was stable to prolonged irradiation through Pyrex or refluxing in toluene. Thus a quantitative yield of **5** could be obtained by exhaustive photolysis of **4**. The tricyclic structure **5** was assigned to the photoproduct on the basis of spectral data. The mass spectrum of **5** is similar to that of **4**, having peaks at m/e 214 (M^+), 196, 109 (base peak), 105, and 94. The nmr spectrum (CCl_4, δ units) of **5** is composed of a sharp aromatic region at 7.1, a broad six proton methylene region, a sharp hydroxyl singlet at 1.65, a three proton methine region, and a methyl singlet (Table I).

Table I. Chemical and Paramagnetic Shifts with Eu(DPM)$_3$ (CCl_4, δ units)

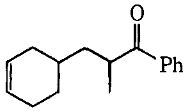
Compd	Proton	CH_3	H_1	H_5	H_6
5	Chemical shift	1.24	2.15	2.65	2.45
	with Eu(DPM)$_3$	2.28	2.52	4.25	4.40
	ΔEu(DPM)$_3$	1.04	0.37	1.60	1.95
		CH_3	H_5	H_2	H_7
7	Chemical shift	1.22		(2.1–2.6)	
	with Eu(DPM)$_3$	2.20	2.7	4.3	4.3
	ΔEu(DPM)$_3$	0.98	<0.6	~2.0	~2.0

The hydroxyl proton chemical shift and its lack of significant concentration or solvent dependence are indicative of a hindered hydroxyl group. The ir of **5** (0.13 M in CCl_4) exhibits a free O–H stretch at 3610 cm^{-1} and a weak hydrogen-bonded O–H stretch at 3460 cm^{-1} with $\epsilon(OH)^b/\epsilon(OH)^f = 0.09$. Only the sharp free O–H stretch is observed for 0.018 M **5**. Thus the ir spectra also indicate a very hindered hydroxyl group, as expected for **5** or its C_4 epimer. The assignment of the probable C_4 stereochemistry was facilitated by the use of the contact shift reagent Eu(DPM)$_3$.[5,6] Addition of ~0.15 equiv of Eu(DPM)$_3$ resulted in large shifts for the methyl and two of the three methine protons (Table I), in accord with structure **5**, but not its C_4 epimer.

2-Benzoyl-2-methylbicyclo[2.2.2]octane (**6**) was observed to undergo complete (>90%) and stereoselective conversion to the tricyclo[3.3.1.0^{2,7}]nonane **7** (eq 3). The absence of the expected photoelimination product **8** was demonstrated by vpc coinjection of an authentic sample of **8** with the photolysis mixture. The assignment of structure **7** to the photoproduct follows from its spectral characteristics which are very similar to those of **5**. The nmr spectrum (CCl_4, δ units) of **7** is composed of an aromatic region at 7.1, a broad methylene region, a sharp hydroxyl singlet at 1.6, a three proton methine region, and a methyl singlet (Table I). Addition of 0.15 equiv of Eu(DPM)$_3$ results in large shifts for the methyl and two of the three methine protons, in accord with the assigned structure, but not its C_8 epimer. No diamagnetic shifts with Eu(DPM)$_3$ were observed for either **5** or **7**. The shift reagent results are compatible with the structures assigned to **5** and **7**, but do not constitute an absolute structure proof.



6 **7** (3)



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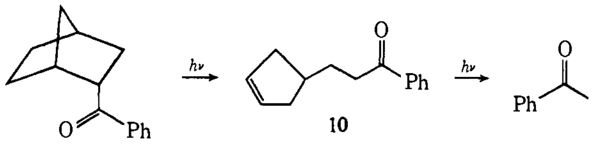
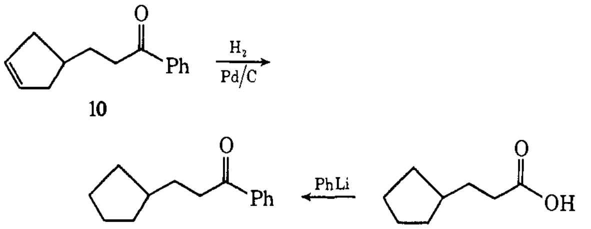
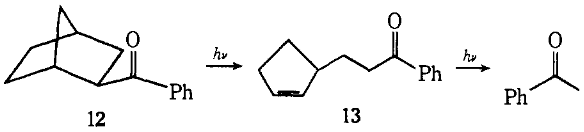
Irradiation of *endo*-2-benzoylnorbornane (**9**) results primarily in the formation of the photoelimination product (**10**). Prolonged irradiation of **9** or irradiation of isolated **10** led to the formation of acetophenone (eq 4). The absence of photocyclization product formation from **9** was deduced from the absence of O–H stretching in the ir spectra of 0.1 M hexane solutions of **9** irradiated to ~40% conversion at 27, 0, and −35°. In view of the thermal and photochemical stability of **5** and **7** it seems highly unlikely that formation of >5% cyclization product from **9** could go undetected. Hydrogenation of **10** over palladium on carbon gave a product having spectral properties and vpc retention time identical with a synthetic sample of **11** (eq 5). Similarly, irradiation of *exo*-2-benzoylnorbornane (**12**) results in formation of the photoelimination product **13**, which is converted to acetophenone upon prolonged irradiation (eq 6) and to **11** upon hydrogenation.



9 **10** (4)

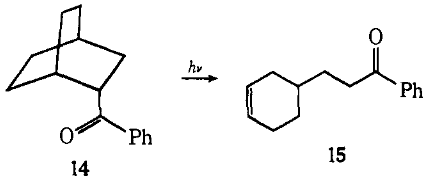


10 **11** (5)



12 **13** (6)

2-Benzoylbicyclo[2.2.2]octane (**14**) has previously been



14 **15** (7)

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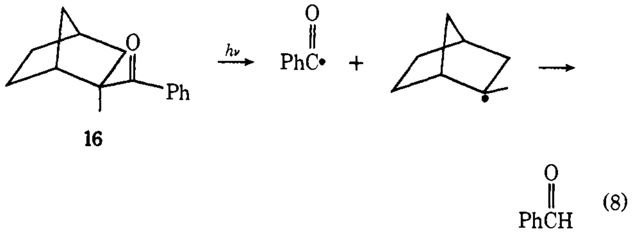
[5] C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

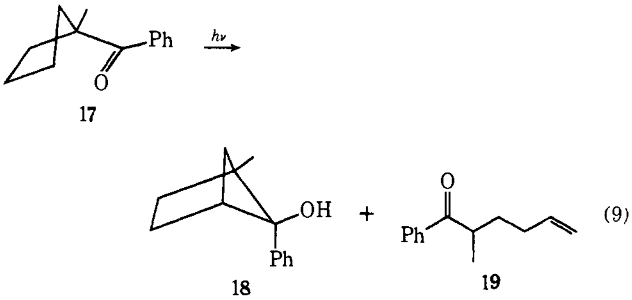
[6] For recent examples of the use of Eu(DPM)$_3$ with alcohols, see (a) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, **92**, 5734 (1970); (b) J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971); (c) B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *ibid.*, **93**, 3281 (1971).

reported to give only the photoelimination product **15** upon irradiation in cyclohexane (eq 7).[7] Irradiation in benzene gave a similar result with no evidence for photocyclization product formation.

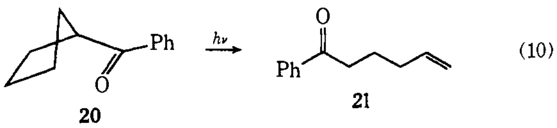
In contrast to the behavior of the other bicycloalkyl phenyl ketones studied, *exo*-2-benzoyl-2-methylnorbornane (**16**) undergoes photochemical α cleavage rather than photoelimination or cyclization. Irradiation of ketone **16** in degassed benzene solution gives benzaldehyde and a number of unidentified alkane and alkene products (eq 8), presumably derived from 2-methylnorbornyl radical.[8]



Irradiation of 1-methylcyclopentyl phenyl ketone (**17**) results primarily in the formation of the bicyclo[2.1.1]hexane **18** (eq 9). Only a small amount (<5%) of the elimination product **19** could be detected by vpc coinjection of the photolysis mixture with an authentic sample of **19**. The ir of **18** (0.10 *M* in CCl_4) exhibits a free O–H stretch at 3610 cm^{-1} and a weak hydrogen-bonded O–H stretch at 3450 cm^{-1}. The nmr spectrum (CCl_4, δ units) of **18** is composed of a sharp aromatic region at 7.34, a broad methine at 2.0, a methyl singlet at 1.42, and a poorly resolved methylene region from 0.8 to 1.9. Lack of resolution of the methylene protons hinders assignment of C_5 stereochemistry, even with the aid of Eu(DPM)$_3$. However, by analogy to **5** and **7** the most probable stereochemistry is that given in **18**. Unlike **5** and **7**, **18** is rather unstable thermally with a half-life of ~30 min in refluxing toluene (111°). The major thermolysis products are **17** and 3-methylcyclopentyl phenyl ketone.



Irradiation of cyclopentyl phenyl ketone (**20**) in benzene solution has been reported to give the photoelimination product **21** and several secondary photoproducts (eq 10).[9] We also observe formation of **21** from **20** with no evidence for photocyclization product formation.



Mechanistic Studies. Degassed 0.05 *M* solutions of ketones **4**, **6**, **9**, **12**, **14**, **16**, **17**, and **20** contained in Pyrex tubes were irradiated using a 450-W, medium-pressure mercury lamp with a filter solution of potassium chromate to isolate the 313-nm line. Light intensities were measured by simultaneous irradiation of the ketones and benzophenone–benzhydrol actinometer solutions[10] at 25°. Product yields were determined by analytical vpc for conversions of <5% in benzene solution and in 67% *tert*-butyl alcohol–benzene solution for ketones **4**, **6**, **9**, and **14** or 3 × 10^{-3} *M* 1-dodecanethiol–benzene for **16**. The resulting quantum yields are given in Table II along with results for valerophenone (**22**).[2b] The quantum yield for formation of **5** from **4** increased with increasing *tert*-butyl alcohol concentration but did not level off to a maximum value. The 3 × 10^{-3} *M* 1-dodecanethiol was sufficient to provide a maximum quantum yield for benzaldehyde formation from ketone **16** (eq 8) and did not lead to competitive photoreduction.

Table II. Quantum Yield and Kinetic Data for Bicycloalkyl and Cyclopentyl Phenyl Ketones

Ketone	Solvent	Φ	$k_q\tau$, M^{-1}	$1/\tau \times 10^{-8}$ sec^{-1}
4, *endo*-2-Benzoyl-2-methylnorborane	C_6H_6 C_6H_6–*t*-BuOH[a]	0.49[c] 0.63	58	0.86
6, 2-Benzoyl-2-methylbicyclo[2.2.2]octane	C_6H_6 C_6H_6–*t*-BuOH[a]	0.13[c] 0.26	16	3.0
9, *endo*-2-Benzoylnorborane	C_6H_6 C_6H_6–*t*-BuOH[a]	0.10[d] 0.13	0.7	70
12, *exo*-2-Benzoylnorborane	C_6H_6	0.13[d]	420	0.12
14, 2-Benzoylbicyclo[2.2.2]octane	C_6H_6 C_6H_6–*t*-BuOH[a]	0.041[d] 0.058	0.5	100
16, *exo*-2-Benzoyl-2-methylnorborane	C_6H_6 C_6H_6–RSH[b]	0.031[e] 0.096	430	0.12
17, 1-Methylcyclopentyl phenyl ketone	C_6H_6	0.19[c]	330	0.15
20, Cyclopentyl phenyl ketone	C_6H_6	0.22[d]	2000	0.025
22, Valerophenone	C_6H_6	0.091[c,f] 0.33[d,f]	36[f]	1.4[f]

[a] 67% *tert*-butyl alcohol–benzene solvent. [b] Benzene containing 3 × 10^{-3} *M* 1-dodecanethiol. [c] Quantum yield for photocyclization. [d] Quantum yield for photoelimination. [e] Quantum yield for benzaldehyde formation. [f] Values from ref 2b.

Photolysis of ketones **4**, **6**, **9**, **12**, **14**, **17**, and **20** in degassed benzene solution in the presence of varying amounts of *trans*-piperylene resulted in linear Stern–Volmer plots (Φ_0/Φ *vs.* [quencher], eq 11). A linear

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \tag{11}$$

Stern–Volmer plot for quenching of benzaldehyde formation from ketone **16** was obtained using naphthalene as the quencher (366-nm irradiation). The slopes of the Stern–Volmer plots are equal to $k_q\tau$ (Table II), where k_q is the rate constant for quenching of the ketone triplet state by piperylene and τ is the ketone triplet lifetime. Assumption of the value 5 × 10^9 M^{-1} sec^{-1}

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(7) C. L. McIntosh, *Can. J. Chem.*, **45**, 2267 (1967).

(8) Reactions of the 2-methylnorbornyl radical have been reviewed; P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 177 (1970).

(9) A. Padwa and D. Eastman, *J. Amer. Chem. Soc.*, **91**, 462 (1969).

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

for k_q[11] allows calculation of τ or $1/\tau$ (Table II). The values for the quantum yield and $1/\tau$ for **20** are lower than those obtained by Padwa and Eastman[9] under considerably different conditions.

All of the ketones studied had normal n,π^* absorption bands with λ_{max} 323–326 nm in hexane solution and showed structured emission similar to that of acetophenone in EPA glasses at 77°K. It is generally assumed that aromatic ketones undergo intersystem crossing more rapidly than photochemical reaction from the n,π^* singlet state.[4,12] In view of the very short lifetimes of **9** and **14** (*vide infra*) it was felt advisable to establish the identity of the reactive excited state. The quantum yield for triplet sensitized cis–trans isomerization of piperylene by **9** was measured as a function of piperylene concentration. A plot of $0.55/\Phi_{c\rightarrow t}$ *vs.* 1/[piperylene] (eq 12)[4] had an intercept of 1.0. Thus

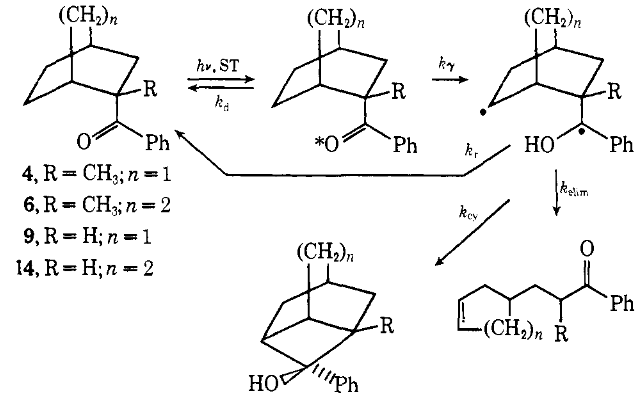
$$\frac{0.55}{\Phi_{c\rightarrow t}} = \frac{1}{\Phi_{ST}}\left(1 + \frac{1}{k_q\tau[Q]}\right) \qquad (12)$$

9 has an intersystem crossing quantum yield of unity. From the slope (1.4) a value of $k_q\tau$, in good agreement with that from piperylene quenching of product formation (Table II), is obtained.

Discussion

The photochemical behavior of the bicycloalkyl phenyl ketones **4**, **6**, **9**, and **14** can be discussed conveniently in terms of Scheme I. Excitation followed by intersystem crossing leads to formation of the reactive n,π^* triplet state. The triplet lifetime (τ) is determined by the rate constants for γ-hydrogen abstraction (k_γ) and nonradiative decay (k_d) ($1/\tau = k_\gamma + k_d$). However, since k_d for most alkyl ketones in benzene solution is much smaller than the values for $1/\tau$ in Table II,[13] the n,π^* triplet lifetime is determined only by the rate constant for γ-hydrogen abstraction ($1/\tau = k_\gamma$). For all the ketones studied the C_γ–H bonds are secondary. Thus the large variation in k_γ ($1/\tau$, Table II) reflects conformational or stereoelectronic requirements for γ-hydrogen abstraction rather than energetic requirements.[2a,4,9,14] Since $k_\gamma \gg k_d$, 1,4-biradical intermediate formation should be totally efficient for the ketones studied. Thus the quantum yields for product formation (eq 13, 14) depend only on the competition between the three biradical reactions and not on the excited state reactivity.

Scheme I



$$\Phi_{cy} = k_{cy}/(k_{cy} + k_{elim} + k_r) \qquad (13)$$

$$\Phi_{elim} = k_{elim}/(k_{elim} + k_{cy} + k_r) \qquad (14)$$

The effects of α-methyl substituents on the behavior of bicycloalkyl phenyl ketones are of two important types: the effect on excited state reactivity and the effect on the behavior of the 1,4-biradical intermediates.

The bicycloalkyl phenyl ketones **9** and **14** undergo γ-hydrogen abstraction approximately 50 times faster than their α-methyl derivatives **4** and **6** or valerophenone (**22**). The rate constants for γ-hydrogen abstraction for ketones **9** and **14** are clearly the most rapid that have been observed for saturated alkyl phenyl ketones and are comparable to those for the highly reactive α-alkoxyacetophenones.[15] These abnormally rapid rate constants may be due to the very favorable conformations of ketones **9** and **14** for γ-hydrogen abstraction. The rigid bicycloalkane structure permits the carbonyl oxygen to come within ~1.7 Å of the γ hydrogen[16] without substantial steric destabilization in the transition state. In the case of the α-methyl ketones **4** and **6**, the transition states for γ-hydrogen abstraction are destabilized by methyl–phenyl eclipsing interactions. Such eclipsing interactions are doubtless important if the carbonyl and phenyl groups remain coplanar in the triplet state.[17]

The large enhancement of k_γ for ketones **9** and **14** relative to valerophenone provides potential insight into the nature of the transition state for γ-hydrogen abstraction. Molecular orbital calculations by Boer, Shannon, and McLafferty[18] support a planar transition state with a O–H_γ distance of 1.1 Å for γ-hydrogen transfer in 2-pentanone. A nonplanar transition state with C_β out of the plane of the carbonyl, C_α, C_γ, and H_γ has a much longer O–H_γ distance (1.8 Å),[18] but does not have most of the 4-kcal methylene eclipsing energy present in the planar transition state. The smaller value of k_γ for valerophenone *vs.* ketones **9** and **14** is consistent with the longer O–H_γ distance for the nonplanar transition state. Strong evidence for a nonplanar transition state for acyclic ketones is provided by the observation that α- and β-methyl substituents do not diminish the rate constant for γ-hydrogen abstraction of alkyl phenyl ketones.[2b,19]

The dependence of k_γ upon O–H_γ distance is further illustrated by the behavior of ketones **12** and **16** (Table II). The O–H_γ bond distances for **12** and **16** (~2.2 Å) are longer than those for **9** and **14**, respectively, whereas other steric and energetic considerations should be similar. Methyl–phenyl eclipsing should make γ-hydrogen abstraction slower for **16** than for **12**. Thus it is not surprising that γ-hydrogen abstraction does not efficiently

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(11) (a) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968); (b) W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969).

(12) R. M. Hochstrasser, *Accounts Chem. Res.*, 1, 266 (1968).

(13) (a) F. D. Lewis, *Tetrahedron Lett.*, 1373 (1970); (b) F. D. Lewis, *J. Phys. Chem.*, 74, 3332 (1970), and references therein.

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

(15) F. D. Lewis and N. J. Turro, *ibid.*, **92**, 311 (1970).

(16) The O–H_γ distances were estimated using Prentice-Hall Framework molecular models. For cyclopentyl phenyl ketone and valerophenone, similar values were obtained with Dreiding models.

(17) R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, 74, 415 (1970).

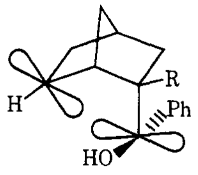
(18) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, 90, 7239 (1968).

(19) The enhanced reactivity of α-alkoxyacetophenones toward photochemical γ-hydrogen abstraction may be due in part to the absence of methylene eclipsing interactions in the six-membered transition state.[15] See, however, ref 4.

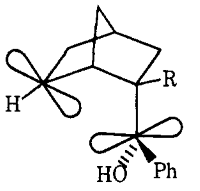
compete with α cleavage for **16**. The rate constant for α cleavage of **16** (0.12×10^8 sec^{-1}) is comparable to those for several other *tert*-alkyl phenyl ketones.[2b,20,21]

For the cyclopentyl phenyl ketones **17** and **20** both the conformational mobility of the molecule and the O–H$_\gamma$ distance are probably important in determining the rate constants for γ-hydrogen abstraction. Padwa[9] has pointed out that an axial benzoyl group in a half-chair conformation is necessary for γ-hydrogen abstraction from **20**. The enhanced reactivity of **17** ($k_\gamma = 0.15 \times 10^8$ sec^{-1}) *vs.* **20** ($k_\gamma = 0.025 \times 10^8$ sec^{-1}), in spite of the introduction of an unfavorable phenyl–methyl interaction, may be due to an increased population of the reactive axial conformation as a result of α-methyl substitution.[23]

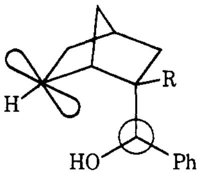
The effect of α-methyl substituents on the behavior of the 1,4-biradical intermediates from bicycloalkyl and cyclopentyl phenyl ketones is even more dramatic than the effect on acyclic alkyl phenyl ketones.[2] Whereas an increase in the percentage of cyclization from 29 to 89% was observed upon going from **2** to **3**, ketones **9**, **12**, **14**, and **20** form <10% and ketones **4**, **6**, and **17** >90% cyclization products. These results can be explained analogously to those for acyclic alkyl phenyl ketones[2] by considering nonbonded interactions in the transition states for biradical cyclization (**22**), elimination (**23**), and reabstraction (**24**). The conformations drawn reflect the requirements of overlap of both radical centers for cyclization, continuous overlap of both radical centers with the σ bond undergoing cleavage for elimination, and a six-membered transition state for reabstraction.[2,4] The fact that little or no cyclization product is formed from **9** and **14** implies that $k_{\text{elim}} \sim k_\text{r} \gg k_{\text{cy}}$ (Scheme I). Inspection of models reveals no particularly unfavorable nonbonded interactions in the transition states for elimination (**23**) and reabstraction (**24**). Thus it is not surprising that these reactions occur more readily than cyclization, for which the phenyl group must be underneath the bicycloalkyl portion of the biradical (**22**). The predominance of cyclization product from **4** and **6** indicates that $k_{\text{cy}} \sim k_\text{r} \gg k_{\text{elim}}$. Since the steric requirements for cyclization are essentially the same as for **9** and **14**, α-methyl substitution must significantly diminish k_r and k_{elim}. Again, the phenyl–methyl eclipsing interactions present in the transition states for elimination (**23**) and reabstraction (**24**) for **4** and **6**, but not for **9** and **14**, can account for the observed effects. Entirely analogous reasoning can be used to explain the effect of an α-methyl substituent on the behavior of the 1,4-biradical intermediate from cyclopentyl phenyl ketone. The increased quantum yields for both cyclization and elimination product formation in *tert*-butyl alcohol–benzene solution (Table II) probably reflect a decrease in k_r due to hydrogen bonding which hinders the reabstraction reaction.[24]



22



23



24

The photochemical synthesis of novel bridged polycyclic cyclobutanols has been the subject of considerable recent attention.[25] The photocyclizations of **4** to **5** (eq 2) and **6** to **7** (eq 3) are of interest in this context since they are essentially quantitative and stereoselective reactions. As such they provide simple, high yield syntheses of a tricyclo[3.2.1.0^{3,6}]octane and a tricyclo[3.3.1.0^{2,7}]nonane. Nonphotochemical syntheses of these ring systems involve multiple steps and low yields.[26,27] The stereoselective formation of the tricyclic compounds with the phenyl trans to the α-methyl and equatorial in the cyclobutyl ring might have been expected on energetic grounds or by analogy to α-methylbutyrophenone (**2**) which forms only *trans*-2-methyl-1-phenylcyclobutanol.[2] 1-Methylcyclopentyl phenyl ketone (**17**) also forms primarily one photocyclization product, presumably the trans isomer **18**. The formation of the more thermodynamically stable of two possible cyclobutanols in the above examples is indicative of a small activation energy for 1,4-biradical cyclization, in agreement with previous results.[28]

In conclusion, the excited state reactivity and product distribution of several bicycloalkyl and cyclopentyl phenyl ketones are profoundly affected by molecular geometry and α-methyl substitution. The effect on the behavior of the biradical intermediates lends support to the transition state arguments used to explain the effects of substituents for methyl substituted butyrophenones.[2] Enhancement of the ratio of photocyclization to photoelimination products by α-methyl substitution of alkyl phenyl ketones appears to be a fairly general phenomenon. Unfortunately, the apparent requirement of an α-methyl phenyl ketone[22] limits the synthetic utility of such photocyclization reactions.

Experimental Section

endo-**2-Benzoyl-2-methylnorbornane (4).** *endo*-5-Methylnorbornene-5-carboxylic acid was prepared by the method of Beckmann, *et al.*[29] Reaction of the acid (1.0 g, 0.0065 mol) with 2 equiv of phenyllithium in ether solution under nitrogen gave after work-up and distillation 0.4 g (30%) of *endo*-5-benzoyl-5-methylnorbornene, bp 98–101° (0.35 mm); uv spectrum, $\lambda_{\max}$ 323 nm, $\epsilon_{\max}$ 85 (hexane); nmr (CCl$_4$) δ 1.2–1.6 (m, 4 H), 1.6 (s, 3 H), 2.8 (m, 1 H), 3.1 (m, 1 H), 6.0 (m, 2 H), 7.4 (m, 3 H), and 7.8 (m, 2 H). Hydrogenation of 0.26 g of unsaturated ketone over palladium on carbon in ethanol

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[20] Small amounts of α cleavage (<5%) were observed for ketone 17 and could have gone undetected for ketones 4 or 6.

[21] It was hoped that the importance of methyl–phenyl eclipsing could be assessed by studying the corresponding bicycloalkyl methyl ketones. Unfortunately, α cleavage is the predominant reaction for α-methylbicycloalkyl methyl ketones as it is for other *tert*-alkyl alkyl ketones,[22] but not for all *tert*-alkyl phenyl ketones.[2b]

[22] N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, **90**, 504 (1968).

[23] Implicit in such an explanation is the assumption that the rate of interconversion of axial and equatorial isomers is rapid compared to the rate of hydrogen abstraction.

[24] For a discussion of solvent effects on quantum yields see (a) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967); (b) P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5383 (1969).

[25] (a) A. Padwa and W. Eisenberg, *ibid.*, **92**, 2590 (1970); (b) R. B. Gagosian, J. C. Dalton, and N. J. Turro, *ibid.*, **92**, 4752 (1970); (c) R. R. Sauers, M. Gorodetsky, J. A. Whittle, and C. K. Hu, *ibid.*, **93**, 5520 (1971); (d) N. Sugiyama, K. Yamada, and H. Aoyama, *J. Chem. Soc. C*, 830 (1971).

[26] For a nonphotochemical synthesis of a tricyclo[3.2.1.0^{3,6}]octane, see R. R. Sauers, R. A. Parent, and S. B. Damle, *J. Amer. Chem. Soc.*, 88, 2257 (1966).

[27] The only other example of a tricyclo[3.3.1.0^{2,7}]nonane of which we are aware is tricycloionone: G. Büchi, E. Koller, and C. W. Perry, *ibid.*, 86, 5646 (1964).

[28] J. A. Barltrop and J. D. Coyle, *ibid.*, 90, 6584 (1968).

[29] S. Beckmann, R. Schaber, and R. Bamberger, *Chem. Ber.*, 87, 997 (1954).

gave, after evaporative distillation, 0.19 g (73%) of colorless **4**: uv spectrum, λ_{max} 326 nm, ϵ_{max} 80 (hexane); nmr (CCl_4) δ 1.3 (s, 3 H), 1.2–1.6 (m, 8 H), 2.3 (m, 1 H), 2.6 (m, 1 H), 7.4 (m, 3 H), and 7.9 (m, 2 H).

2-Benzoyl-2-methylbicyclo[2.2.2]octane (6). A mixture of *endo*- and *exo*-5-methylbicyclo[2.2.2]octane-5-carboxylic acid was prepared by the method of Boehme, *et al.*[30] Hydrogenation of the mixture over palladium on carbon gave 2-methylbicyclo[2.2.2]-octane-2-carboxylic acid, mp 119–121° (lit.[30] 122–123°). Reaction of the acid (1.7 g, 0.01 mol) with phenyllithium gave after work-up and distillation 1.3 g (56%) of colorless **6**: bp 141–143° (1.2 mm); uv spectrum, λ_{max} 324 nm, ϵ_{max} 93 (hexane); nmr (CCl_4) δ 1.4 (s, 3 H), 1.2–1.7 (m, 10 H), 2.2 (m, 1 H), 2.5 (m, 1 H), 7.4 (m, 3 H), and 7.8 (m, 2 H).

***endo*-2-Benzoylnorbornane (9).** Diels–Alder reaction of acrylic acid with cyclopentadiene followed by several recrystallizations from pentane gave *endo*-5-norbornenecarboxylic acid, mp 44° (lit. 39°,[31] 40–41.5°[32]). Reaction of the acid (5.8 g, 0.042 mol) with phenyllithium followed by hydrogenation over palladium on carbon gave 5.8 g (74%) of colorless **9**: uv spectrum λ_{max} 324, ϵ_{max} 62; nmr (CCl_4) δ 1.2–1.6 (m, 8 H), 2.3 (m, 1 H), 2.6 (m, 1 H), 3.6 (m, 1 H), 7.3 (m, 3 H), and 7.8 (m, 2 H).

***exo*-2-Benzoylnorbornane (12).** Reaction of a mixture of *exo*- and *endo*-5-norbornenecarboxylic acids with phenyllithium followed by stirring with 0.3 *M* sodium methoxide in methanol gave a ∼4:1 mixture of *exo*- and *endo*-5-benzoylnorbornenes. Partial photolysis of this mixture in 1 *M* piperylene–benzene followed by chromatography on silica gel (hexane solvent) gave pure (>98% by vpc) *exo*-5-benzoylnorbornene. This procedure takes advantage of the very rapid intramolecular oxetane formation of the endo isomer[33] and avoids the highly objectionable odors encountered when the corresponding carboxylic acids are separated. Hydrogenation of *exo*-5-benzoylnorbornene over palladium on carbon gave colorless **12**; uv spectrum, λ_{max} 325 nm, ϵ_{max} 72 (hexane); nmr (CCl_4) δ 1.0–2.0 (m, 8 H), 2.3 (m, 1 H), 2.5 (m, 1 H), 3.1 (m, 1 H), 7.3 (m, 3 H), and 7.8 (m, 2 H).

2-Benzoylbicyclo[2.2.2]octane (14). Diels–Alder reaction of acrylic acid with 1,3-cyclohexadiene followed by hydrogenation over palladium on carbon gave bicyclo[2.2.2]octane-2-carboxylic acid, mp 79–81° (lit.[7] 84–85°). Reaction of the acid (2.7 g, 0.017 mol) with phenyllithium gave after recrystallization from methanol 1.9 g (50%) of white crystalline **12**, mp 93–94° (lit.[7] 89–90°).

***exo*-2-Benzoyl-2-methylnorbornane (16)** was prepared from *exo*-5-methylnorbornene-5-carboxylic acid[29] by reaction with phenyllithium followed by hydrogenation of the unsaturated ketone over palladium on carbon: nmr (CCl_4) δ 1.4 (s, 3 H), 1.1–1.6 (m, 8 H), 2.2 (m, 1 H), 2.8 (m, 1 H), 7.2 (m, 3 H), and 7.7 (m, 2 H); uv spectrum λ_{max} 325 nm, ϵ_{max} 79 (hexane).

1-Methylcyclopentyl Phenyl Ketone (17). 1-Methylcyclopentanecarboxylic acid[34] was prepared by reaction of 2-methyl-2-acetylcyclohexanone[35] with aqueous peroxide. Reaction of the acid (1.4 g, 0.01 mol) with phenyllithium followed by distillation gave 1.2 g (60%), bp 85–89° (0.25 mm), of colorless **14**; uv spectrum λ_{max} 324, ϵ_{max} 30; nmr (CCl_4) δ 1.4 (s, 3 H), 1.5–1.8 (m, 6 H), 2.2–2.5 (m, 2 H), 7.3 (m, 3 H), and 7.8 (m, 2 H).

Cyclopentyl phenyl ketone (20) was prepared from cyclopentanecarboxylic acid (Aldrich) by the method of Padwa and Eastman.[9]

1-Phenyl-3-cyclopentylpropan-1-one (11). Reaction of (1.0 g, 0.007 mol) 3-cyclopentylpropanoic acid (Chemical Samples) with phenyllithium gave 0.68 g (47%) of colorless **11**, bp 130° (1 mm): ir spectrum 5.97 μ; nmr (CCl_4) δ 1.2–1.9 (m, 10 H), 2.2 (m, 1 H), 2.8 (t, 2 H), 7.3 (m, 3 H), and 7.8 (m, 2 H).

1-Phenyl-3-(Δ^3-cyclohexenyl)propan-1-one (15). β-(Δ^3-Cyclohexenyl)propionic acid was prepared by the method of Finkbeiner and Cooper.[36] Reaction of this acid with phenyllithium gave colorless **15**, bp 120° (0.4 mm); nmr (CCl_4) δ 1.2–2.2 (m, 9 H), 2.9 (t, 2 H), 5.7 (s, 2 H), 7.5 (m, 3 H), and 8.0 (m, 2 H).

1-Phenyl-2-methyl-3-(Δ^3-cyclohexenyl)propan-1-one (8). Reaction of **15** with 1 equiv of sodium hydride and methyl iodide in dimethoxyethane gave **8**: nmr (CCl_4) δ 1.2 (d, 3 H), 1.0–2.0 (m, 9 H), 3.2 (m, 1 H), 5.5 (s, 2 H), 7.4 (m, 3 H), and 7.8 (m, 2 H).

1-Phenyl-2-methyl-5-hexen-1-one (19). 1-Phenyl-5-hexen-1-one (**21**) was prepared by the method of Padwa and Eastman.[9] Alkylation with 1 equiv of sodium hydride and methyl iodide gave **19**; nmr (CCl_4) δ 1.2 (d, 3 H), 7.8 (m, 4 H), 3.2 (m, 1 H), 4.8 (m, 1 H), 5.0 (m, 1 H), 5.6 (m, 1 H), 7.3 (m, 3 H), and 7.8 (m, 2 H).

Preparative Scale Irradiations. Solutions of ∼0.2 g of ketone in 20–50 ml of benzene were irradiated under nitrogen or argon with a 450-W, medium-pressure mercury lamp in a Pyrex immersion well. Ketones **4** and **6** were photolyzed to essentially complete conversion. The tricyclic alcohols **5** and **7** were purified by chromatography on silica gel with hexane solvent to remove trace impurities and characterized by their spectral data (see Results section). Ketones **9**, **12**, and **17** were photolyzed to about 60% conversion and the products isolated by silica gel chromatography with hexane or hexane–ethyl acetate solvent. The products were identified by comparison of spectral properties and vpc retention time with authentic samples. Infrared spectra were recorded on a Beckman IR 5 spectrophotometer, nmr spectra on a Varian A-60 or T60 spectrometer, emission spectra on a Perkin-Elmer MPF-2A with phosphorescence attachment, ultraviolet spectra on a Cary 14 spectrophotometer, and mass spectra on a CEC 21-104 mass spectrometer with an ionization voltage of 15 eV.

Quantum yields and rate constants were determined as previously described.[2b,37] Photolyzed solutions were analyzed with a calibrated 5 ft × $^1/_8$ in. column of 4% QF1 and 1% Carbowax 20M on Chromosorb G or a 5 ft × $^1/_8$ in. column of 5% SF 96 on Chromosorb G.

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