

Conformational Control of Photochemical Behavior. Competitive α Cleavage and γ -Hydrogen Abstraction of Alkyl Phenyl Ketones¹

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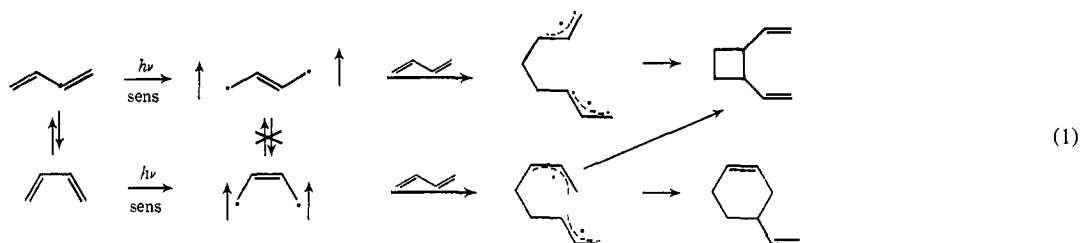
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Abstract: The photochemical α cleavage and γ -hydrogen abstraction reactions of several acyclic and cycloalkyl phenyl ketones have been investigated. Photochemical reactions of cyclohexyl phenyl ketones are more rapid than ring inversion. As a consequence, product compositions are determined by ground state conformational populations. In contrast, pseudorotation in cyclopentyl phenyl ketones and bond rotations in acyclic ketones are more rapid than photochemical reactions. The Curtin-Hammett principle applies to the reactions of these ketones. Product compositions are determined by relative rates of the competitive primary photoprocesses rather than conformational populations. For cyclohexyl phenyl ketone isoenergetic energy transfer from the long-lived equatorial excited state to the highly reactive axial conformer is observed to occur with a rate constant of $1.2 \times 10^8 M^{-1} \text{ sec}^{-1}$.

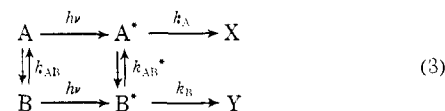
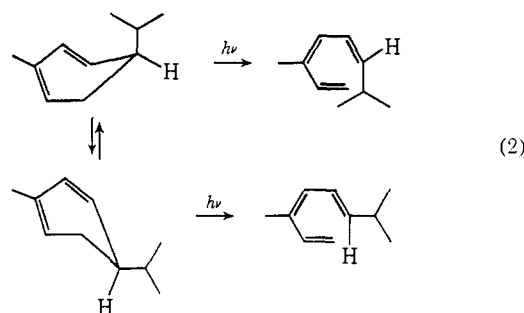
There is an increasing number of photochemical reactions for which the product composition apparently depends upon ground-state molecular conformation.³⁻⁶ The first example where such a relationship was postulated is the sensitized dimerization of butadiene (eq 1).³ Formation of vinylcyclohexene only upon

mobile system (*cf.* eq 1 and 2), energy barriers for conformational isomerization in the ground and excited state will not necessarily be the same.

The simplest situation for studying conformational effects in photochemistry occurs when two conformers give rise to different photoproducts (eq 3). Two limiting



excitation of the s-cis diene requires that the cis and trans triplets do not interconvert prior to addition. Conformational control of product compositions in the photoisomerization of 1,3-cyclohexadienes to 1,3,5-hexatrienes has been extensively investigated.⁴ The mode of conrotatory ring opening is found to be accordant with the conformation of the nonplanar cyclohexadiene (eq 2). Conformational effects have been implicated in a number of other photochemical reactions.⁵ Lack of knowledge about the conformations of excited states has made quantitative studies of conformational effects difficult or impossible. In cases where the chromophore is part of the conformationally



cases are possible for such a scheme. In case I the activation energy for conformational isomerization is lower than those for formation of X or Y ($k_{AB}^* \gg k_A, k_B$). In this case the ratio of products will depend upon the difference in energy for the transition states leading to X and Y (Curtin-Hammett principle⁶), and the lifetimes of both excited state conformers will be the same. In case II the activation energy for conformational isomerization is greater than those for formation of X or Y ($k_{AB}^* \ll k_A, k_B$). In this case the ratio of products will depend upon the population of A^* and B^* and their efficiencies of product formation. Since electron excitation is much faster than nuclear motion,

(1) (a) The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and PPG Industries for support of this research. (b) Presented in part at the IVth IUPAC Photochemistry Symposium, Baden-Baden, Germany, July 1972.

(2) (a) Camille and Henry Dreyfus Teacher-Scholar 1973-1978; (b) Petroleum Research Fund Graduate Fellow, 1973-1974.

(3) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

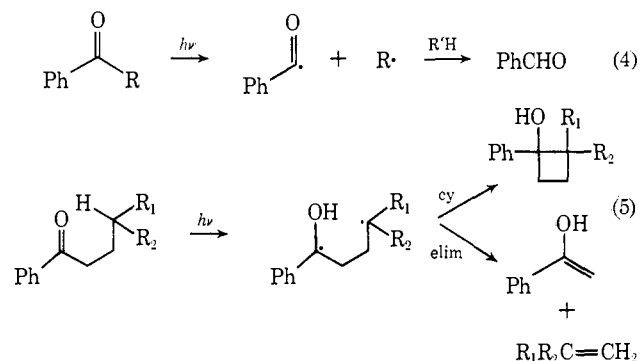
(4) (a) J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 6444 (1969); (b) C. W. Spangler and R. P. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972); (c) W. G. Dauben, R. G. Williams, and R. D. McKelvey, *J. Amer. Chem. Soc.*, **95**, 3932 (1973), and references therein.

(5) (a) R. M. Moriarty and R. C. Reardon, *Tetrahedron*, 1379 (1970); (b) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971); (c) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972); (d) R. C. Hahn and D. W. Kurtz, *ibid.*, **95**, 6723 (1973).

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 151, 237.

the initial populations of A^* and B^* will be determined by ground state conformational populations and extinction coefficients. In case II, the lifetimes of A^* and B^* need not be the same.

In order to provide quantitative information about the effects of molecular conformation on photochemical behavior, the photochemistry of several cycloalkyl phenyl ketones has been investigated in some detail.⁷ The well-known α cleavage (type I) and γ -hydrogen abstraction (type II) reactions of alkyl phenyl ketones (eq 4 and 5) have been employed as probes for conformational effects.

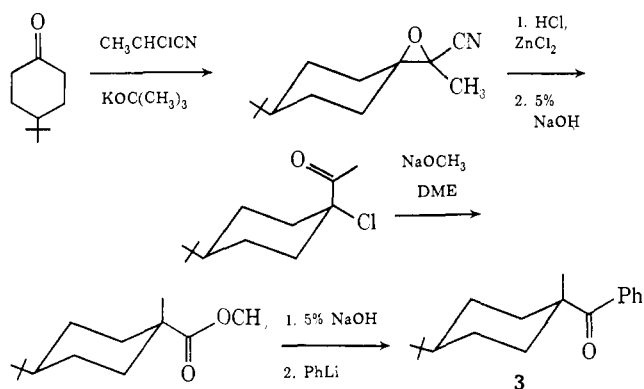


Results

Synthesis and Spectral Properties of Reactants.

1-Methylcyclohexyl phenyl ketone (**1**) and *cis*-4-*tert*-butyl-1-methylcyclohexyl phenyl ketone (**2**) were prepared by methylation of the corresponding cyclohexyl phenyl ketones. The stereochemistry of **2** is assigned on the basis of the known preference of cyclohexyl enolates toward equatorial methylation.⁸ The synthesis of *trans*-4-*tert*-butyl-1-methylcyclohexyl phenyl ketone (**3**) is outlined in Scheme I. This synthesis utilizes

Scheme I. Synthesis of *trans*-4-*tert*-Butyl-1-methylcyclohexyl Phenyl Ketone



three consecutive stereoselective reactions. α -Halo ketone formation from the glycidonitrile proceeds with inversion⁹ as does the subsequent Favorskii rearrangement.¹⁰ The chemical shift of the methyl protons of **3** (δ 1.28) is at slightly higher field than that of **2** (δ 1.34). The same relationship has been reported for the corresponding methyl ketones.⁸ The stereochemical assign-

(7) For preliminary reports of portions of this work, see (a) F. D. Lewis and R. W. Johnson, *J. Amer. Chem. Soc.*, **94**, 8914 (1972); (b) *Tetrahedron Lett.*, 2557 (1973).

(8) H. O. House and T. M. Bare, *J. Org. Chem.*, **33**, 943 (1968).

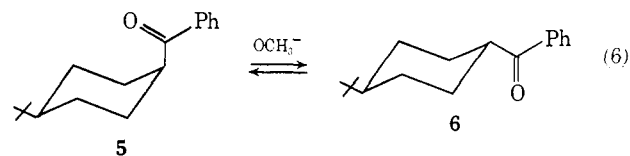
(9) G. Stork, W. S. Worrall, and J. J. Pappas, *J. Amer. Chem. Soc.*, **82**, 4315 (1960).

(10) H. O. House and W. F. Gilmore, *J. Amer. Chem. Soc.*, **83**, 3980 (1961).

ments for **2** and **3** are corroborated by their photochemical behavior.

The conformational preference of ketone **1** was established by low temperature Fourier transform ^{13}C nmr spectroscopy.¹¹ The carbonyl resonance appears as a singlet at 206.8 ppm in the proton decoupled spectrum above -28° . Below the coalescence temperature it appears as a doublet (203.1, 207.2 ppm). Assignment of the stronger downfield signal to the equatorial benzoyl conformation is based upon the general observation that axial carbons bonded to cyclohexane absorb at higher field than equatorial carbons.¹² From the average of six low temperature spectra a value of $A = 0.51 \pm 0.04$ was calculated, in accord with the slightly larger A value for benzoyl *vs.* methyl (*vide infra*).¹³ The free energy of activation at the coalescence temperature (9.9 ± 0.5 kcal/mol) is similar to those for a number of substituted cyclohexanes.¹⁴

Cyclohexyl phenyl ketone (**4**) and *cis*-4-*tert*-butylcyclohexyl phenyl ketone (**5**) were prepared by the acylation of benzene with the appropriate acid chloride.¹⁵ Base catalyzed isomerization of **5** provided *trans*-4-*tert*-butylcyclohexyl phenyl ketone (**6**). The conformational preference of the benzoyl group was estimated by equilibration of **5** and **6** (eq 6). Degassed



solutions of the pure ketones in 0.07 *M* NaOCH_3 - CH_3OH were maintained at $56 \pm 0.5^\circ$ for 144 hr. Analysis of the resulting solutions by vpc showed a *cis*/*trans* ratio of 0.066 ± 0.001 . From this ratio an A value (1.79) slightly larger than those for acetyl (1.52¹⁶) and methyl (1.6–1.7¹⁷) is obtained. In view of the similar A values for benzoyl and methyl, it seems probable that the lowest energy conformation of **5** will be a chair. The syntheses of 1-methylcyclopentyl phenyl ketone (**7**) and cyclopentyl phenyl ketone (**8**) have been described.^{18b}

Ultraviolet absorption data for ketones **1**–**8** are given in Table I. All the ketones show normal n, π^* lowest energy absorption bands at $\lambda_{\text{max}} 324 \pm 3$ nm in hexane solution. The *tert*-alkyl phenyl ketones **1**–**3** and **7** show somewhat stronger absorbance than their secondary counterparts. From the point of view of quantitative discussion of photochemical behavior, the important comparison is between molar extinction co-

(11) The methyl signal in the 90-MHz pmr spectrum appears as a singlet down to -90° . Apparently the axial and equatorial methyls have identical chemical shifts. The methyl chemical shifts for ketones **2** and **3** differ only by 0.06 ppm.

(12) H. Brouwer and J. B. Strothers, *Can. J. Chem.*, **50**, 601 (1972).

(13) Calculation of an A value from ^{13}C peak areas requires the assumption that axial and equatorial carbonyl carbons have similar relaxation times and nuclear Overhauser effects. G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, p 30.

(14) I. O. Sutherland, *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, **4**, 71 (1971).

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

(16) E. L. Eliel and M. C. Reese, *J. Amer. Chem. Soc.*, **90**, 1560 (1968).

(17) F. A. L. Anet, C. H. Bradley, and C. W. Buchanan, *J. Amer. Chem. Soc.*, **93**, 259 (1971).

(18) (a) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972); (b) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *ibid.*, **94**, 4292 (1972).

Table I. Absorption Spectral Data for Cycloalkyl Phenyl Ketones

| Ketone | λ_{\max} , nm | ϵ | λ_{br} , nm | ϵ |
|--------|-----------------------|------------|----------------------------|------------|
| 1 | 321 | 111 | 365 | 13 |
| 2 | 324 | 111 | 365 | 13 |
| 3 | 327 | 98 | 365 | 11 |
| 4 | 323 | 66 | 313 | 54 |
| 5 | 325 | 73 | 313 | 57 |
| 6 | 321 | 67 | 313 | 57 |
| 7 | 324 | 76 | 365 | 10 |
| 8 | 324 | 58 | 313 | 52 |

efficient at the wavelength of irradiation. The values for 4–6 are within $\pm 5\%$ of each other. Thus the axial and equatorial conformers of ketone 4 should absorb equally. The agreement for ketones 1–3 is not as good; however, the absorbance of the axial conformer of 1 should be no more than 20% greater than that of the equatorial conformer.

The 77°K phosphorescence data for ketones 1–8 are given in Table II. Triplet energies were estimated from

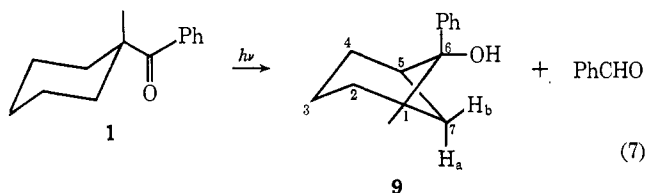
Table II. Phosphorescence Data for Cycloalkyl Phenyl Ketones

| Ketone | Solvent ^a | E_T , kcal/mol ^b | τ , msec |
|--------|----------------------|-------------------------------|---------------|
| 1 | EPA | 72.1 | 5.3 |
| | MC | 71.4 | 3.6 |
| 2 | EPA | 72.1 | 5.4 |
| | MC | 71.4 | 3.5 |
| 4 | EPA | 73.3 | 3.4 |
| | MC | 72.7 | 1.9 |
| 5 | EPA | 72.3 | 1.7 |
| | MC | 71.5 | 1.2 |
| 6 | EPA | 73.3 | 3.6 |
| | MC | 72.7 | 2.1 |
| 7 | EPA | 72.1 | 3.7 |
| | MC | 71.4 | 2.1 |
| 8 | EPA | 73.7 | 3.3 |
| | MC | 73.1 | 2.7 |

^a EPA is ether-isopentane-ethanol and MC is methylcyclohexane. ^b Estimated from the highest energy emission maximum at 77°K.

the position of the highest energy emission maxima. Triplet lifetimes were measured by the flash-emission technique. Emission occurs predominantly from a single short-lived excited state in both polar (EPA) and nonpolar (MC) solvents. The short lifetimes and structured emission are indicative of lowest n, π^* triplet states for all of these ketones.¹⁹

Product Studies. Preparative photolyses were carried out on dilute benzene or 1-propanol solutions under a nitrogen or argon atmosphere using a 450-W medium-pressure mercury lamp in a Pyrex immersion well. Irradiation of 1 in benzene gives the bicyclic alcohol 9 and benzaldehyde as the only primary products (eq 7).²⁰ Addition of 1-dodecanethiol (0.01 M)

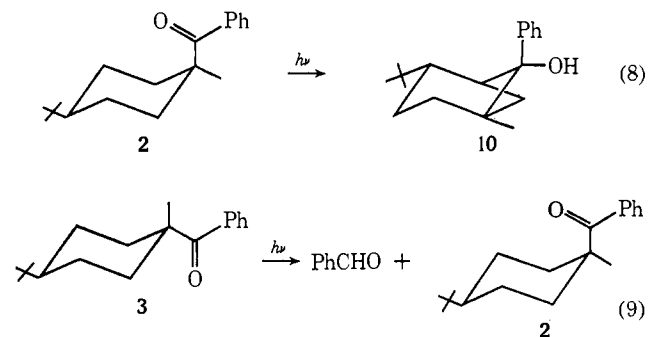


(19) P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5269 (1970).

(20) *tert*-Alkyl phenyl ketones have previously been observed to give mainly photocyclization and little or no photoelimination product.¹⁸

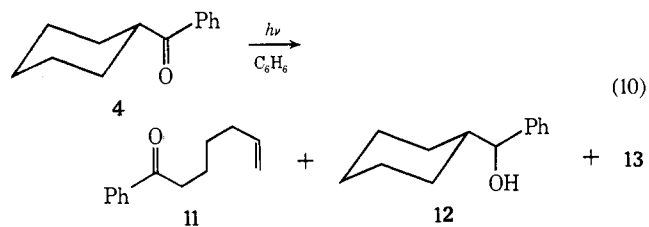
increases the yield of benzaldehyde without diminishing the yield of 9. Alkane thiols are known to be efficient scavengers of benzoyl radicals.²¹ The structure of 9 is assigned on the basis of spectroscopic data (see Experimental Section). The nmr assignments are consistent with previous reports for bicyclo[3.1.1]heptan-6-ols.²²

The only product observed upon irradiation of ketone 2 in benzene is the bicyclic alcohol 10 (eq 8). Neither the isomeric ketone 3 nor benzaldehyde could be detected, with or without added 1-dodecanethiol. In contrast, irradiation of ketone 3 in benzene gives benzaldehyde and ketone 2 as the primary products (eq 9).



Prolonged photolysis results in conversion of ketone 2 into 10 (eq 8). Addition of 0.01 M thiol greatly reduces the yield of 2 and increases the yield of benzaldehyde.

The photochemical behavior of cyclohexyl phenyl ketone (4) proved to be far more complicated than that of ketones 1–3. Irradiation in degassed benzene results in the formation of 1-phenyl-6-hepten-1-one (11), cyclohexylphenylcarbinol (12), and an unidentified product (13) in an approximate ratio 3:1:1 (eq 10).



The elimination product 11 reaches its maximum concentration at <2% conversion and thereafter is converted to acetophenone as rapidly as it is formed. Thus acetophenone is the major product of prolonged photolysis in benzene, as previously reported.²³ Irradiation in degassed 1-propanol results in much more rapid formation of 11 and the absence of product 13. The yield of carbinol 12 is insensitive to solvent. The ratio of 11 to 12 is approximately 30:1 in 1-propanol at low conversions. The ir, nmr,²⁴ and mass spectra of the unknown product 13 are indicative of an α -tetralone structure. Particularly informative is the mass spectrum of 13 which, aside from the molecular ion (m/e 186), closely resembles the spectrum of α -tetralone with

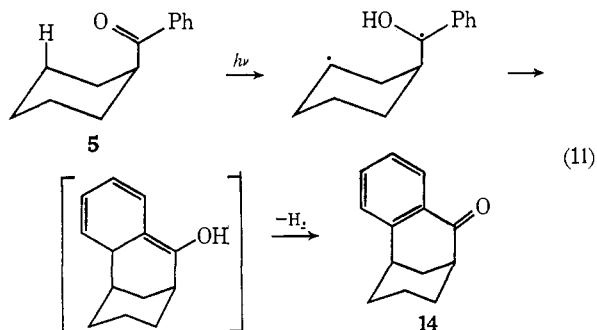
(21) (a) F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, **37**, 2102 (1972); (b) H.-G. Heine, W. Hartmann, D. R. Kory, J. G. Magyar, C. E. Hoyle, J. K. McVey, and F. D. Lewis, *ibid.*, **39**, 691 (1974).

(22) (a) K. B. Wiberg and B. A. Hess, *J. Org. Chem.*, **31**, 2250 (1966); (b) K. B. Wiberg and W. Chen, *ibid.*, **37**, 3235 (1972).

(23) J. H. Stocker and D. H. Kern, *Chem. Commun.*, 204 (1969). No attempt was made to isolate the pinacols of ketone 4 obtained by these workers.

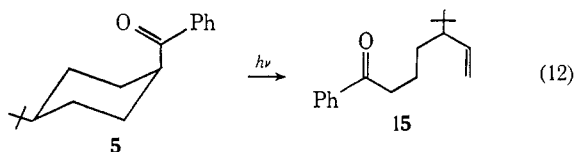
(24) L. M. Jackman and S. Sternhell, "Nmr Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, England, 1969, p 197.

major fragments at m/e 118 (base peak) and 90.²⁵ We suspected that tetralone **14** might be formed by an unusual reaction of the biradical intermediate as shown in eq 11.²⁶ However, the spectra of **13** and an authentic

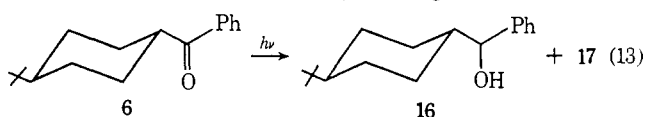


sample of **14**²⁷ were similar but not identical. The isomeric hexahydrofluorenones were also ruled out as possible structures for **13** on the basis of comparison with authentic samples.²⁸

Irradiation of ketone **5** in either benzene or 1-propanol solution results in formation of the elimination product **15** as the only primary photoproduct observed by gc or nmr analysis of the reaction mixture (eq 12).

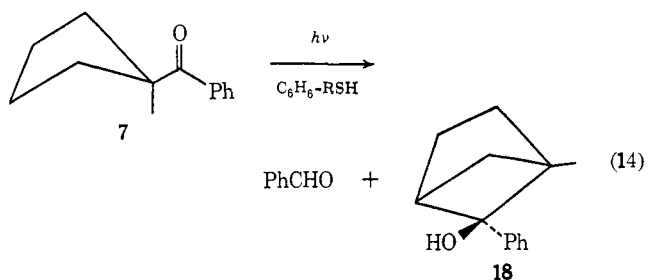


Prolonged irradiation leads to conversion of **15** to acetophenone. Analysis of the reaction mixture by ir confirms the absence of alcoholic products.¹⁸ Irradiation of ketone **6** results in a complex mixture of products even at low conversion. The two major products detected by gc are the carbinol **16** and a tetralone (**17**) of unknown structure (eq 13). Assignments are based



on analogous mass spectral fragmentation for **16** and **12** and for **17** and **13**.

The photochemistry of 1-methylcyclopentyl phenyl ketone (**7**) was reinvestigated^{18b} in order to determine the extent of α cleavage. Irradiation of **7** in 0.01 *M* 1-dodecanethiol-benzene resulted in the formation of benzaldehyde in addition to the previously observed bicyclo[2.1.1]hexan-5-ol (**18**) (eq 14).



(25) J. H. Bowie, *Aust. J. Chem.*, **19**, 1619 (1966).

(26) Pitts postulated a similar sequence for the formation of an unidentified ortho-disubstituted aromatic ketone from butyrophenone. E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 2652 (1966).

(27) J. C. Bardhan and R. C. Banerjee, *J. Chem. Soc.*, 1809 (1956).

(28) H. O. House, V. Paragamian, R. S. Ro, and D. J. Wluka, *J. Amer. Chem. Soc.*, **82**, 1457 (1960).

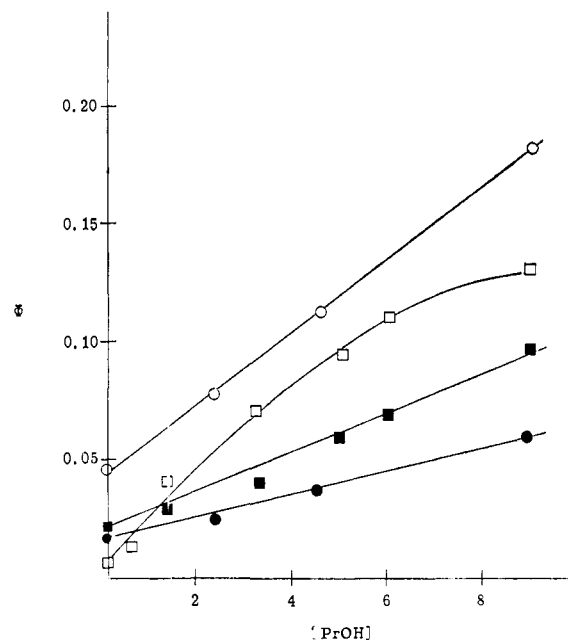


Figure 1. Variation in quantum yields for type II product formation in benzene with added 1-propanol for ketones **1** (○), **2** (●), **4** (□), and **5** (■).

Product Quantum Yields. The quantum yields for product formation from ketones **1–7** are given in Table III. In the case of ketone **6** for which product quan-

Table III. Quantum Yield and Kinetic Data for Cycloalkyl Phenyl Ketones

| Ketone, [M] | Solvent | Φ_{α}^a | Φ_{γ}^b | $k_q\tau, M^{-1}$ | $10^{-8}(1/\tau), \text{sec}^{-1}$ |
|-------------|-----------------------------|-------------------|-------------------|------------------------------------|------------------------------------|
| 1[0.15] | C_6H_6 -RSH | 0.20 | 0.045 | 200 ^c (29) ^d | 0.25 (1.7) |
| | PrOH | | 0.18 | | |
| 2[0.15] | C_6H_6 | | 0.019 | 7.3 | 6.9 |
| | PrOH | | 0.060 | | |
| 3[0.15] | C_6H_6 -RSH | 0.31 | | 240 | 0.21 |
| | C_6H_6 | | 0.008 | 765 (2.9) ^e | 0.066 (17) |
| 4[0.044] | PrOH | | 0.13 | | |
| | C_6H_6 | | 0.024 | 0.74 | 68 |
| 5[0.035] | PrOH | | 0.098 | | |
| | C_6H_6 | | 0.10 | 670 | 0.075 |
| 7[0.050] | C_6H_6 -RSH | 0.03 | 0.19 | 380 | 0.13 |

^a Quantum yield for benzaldehyde formation in 0.01 *M* dodecanethiol-benzene. ^b Quantum yield for type II products in benzene or 8.9 *M* 1-propanol-benzene. ^c Slope of Stern-Volmer plot for quenching of benzaldehyde formation. ^d Slope of Stern-Volmer plot for quenching of cyclization. ^e Stern-Volmer slopes for equatorial and axial excited states obtained from eq 25 and 26. The lifetime of the equatorial excited state is concentration dependent; see text.

tum yields could not be measured by our standard techniques, the quantum yield for loss of starting material extrapolated to zero conversion is given. Quantum yields for type II cyclization from ketones **1** and **2** and elimination from ketones **4** and **5** (Φ_{γ}) increase with added 1-propanol.²⁹ The dependence of quantum yield upon 1-propanol concentration is shown in Figure 1. The quantum yields do not attain

(29) Solvent effects on the type II reaction have been extensively studied by Wager and coworkers. Alcohol solvents increase quantum yields by inhibiting reversion of the biradical intermediate to ground state ketone. P. J. Wagner, I. E. Kochevar, and A. E. Kempainen, *J. Amer. Chem. Soc.*, **94**, 7489 (1972).

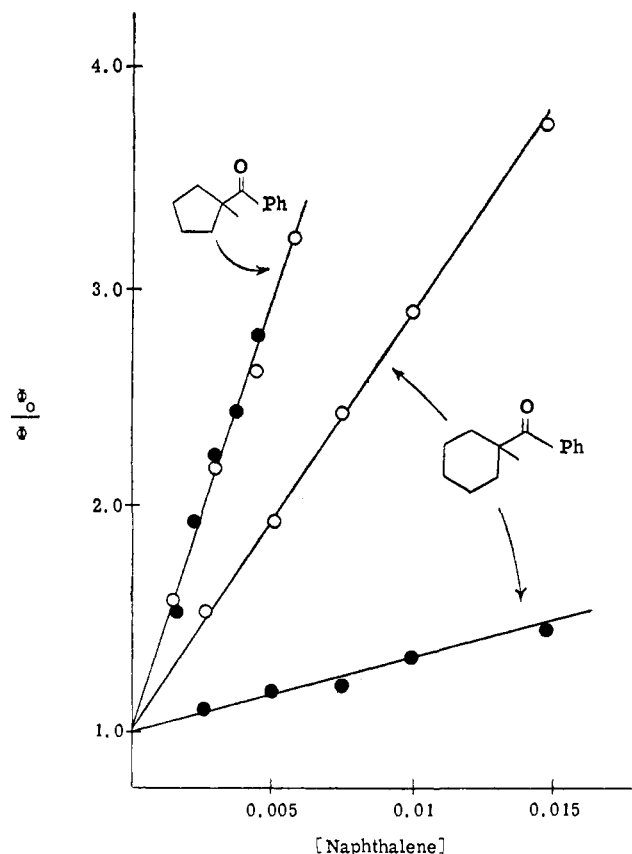


Figure 2. Stern-Volmer plots for quenching of benzaldehyde (O) and bicyclobutanol (●) formation from 1-methylcyclopentyl phenyl ketone and 1-methylcyclohexyl phenyl ketone.

a maximum value in 8.9 *M* 1-propanol-benzene. Thus the quantum yields for type II elimination or cyclization given in Table III provide a lower limit for the γ -hydrogen abstraction quantum yield. The quantum yield for photoelimination from ketone 4 is dependent upon initial ketone concentration. Results obtained in 4.5 *M* 1-propanol-benzene are given in Table IV.

Table IV. Variation in Quantum Yield for Formation of 1-Phenyl-6-hepten-1-one (11) with Concentration for Cyclohexyl Phenyl Ketone (4)

| [Ketone], <i>M</i> | Φ | [Ketone], <i>M</i> | Φ |
|--------------------|--------|--------------------|--------|
| 0.030 | 0.052 | 0.16 | 0.13 |
| 0.060 | 0.098 | 0.21 | 0.15 |
| 0.090 | 0.11 | 0.30 | 0.17 |

Quantum yields for benzaldehyde formation were measured in 0.01 *M* dodecanethiol-benzene. Scavenging of noncage benzoyl radicals is quantitative under these conditions.²¹ Since cage recombination of benzoyl and *tert*-alkyl radicals is known to compete with diffusion,³⁰ the quantum yields for benzaldehyde formation given in Table III are lower than the actual α cleavage quantum yields.

Triplet lifetimes (τ) for ketones 1-7 were determined by standard Stern-Volmer quenching techniques. Naphthalene was used as the quencher and 0.01 *M* dodecanethiol-benzene as the solvent for those ketones

(30) (a) F. D. Lewis and J. G. Magyar, *J. Amer. Chem. Soc.*, **95**, 5973 (1973); (b) K. Müller and G. L. Closs, *ibid.*, **94**, 1002 (1972).

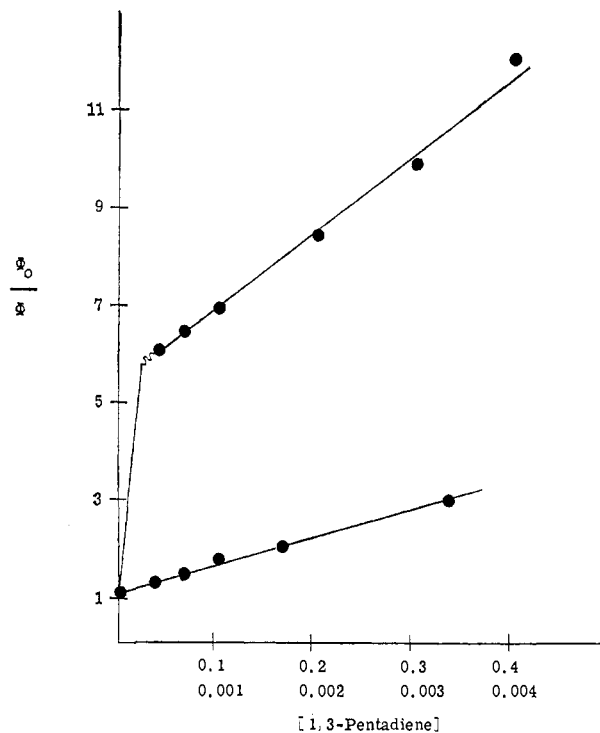


Figure 3. Stern-Volmer plots for quenching of photoelimination from cyclohexyl phenyl ketone using high (upper curve) and low (lower curve) concentrations of 1,3-pentadiene.

which undergo α cleavage (1, 3, 7). *trans*-1,3-Pentadiene was used as the quencher for the other ketones and either benzene or 4.5 *M* 1-propanol-benzene (for ketones 4 and 5) was the solvent. Plots of Φ_0/Φ for product formation *vs.* quencher concentration (eq 15) were

$$\frac{\Phi_0}{\Phi} = 1 + k_q\tau[Q] \quad (15)$$

linear except in the case of ketone 4. From the slopes of the Stern-Volmer plots ($k_q\tau$) and the assumption that $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for exothermic quenching in benzene,³¹ the values of $1/\tau$ in Table III were obtained. Ketones 1 and 7 undergo both α cleavage and γ -hydrogen abstraction. The $k_q\tau$ values for quenching of these two reactions are identical for ketone 7 but different for ketone 1 (Figure 2). The quenching plot for ketone 4 (Figure 3) is unusual in that there are two linear portions, indicating that two excited states with different lifetimes are involved in product formation.³²

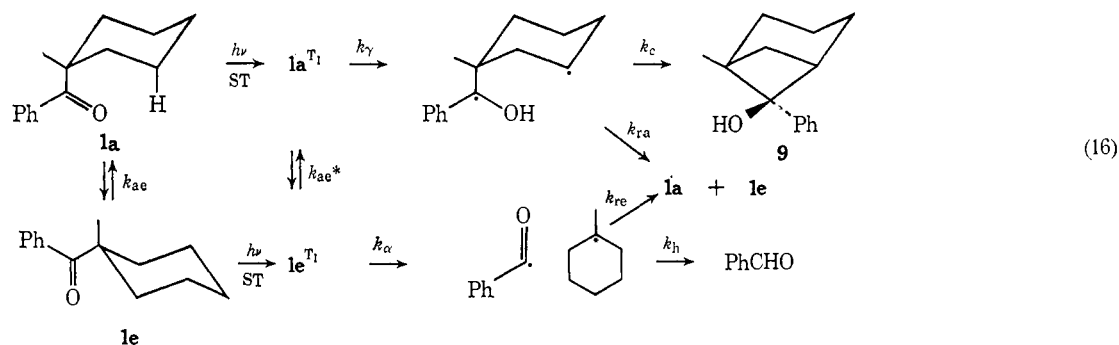
Discussion

Conformational Control of Product Composition.

Quantitative understanding of the effects of conformation upon photochemical behavior requires detailed information about both the conformational properties and photochemical reactions of the molecules being investigated. 1-Methylcyclohexyl phenyl ketone (1) proved to be particularly well suited for such a study for several reasons. Conformational analysis of ground-state cyclohexanes is reasonably straightforward.

(31) It is assumed that the rate constant for quenching of ketones 1-7 is independent of structure. See P. J. Wagner, J. M. McGrath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972).

(32) (a) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970); (b) M. D. Shtlar, *ibid.*, **5**, 311 (1973); (c) P. J. Wagner in "Creation and Detection of the Excited State," A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 4.



ward. Electronic excitation of ketone **1** would not be expected to perturb conformational isomerization since the chromophore does not include the cyclohexane ring. The photochemistry of alkyl phenyl ketones is relatively well understood.^{18, 21, 33} Due to very rapid intersystem crossing^{34a} only one excited state, the n, π^* triplet, is normally responsible for product formation. Finally, rigid models for the axial and equatorial conformers of ketone **1** are provided by the 4-*tert*-butyl derivatives **2** and **3**.

The only products observed upon irradiation of the model compounds **2** and **3** are those resulting from γ -hydrogen abstraction and α cleavage, respectively (eq 8 and 9). The rate constants for triplet decay ($1/\tau$) given in Table III are much larger than non-radiative decay rate constants for normal alkyl phenyl ketones.^{21a} Thus the triplet lifetimes are determined only by the rate constants for γ -hydrogen abstraction ($1/\tau = k_\gamma$) or α cleavage ($1/\tau = k_\alpha$). The absence of type II products from ketone **3** is due to the prohibitively large O-H γ distance^{18b, 34b} rather than stereoelectronic factors.^{15, 35} Both the rate constant for α cleavage and the quantum yield for benzaldehyde formation from ketone **3** are similar to those for an acyclic *tert*-alkyl phenyl ketone, pivalophenone (**19**) (Table V).

Table V. Quantum Yields^a and Kinetic Data for Model Alkyl Phenyl Ketones

| Ketone | Φ_α | Φ_γ | $1/\tau, \text{sec}^{-1}$ |
|---|---------------|---------------|---------------------------|
| Pivalophenone ^b (19) | 0.30 | | 1.1×10^7 |
| Valerophenone ^c (20) | | 1.0 | 1.4×10^8 |
| 2-Benzoyl-2-methylbicyclo-[2.2.2]octane ^d (21) | | 0.26 | 3.0×10^8 |
| 2-Benzoylbicyclo[2.2.2]-octane ^d (22) | | 0.058 | 1.0×10^{10} |
| α, α -Dimethylvalerophenone ^{c, e} (25) | 0.06 | 0.45 | 1.1×10^8 |

^a Quantum yields for benzaldehyde formation (Φ_α) measured in 0.01 M 1-dodecanethiol-benzene and for type II products (Φ_γ) in alcohol-benzene solutions. ^b Values from ref 21a. ^c Values from ref 33. ^d Values from ref 18b. ^e Values from ref 18a.

The absence of α cleavage products from ketone **2** reflects the 30-fold faster rate constant for γ -hydrogen abstraction. The rate of γ -hydrogen abstraction for ketone **2** is faster than that for valerophenone (**20**) but similar to that for the rigid α -methyl ketone **21** (Table V).

Formation of both the cyclobutanol **9** and benzalde-

hyde upon irradiation of ketone **1** can be described in terms of eq 16. By analogy to the model compounds **2** and **3**, the axial conformer **1a** would be expected to undergo γ -hydrogen abstraction more rapidly than α cleavage, whereas **1e** should α cleave exclusively. Both α cleavage and γ -hydrogen abstraction should be more rapid than cyclohexane ring inversion. The value of $\Delta G^\ddagger = 9.9$ kcal/mol for inversion of ketone **1** is much larger than the activation energy ($E_a \sim 3.5$ kcal/mol) for γ -hydrogen abstraction by valerophenone (**20**) or norbornyl phenyl ketone.³⁶ The activation energy for α cleavage of *tert*-alkyl phenyl ketones has not been measured but certainly is less than 10 kcal/mol. Thus, barring a large increase in k_α upon excitation, conformers **1a*** and **1e*** should react more rapidly than invert ($k_{ae}^* \ll k_\gamma, k_\alpha$). This prediction is born out by the markedly different slopes of the Stern-Volmer plots for quenching of bicyclobutanol and benzaldehyde formation (Figure 2). From these slopes values of $1/\tau_a = k_\gamma = 1.7 \times 10^8 \text{ sec}^{-1}$ and $1/\tau_b = k_\alpha = 2.5 \times 10^7 \text{ sec}^{-1}$ are obtained. The Stern-Volmer plot for benzaldehyde is linear to >90% quenching indicating that <10% of the α cleavage occurs from the axial conformer **1a***. The rate constant for α cleavage from **1e*** is similar to those for the rigid model **3** and pivalophenone (**19**).³⁷ The rate constant for γ -hydrogen abstraction from **1a*** is somewhat slower than for the rigid model **2**. This difference may be due to slightly different bond angles and O-H γ distances for **1a** and **2**.

Since the axial and equatorial conformers of ketone **1** react more rapidly than interconvert, it follows that the product quantum yields should depend upon conformational populations and the efficiency of product formation from the excited state conformers but not upon the relative rate constants k_α and k_γ . Correction of the ground state conformational populations for the somewhat greater absorption of the axial *vs.* equatorial model compound (Table I) gives excited state populations of **1a*** $\sim 35\%$ and **1e*** $\sim 65\%$. The quantum yield for benzaldehyde formation from **1** (0.20) is precisely 65% of the value for the model ketone **3**, in accord with the hypothesis that conformational populations influence the product quantum yields. Interpretation of the quantum yield data in Table III is

(36) F. D. Lewis, R. W. Johnson, and D. R. Kory, *J. Amer. Chem. Soc.*, **95**, 6470 (1973).

(37) The shorter lifetime of **1e*** *vs.* pivalophenone could result from quenching of the equatorial excited state by the axial ground state. Assuming the rate constant for this process is similar to that observed for ketone **4** (eq 29), a value of $k_{e[1a]} = 5 \times 10^6 \text{ sec}^{-1}$ is obtained. Since $1/\tau = 2.5 \times 10^7 \text{ sec}^{-1}$ for **1e***, approximately 20% of the excited equatorial molecules may be quenched by the ground state axial conformer. The moderately large quantum yield for α cleavage and the linearity of the Stern-Volmer plot for cyclobutanol formation (Figure 2) indicate that energy transfer between conformers is not an important reaction for ketone **1**.

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

(34) (a) P. M. Rentzepis and G. E. Busch, *Mol. Photochem.*, **4**, 353 (1972); (b) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 7239 (1968).

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

complicated by the fact that the biradical formed upon γ -hydrogen abstraction can revert to ground state ketone^{29,33} and the radical pair formed upon α cleavage can undergo cage recombination.³⁰ An estimate of the quantum yield for α cleavage from **1** ($\phi_\alpha \sim 0.4$) can be obtained from the quantum yield for benzaldehyde formation and the assumption that 50% of the benzoyl-*tert*-alkyl radical pairs undergo cage recombination.³⁰ If the rate constants k_α and k_γ determined the product ratios, the maximum quantum yield for α cleavage would be $k_\alpha/(k_\alpha + k_\gamma) = 0.13$.

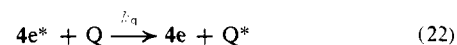
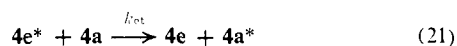
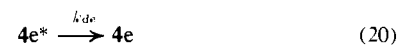
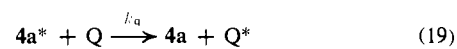
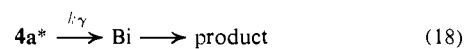
The photochemistry of cyclohexyl phenyl ketone has been investigated several times prior to the present study.^{15,23,38} The type II elimination product **11** (eq 10) has not been previously detected; however, Stocker and Kern²³ correctly postulated its intermediacy in the formation of acetophenone upon prolonged irradiation. The reported absence of type II products from cyclohexyl phenyl ketone (**4**) and *cis*-4-*tert*-butylcyclohexyl phenyl ketone (**5**) was attributed to the lowest energy conformations (equatorial chair and twist boat) in which the γ -hydrogens are inaccessible to the carbonyl n,π^* excited state.^{15,38} Conformational studies on the benzoyl group indicated that ketone **5** should have a lowest energy chair conformation and that the axial population of ketone **4** should be significant (4–5%). Since the results for 1-methylcyclohexyl phenyl ketones showed the axial benzoyl conformation to be highly reactive toward γ -hydrogen abstraction, we decided to reinvestigate the behavior of ketone **4** and its rigid models **5** and **6**.

The only primary product observed upon irradiation of ketone **5** is the photoelimination product **15**. The quantum yield for formation of **15** is low even in 8.9 *M* 1-propanol–benzene (Figure 1). The low quantum yield is not due to an unfavorable conformation for γ -hydrogen abstraction^{15,38} or low triplet reactivity. In fact the triplet lifetime of **5** is comparable to that for 2-benzoylbicyclooctane (**22**) (Table V) and is among the shortest reported for alkyl phenyl ketones.¹⁸ It seems likely that the low quantum yields for both **5** and **22** are due to efficient reversion of the biradical intermediate to ground state ketone. The same rigid structure that facilitates γ -hydrogen abstraction³⁶ also provides the best geometry for reverse hydrogen transfer. Rapid abstraction–reabstraction provides an efficient pathway for nonradiative triplet decay which precludes competition by slower photochemical processes such as reduction.

Since *trans*-4-*tert*-butylcyclohexyl phenyl ketone (**6**) can neither abstract a γ -hydrogen nor α cleave,²¹ we were at first surprised to find it to be less stable ($\Phi = 0.1$ for loss of ketone) than ketone **5**. The rate constant for triplet reaction of ketone **6** is 300 times less than that for ketone **5** (Table III), but faster than nonradiative decay rate constants for alkyl phenyl ketones.^{21a} The complex product mixture did not contain normal α cleavage or γ -hydrogen abstraction products. Photo-reduction apparently is a major process even in benzene solution.

Type II elimination is the predominant primary process for cyclohexyl phenyl ketone (eq 10). The marked increase in quantum yield with added 1-propanol (Figure 1) indicates that the biradical intermediate re-

verts efficiently to ground state ketone in benzene solution. Since the quantum yield for photoelimination in 8.9 *M* 1-propanol–benzene (0.13) is distinctly larger than the ground state population of the axial conformer **4a** (4–5%), excitation of the equatorial conformer **4e** must lead to product formation. The non-linearity of the Stern–Volmer plot (Figure 3) also indicates that product formation occurs from short-lived and long-lived excited states which do not equilibrate prior to γ -hydrogen abstraction.³² By analogy to the behavior of 1-methylcyclohexyl phenyl ketone, the short- and long-lived excited states of ketone **4** are most likely the excited axial (**4a***) and equatorial (**4e***) conformers. Photoelimination directly from **4e*** is geometrically unfeasible and cyclohexane ring inversion is too slow to occur within the lifetime of either **4e*** or **4a*** (*vide infra*).³⁹ In view of the concentration dependence of the photoelimination quantum yield (Table IV), energy transfer from excited **4e*** to ground state **4a** is the most probable explanation for product formation from **4e***. A simplified mechanism which accounts for product formation from both **4a*** and **4e*** is given in eq 17–22, where the rate constants k_{da} and k_{de} (eq 17



and 20) include all decay processes other than γ -hydrogen abstraction (eq 18). The quantum yield for product formation can be expressed as a sum of quantum yields from **4a*** and **4e*** as shown in eq 23.

$$\Phi = \Phi_a + \Phi_e = X_a \phi_a P + X_e \phi_{et} \phi_a P \quad (23)$$

where X_a and X_e are ground state populations, ϕ_a is the quantum yield for γ -hydrogen abstraction, ϕ_{et} is the quantum yield for energy transfer, and P is the probability of product formation from the biradical intermediate. Substitution of kinetic parameters for quantum yields gives eq 24 for the quantum yield in the ab-

$$\Phi^0 = X_a \left(\frac{k_\gamma}{k_\gamma + k_{da}} \right) P + X_e \times \left(\frac{k_{et}[4a]}{k_{et}[4a] + k_{de}} \right) \left(\frac{k_\gamma}{k_\gamma + k_{da}} \right) P \quad (24)$$

sence of added quencher. A similar expression can be written for the quantum yield in the presence of added quencher. The large difference in the lifetimes of the two excited states makes possible the derivation of simplified Stern–Volmer equations for the axial (eq 25)

$$\frac{\Phi_a^0}{\Phi_a} = \frac{\Phi^0 - \Phi_e^0}{\Phi - \Phi_e} = 1 + \frac{k_q[Q]}{k_\gamma + k_{da}} = 1 + k_q \tau_a [Q] \quad (25)$$

and equatorial (eq 26) excited states. At high

(39) The rate constant for inversion of 1,1-dimethylcyclohexane at 25° is $\sim 7 \times 10^4 \text{ sec}^{-1}$; D. K. Dalling, D. M. Grant, and L. F. Johnson, *J. Amer. Chem. Soc.*, **93**, 3678 (1971).

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

$$\frac{\Phi_e^0}{\Phi_e} = \frac{\Phi^0 - \Phi_a^0}{\Phi - \Phi_a} = \left(1 + \frac{k_q[Q]}{k_{et}[4a] + k_{de}}\right) \left(1 + \frac{k_q[Q]}{k_\gamma + k_{da}}\right) = \left(1 + \frac{k_q[Q]}{k_{et}[4a] + k_{de}}\right) \quad (26)$$

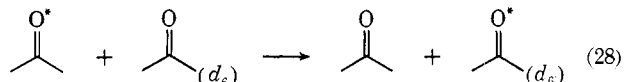
quencher concentrations ($>0.1 M$) the long-lived excited state is completely quenched ($\Phi_e = 0$), while at low quencher concentrations ($<0.002 M$) the short-lived excited state is quenched to an insignificant extent ($k_\gamma + k_d \gg k_q[Q]$, $\Phi_a = \Phi_a^0$). From the extrapolated intercept of the high quencher portion of Figure 3 ($\Phi_0/\Phi = 5.3$) and the total quantum yield in the absence of quencher (0.089), values of $\Phi_a^0 = 0.017$ and $\Phi_e^0 = 0.072$ can be obtained.

When the data in Figure 3 are replotted according to eq 25 and 26, linear Stern-Volmer plots with intercepts of 1.0 and the slopes given in Table III are obtained.⁴⁰ The lifetime of **4a*** is similar to that of the model ketone **5** and is primarily determined by the rate of γ -hydrogen abstraction. The lifetime of **4e*** is dependent upon ketone concentration ($1/\tau = k_{de} + k_{et}[4a^*]$). Modification of eq 24 as given in eq 27 allows analysis of the

$$\frac{1}{\Phi_e} = \frac{1}{\Phi - \Phi_a} = \frac{1}{X_e P} \left(1 + \frac{k_{de}}{k_{et}[4a]}\right) \quad (27)$$

concentration dependence of the quantum yield. Since the value of Φ_a does not vary with concentration, a plot of $1/(\Phi - \Phi_a)$ vs. $[4a]^{-1}$ will be linear and have an intercept of $1/X_e P$ and a slope of $(1/X_e P)(k_{de}/k_{et})$. The slope/intercept ratio of Figure 4 gives a value of $k_{de}/k_{et} = 1.5 \times 10^{-2}$. From the lifetime of **4e*** ($1/\tau = k_{de} + k_{et}[4a] = 6.6 \times 10^6 \text{ sec}^{-1}$ for 0.04 M ketone) values of $k_{de} = 1.8 \times 10^6 \text{ sec}^{-1}$ and $k_{et} = 1.2 \times 10^8 M^{-1} \text{ sec}^{-1}$ are obtained. The lifetimes of **4e** and the rigid model ketone **6** are similar.

Energy transfer between identical molecules in solution has not been widely investigated due to the difficulty in distinguishing donor and acceptor molecules.⁴¹⁻⁴³ Turro and Lechtken⁴³ have investigated "energy-hopping" between acetone (generated by decomposition of tetramethyldioxetane) and acetone-*d*₆ (eq 28). They report rate constants of $\sim 3 \times 10^6 M^{-1}$



sec^{-1} for both singlet and triplet energy transfer. The rate constant we observe for equatorial to axial energy transfer (eq 29) is 40 times more rapid. Our result is in good accord with the expected value for isoenergetic transfer.⁴⁴ The smaller rate constant for energy hopping in acetone may be due to unfavorable Franck-Condon factors for transfer from a nonplanar excited state to a planar ground state, as earlier suggested by Borkman and Kearns.⁴¹

(40) The Stern-Volmer plots show curvature if too large or too small values of Φ_e^0 are used. Best least-squares fits are obtained for $19 \pm 2\%$ axial product formation, in agreement with the quantum yields obtained from the extrapolated intercept in Figure 3.

(41) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

(42) P. J. Wagner, *J. Amer. Chem. Soc.*, **88**, 5672 (1966).

(43) P. Lechtken and N. J. Turro, *Angew. Chem., Int. Ed. Engl.*, **12**, 314 (1973).

(44) A. A. Lamola, *Tech. Org. Chem.*, **14**, 17 (1969).

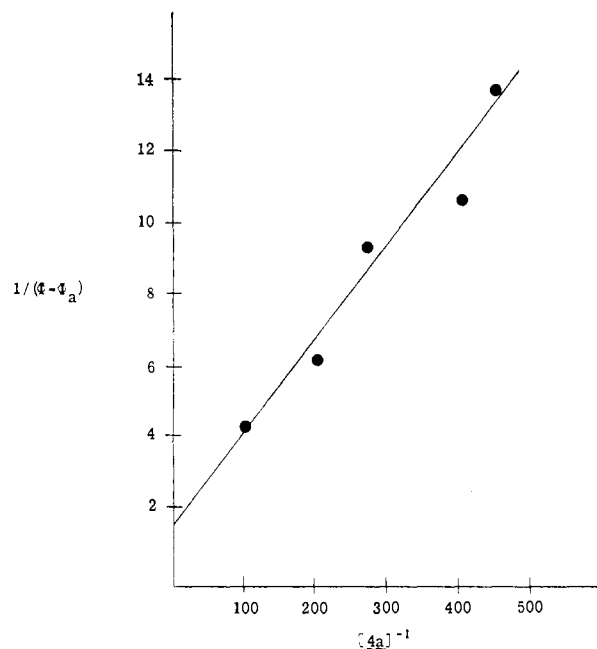
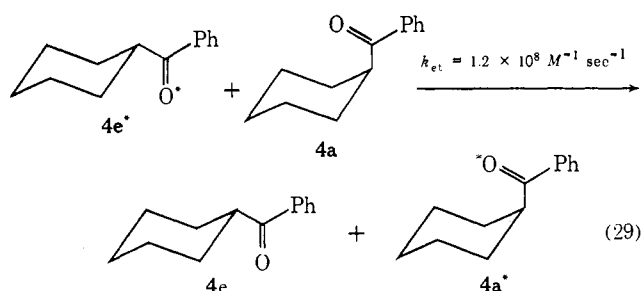
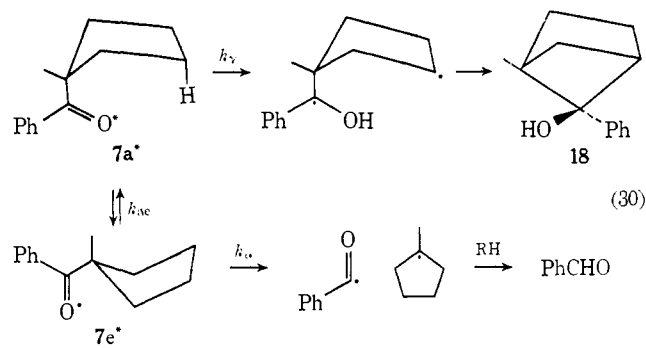


Figure 4. Variation in photoelimination quantum yield for cyclohexyl phenyl ketone with concentration according to eq 27.

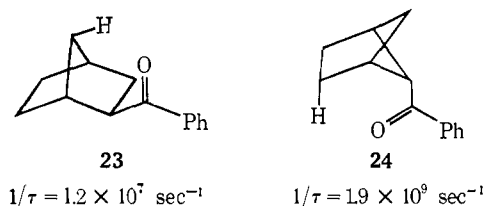


Curtin-Hammett Reactions. The axial and equatorial conformations of ketones **1** and **4** react more rapidly than cyclohexane ring inversion. Consequently they belong to case II as defined in the introductory section and the product ratios are determined by conformational populations. The energy barrier for cyclopentane pseudorotation is considerably smaller than that for cyclohexane ring inversion.⁴⁵ Thus it appeared possible that pseudorotation might compete efficiently with α cleavage and γ -hydrogen abstraction for 1-methylcyclopentyl phenyl ketone (**7**). As is the case for the cyclohexyl phenyl ketones, γ -hydrogen abstraction requires an axial benzoyl conformation (**7a**) whereas α -cleavage can occur from any conformation (eq 30). Quenching of benzaldehyde and bicyclo-



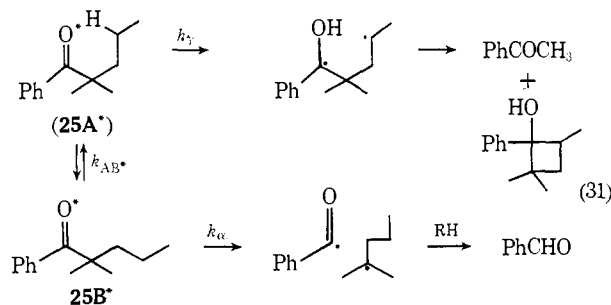
(45) Reference 6, p 248.

butanol formation from ketone **7** gave Stern–Volmer plots with identical slopes (Figure 2). Thus the lifetimes of **7a*** and **7e*** must be the same ($\tau_a = \tau_e = (k_\alpha + k_\gamma)^{-1}$). The observed lifetime ($1/\tau = 2.5 \times 10^7 \text{ sec}^{-1}$) indicates that both γ -hydrogen abstraction and α cleavage^{21b} must be slower for **7** than for **1** (Table III). As we previously pointed out,^{15b} the small rate constant for γ -hydrogen abstraction could reflect either the low conformational population of **7a** or an unusually long O–H $_\gamma$ distance. The two available rigid models for cyclopentyl phenyl ketone (**23**^{18b} and **24**⁴⁶) have



markedly different lifetimes making comparisons with ketone **7** impossible.

Acyclic *tert*-alkyl phenyl ketones can also undergo competitive photochemical γ -hydrogen abstraction and α cleavage (eq 31).^{20, 47} γ -Hydrogen abstraction re-



quires a six-membered transition state (**25A**), whereas α cleavage should occur equally well from all conformations. Energy barriers for rotation about single bonds (3.5–4.5 kcal/mol)⁴⁸ are comparable to those for γ -hydrogen abstraction;³⁶ however, the entropy of activation is more negative for the latter processes. Thus we expected conformational isomerization to be more rapid than photochemical reaction ($k_{AB^*} > k_\alpha, k_\gamma$). For both α, α -dimethylbutyrophenone and α, α -dimethylvalerophenone (**25**) Stern–Volmer plots for quenching of benzaldehyde and cyclobutanol formation have identical slopes.^{18a, 47}

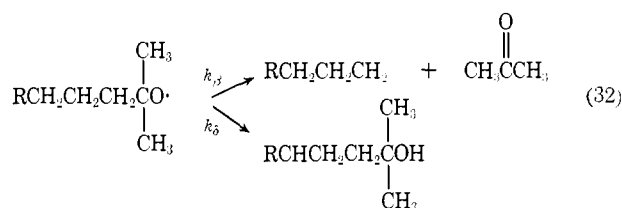
If conformational isomerization of acyclic ketones is more rapid than their chemical reactions, the Curtin–Hammett principle requires that the product composition depends upon the relative rates of formation of the products and not upon conformational populations. The results shown in Table V indicate that this is indeed the case. Assuming $\sim 50\%$ cage recombination the quantum yield for α cleavage is ~ 0.06 . This value is in good accord with the ratio of rate constants $k_\alpha/k_\gamma = 0.08$ for the model compounds **19** and **20**. If conformational populations affected the product ratio, α cleavage would have been expected to be the predominant reaction.

(46) A. Padwa and W. Eisenberg, *J. Amer. Chem. Soc.*, **94**, 5859 (1972).

(47) P. J. Wagner and J. M. McGrath, *J. Amer. Chem. Soc.*, **94**, 3849 (1972).

(48) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).

It is interesting to compare our results for α cleavage and γ -hydrogen abstraction of acyclic ketones with those for the analogous β -scission and δ -hydrogen abstraction reactions of *tert*-alkoxy radicals (eq 32).



Walling and Padwa⁴⁹ suggested that these reactions occur *more* rapidly than alkyl side-chain conformational changes. This would require energy barriers of < 3 kcal/mol for the free radical reactions.

Conclusions

The competitive α cleavage and γ -hydrogen abstraction reactions of alkyl phenyl ketones have been used to probe the effects of molecular conformation upon photochemical behavior. Conformational isomerization is found to be slower than photochemical reactions in some cases (cyclohexyl ketones) and faster in others (cyclopentyl and acyclic ketones). In the former case ground-state conformational populations control product ratios, but in the latter they do not. An approximate knowledge of the relative rate constants for excited state reactions and conformational isomerization is necessary to predict what effect, if any, ground-state conformation will have on photochemical behavior.

For the acyclic alkyl phenyl ketones, product ratios are not determined by conformational populations. However, the rate constant for a conformationally restricted reaction such as γ -hydrogen abstraction should be dependent upon conformational populations or rotamer distributions.⁵⁰ According to the Winstein–Holness relationship (eq 33)⁶ the observed rate will be

$$\text{rate} = k_\gamma X_\gamma \quad (33)$$

equal to the rate of abstraction for rotamers with an optimal O–H $_\gamma$ distance times the equilibrium mole fraction of such rotamers. Expressed in terms of transition-state theory, there should be a negative entropy of activation associated with freezing out internal rotations in the γ -hydrogen abstraction reaction. Entropic control of excited state reactivity is discussed in the accompanying paper.

Experimental Section

1-Methylcyclohexyl Phenyl Ketone (1). Cyclohexyl phenyl ketone (1.0 g, 0.005 mol) and sodium hydride (0.5 g) in 35 ml of dimethoxyethane were refluxed for 4 hr under a nitrogen atmosphere. The mixture was cooled on an ice bath, methyl iodide (1.5 g, 0.01 mol) was added, and stirring was continued for 30 min. Additional sodium hydride (0.2 g) was added and the mixture was refluxed for 1.5 hr prior to cooling and the addition of 0.5 g of methyl iodide. After cautious addition of 30 ml of water, the reaction mixture was extracted with pentane and dried, and the solvent was removed. Chromatography on 40 g of alumina using hexane as the eluent was necessary to remove the residual nonalkylated ketone. 1-Methylcyclohexyl phenyl ketone was obtained as a

(49) (a) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1597 (1963); (b) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967).

(50) T. C. Bruce and U. K. Pandit, *J. Amer. Chem. Soc.*, **82**, 5858 (1960).

colorless oil: ir spectrum 5.95μ ; pmr (CCl_4) δ 1.28 (s, 3 H), 1.40 (m, 10 H), 7.2 (m, 3 H), 7.5 (m, 5 H); ^{13}C nmr (Freon, TMS) δ 24.9 ($\text{C}_{3,\dots}$), 27.6 (C_4), 27.8 (CH_3), 38.0 ($\text{C}_{2,\dots}$), 49.5 (C_1), 206.8 (CO).

cis-4-tert-Butyl-1-methylcyclohexyl phenyl ketone (2) was prepared by alkylation of ketone 5. A procedure analogous to that for conversion of 4 to 1 was used. Crystallization from hexane gave 2 as colorless plates: mp 58–62°; ir spectrum 5.93μ ; pmr (CCl_4) δ 0.75 (s, 9 H), 1.34 (s, 3 H), 0.9–1.6 (m, 7 H), 2.5 (m, 2 H), 7.28 (m, 3 H), 7.58 (m, 2 H).

trans-4-tert-Butyl-1-methylcyclohexyl phenyl ketone (3), **cis-4-tert-Butyl-1-chloro-1-acetylcyclohexane** was prepared by the procedure of Stork, Worrall, and Pappas.⁹ 4-tert-Butylcyclohexanone (31.8 g, 0.21 mol), α -chloropropionitrile⁹ (19 g, 0.21 mol), and 0.23 mol of potassium *tert*-butoxide in 200 ml of *tert*-butyl alcohol were stirred overnight. Following work-up and recrystallization from hexane 17.3 g (0.084 mol, 40%) of the glycidonitrile was obtained as pale yellow crystals. This material and anhydrous zinc chloride (13.6 g, 0.1 mol) in 250 ml of anhydrous ether were cooled on an ice bath and bubbled with gaseous hydrogen chloride. Aqueous work-up followed by distillation gave 10.8 g (65%) of pure **cis-4-tert-butyl-1-chloro-1-acetylcyclohexane**, bp 102–108° (0.2 mm). The α -chloro ketone was converted to **trans-4-tert-butyl-1-methylcyclohexanecarboxylic acid** by the method of House and Gilmore.¹⁰ Reaction of the acid with 2 equiv of phenyllithium followed by chromatography of the crude reaction mixture on silica gel (hexane–benzene) gave after evaporative distillation 0.8 g of pure 6 as a low melting colorless solid: pmr (CCl_4) δ 0.82 (s, 9 H), 1.28 (s, 3 H), 1.0–2.0 (m, 9 H), 7.28 (m, 3 H), 7.58 (m, 2 H).

Cyclohexyl Phenyl Ketone (4). Either Friedel–Crafts acylation of benzene with cyclohexanecarboxyl chloride⁵¹ or reaction of cyclohexanecarboxylic acid (Aldrich) with phenyllithium was used to prepare 1. Reaction of the acid (3.0 g, 0.023 mol) with 0.05 mol of phenyllithium in 300 ml of anhydrous ether gave after work-up and recrystallization from hexane 2.7 g (63%) of 1: mp 55° (lit.⁵¹ 54–55°); ^{13}C nmr (Freon, TMS) δ 28.0 ($\text{C}_{3,\dots}$), 31.3 ($\text{C}_{2,\dots}$), 46.7 (C_1), 201.3 (CO).

cis-4-tert-Butylcyclohexyl phenyl ketone (5) was prepared by the method of Padwa and Eastman,¹⁵ mp 110° (lit.¹⁵ 108–109°).

trans-4-tert-Butylcyclohexyl Phenyl Ketone (6). A solution of 2 and 0.1 M NaOCH_3 in methanol was refluxed for 24 hr. After work-up and crystallization from hexane, 3 was obtained as colorless plates, mp 80–82° (lit.⁵¹ 82–83°).

1-Phenyl-6-hepten-1-one (11). Reaction of (8.3 g, 0.05 mol) 6-bromo-1-hexene (Chemical Samples, 68%) with magnesium in ether followed by addition of benzonitrile gave after hydrolytic work-up 4.2 g (56%) of colorless 11, bp 148–150° (6 mm): nmr (CCl_4) δ 1.6 (m, 4 H), 2.05 (t, 2 H), 2.9 (t, 2 H), 4.8–5.9 (m, 3 H), 7.4 (m, 3 H), 7.8 (m, 2 H); mass spectrum m/e 188 (M^+), 133, 120, 105 (base peak), 77.

Cyclohexylphenylcarbinol (12). Reduction of ketone 4 with sodium borohydride in ethanol afforded 12 as a colorless oil: ir spectrum (film) 3350 cm^{-1} ; nmr (CCl_4) δ 0.9–1.8 (m, 11 H), 1.9 (s, OH), 4.2 (d, 1 H), 7.2 (m, 5 H); mass spectrum m/e 190 (M^+), 107 (base peak), 79, 77.

Irradiation of 1-Methylcyclohexyl Phenyl Ketone (1). A solution of 1.0 g of 1 and 0.25 ml of 1,3-pentadiene⁵² in 100 ml of benzene was bubbled with nitrogen and irradiated for 3.5 hr. Repeated chromatography first on silica gel and then on alumina using ethyl acetate–hexane eluent was necessary to separate unreacted ketone from 6-phenyl-1-methylbicyclo[3.1.1]heptan-6-ol (9) which was obtained as a low melting solid: ir spectrum (0.01 M CCl_4) 3610 cm^{-1} free OH; nmr (90 MHz, CCl_4) δ 1.22 (s, CH_3), 1.64 (s, OH), 1.20 (d,

H_a), 2.28 (t, H_b , $J_{a,b} = 8.0 \text{ Hz}$), 2.48 (m, C_3H), 1.6–2.1 (m, 6 H), 7.2 (m, 5 H). Addition of 0.2 equiv of $\text{Eu}(\text{DPM})_3$ resulted in the following LIS values (ppm): CH_3 1.08, H_a 0.80, H_b 2.0, H_3 2.0, methylene protons ≤ 0.5 .

Irradiation of cis-4-tert-Butyl-1-methylcyclohexyl Phenyl Ketone (2). A solution of 0.2 g of ketone 2 in 25 ml of 1-propanol–benzene was bubbled with argon and irradiated for 1 hr. Silica gel chromatography (hexane) followed by evaporative distillation gave the bicyclic alcohol 10 (0.064 g, 32%) as a colorless oil: ir spectrum (CCl_4) 3610 cm^{-1} ; nmr (CCl_4) δ 0.65 (s, 9 H), 1.15 (s, 3 H), 2.6 (m, 1 H), 7.2 (m, 5 H); mass spectrum m/e 258 (M^+), 256, 242, 145, 143, 129, 91 (base peak); 81, 77.

Irradiation of Cyclohexyl Phenyl Ketone (4). A solution of 1.0 g of ketone in 100 ml of benzene was bubbled with nitrogen and irradiated for 9 hr. Evaporative distillation at 150° (0.1 mm) gave 0.3 g of volatile material and a glassy residue. Chromatography on silica gel (benzene–hexane) gave as the major product an unidentified ketone 13: ir spectrum (CCl_4) 1680 cm^{-1} ; nmr (CCl_4) δ 1.7 (m, 8 H), 3.0 (m, 2 H), 7.2 (m, 3 H), 7.9 (m, H); mass spectrum m/e 186 (M^+), 168, 158, 145, 118 (base peak), 90. Further elution gave an alcoholic product identified as cyclohexylphenylcarbinol (12) by comparison with an authentic sample.

Irradiation of ketone 4 in 1-propanol solution gave 1-phenyl-6-hepten-1-one (11) as the major product. Ketone 11 was identified by comparison of vpc retention time and mass spectra with an authentic sample.

Irradiation of cis-4-tert-Butylcyclohexyl Phenyl Ketone (5). A solution of 0.15 g of ketone 5 in 15 ml of 33% 1-propanol–benzene was irradiated for 3.5 hr. Chromatography on silica gel (hexane–benzene) gave 1-phenyl-5-*tert*-butyl-6-hepten-1-one (15) as a colorless oil: ir spectrum (film) 1680 cm^{-1} ; nmr (CCl_4) δ 0.85 (s, 9 H), 1.4 (m, 4 H), 2.1 (m, 1 H), 2.82 (t, 2 H), 4.8–5.9 (m, 3 H), 7.4 (m, 3 H), 7.9 (m, 2 H); mass spectrum m/e 244 (M^+), 188, 133, 120, 105 (base peak), 77.

Irradiation of trans-4-tert-Butylcyclohexyl Phenyl Ketone (6). Irradiation of a benzene solution resulted in the formation of two products with longer vpc retention time. Repeated attempts to isolate the products by column, thick layer, or preparative vapor phase chromatography were unsuccessful. Analysis of the products by gc–mass spectroscopy showed them to be an unidentified ketone (17) (mass spectrum m/e 242 (M^+), 188, 186, 168, 158, 157, 145, 119, 118 (base peak)) and 4-*tert*-butylcyclohexylphenylcarbinol (16) (mass spectrum m/e 246 (M^+), 107 (base peak), 79, 77).

General Procedures. Preparative scale irradiations were carried out in a Pyrex annulus using a 450-W Hanovia medium-pressure mercury lamp in a Pyrex immersion well. Solutions were analyzed for product formation on a Hewlett-Packard 5750 dual flame gas chromatograph using 5 ft \times $1/8$ in. columns of 5% Carbowax 20 M, 5% SF 96 or 4% QF 1 and 1% Carbowax 20M on Chromosorb G. Quantum yields and rate constants were determined as previously described.^{18a} Infrared spectra were recorded on a Beckman IR 10 or IR 5 spectrophotometer, pmr spectra on a Perkin–Elmer R20B 60 MHz or Bruker 90 MHz spectrometer, 22.6 MHz ^{13}C nmr spectra on a Bruker spectrometer with Fourier transform attachment, ultraviolet spectra on a Cary 14 spectrophotometer, emission spectra on a Perkin–Elmer MPF-2A with phosphorescence attachment, and mass spectra on a Hewlett-Packard 5930A mass spectrometer. Phosphorescence lifetimes were measured as previously described.^{21b}

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(52) This concentration of pentadiene was sufficient to quench most of the α cleavage without affecting γ -hydrogen abstraction.