Photoreduction and α Cleavage of Aryl Alkyl Ketones[1]

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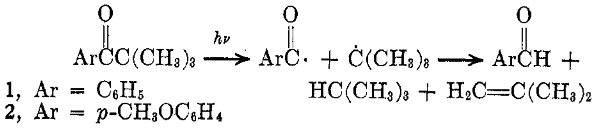
The photochemical α cleavage and reduction reactions of several aryl alkyl ketones have been investigated. Electron-releasing aromatic substituents decrease the excited state reactivity of *tert*-alkyl aryl ketones toward both primary photoprocesses to a similar extent. The aromatic carbonyl $^3(n,\pi^*)$ state is concluded to be responsible for α cleavage as well as hydrogen abstraction reactions. The rate constant for intermolecular hydrogen abstraction by the carbonyl triplet state decreases with α-methyl substitution. Pinacol and carbinol products are formed *via* the combination and disproportionation of ketyl radicals. A primary deuterium isotope effect on isobutyrophenone ketyl radical disproportionation of 2.7 is observed. α-Methyl substituents increase the percentage of carbinol products due to steric hindrance of free-radical combination.

Synthetic[3,4] and mechanistic[5-7] aspects of aryl alkyl ketone photoreduction have been extensively investigated. A number of α-substituted acetophenones form pinacols upon irradiation in 2-propanol or other suitable hydrogen-donor solvents;[3,4] however, quantitative data on such ketones was unavailable prior to our investigation.[7] The elegant studies of Yang and coworkers[5] on aryl-substituted acetophenones established that the carbonyl $^3(n,\pi^*)$ excited state is responsible for the primary photochemical process, intermolecular hydrogen abstraction. The reactivity of the n,π^* state toward inter- or intramolecular hydrogen abstraction is generally attributed to the half-vacant nonbonding orbital on oxygen, which gives the excited state properties similar to those of alkoxy radicals.[8] The half-vacant nonbonding orbital on oxygen also has been postulated to be responsible for α cleavage;[9,10] however experimental evidence on this point has been lacking. In fact the α-cleavage reactions of aryl alkyl ketones remain largely uninvestigated. Aside from *tert*-alkyl phenyl ketones,[11-14] only several deoxybenzoins[15] have been reported to undergo α cleavage.

Results

α Cleavage.—Irradiation of pivalophenone (**1**) and *p*-methoxypivalophenone (**2**) in degassed benzene solution gives benzaldehyde and *p*-methoxybenzaldehyde, respectively, along with isobutane and isobutylene (eq 1). No other products are formed in amounts >5% of benzaldehyde formation. *p*-Phenylpivalophenone (**3**) remains unchanged after prolonged irradiation in degassed benzene or 2-propanol solution. Photolysis of ketones **1** and **2** in nondegassed solution results in more complex product mixtures, presumably due to reaction of the intermediate free radicals with oxygen.[12,15]



$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{C(CH_3)_3} \xrightarrow{h\nu} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot + \dot{\mathrm{C}}\mathrm{(CH_3)_3} \longrightarrow \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} + \mathrm{HC(CH_3)_3} + \mathrm{H_2C{=}C(CH_3)_2} \quad (1)$$

1, Ar = C_6H_5
2, Ar = p-$CH_3OC_6H_4$

Quantum yields for benzaldehyde formation were determined for 0.05 *M* ketone solutions in benzene or benzene containing 3×10^{-3} *M* 1-dodecanethiol using 313-nm irradiation (Table I). Light intensities were measured by simultaneous irradiation of the ketone solutions and benzophenone–benzhydrol actinometer solutions[16] on a merry-go-round apparatus at 25°. Product yields were determined by analytical vpc after <2% conversion of starting ketone. Quantum yields diminished markedly at higher conversions, principally due to quenching by photoproducts.[17] Quantum yields for benzaldehyde formation increased with added 1-dodecanethiol. No increase was observed at concentrations greater than 10^{-3} *M*. Such low mercaptan concentrations did not lead to formation of photoreduction products.

TABLE I

QUANTUM YIELDS AND KINETIC DATA FOR α CLEAVAGE OF *tert*-BUTYL ARYL KETONES

Ketone	$\Phi_{C_6H_6}{}^a$	$\Phi_{C_6H_6}{}^b$ RSH	$k_Q\tau^c$	$1/\tau \times 10^{-5}$, sec^{-1}
$PhCOC(CH_3)_3$ (**1**)	0.163	0.300	447	110
p-$MeOPhCOC(CH_3)_3$ (**2**)	0.081	0.174	7360	6.8
p-$PhPhCOC(CH_3)_3$ (**3**)	<0.001	<0.001		

[a] Quantum yield for benzaldehyde formation in benzene solution. [b] Quantum yield for benzaldehyde formation in benzene containing 3×10^{-3} *M* 1-dodecanethiol. [c] Least-squares slopes of Stern–Volmer plots, limits of error ±10%.

The triplet lifetimes of ketones **1** and **2** were determined by the usual Stern–Volmer treatment. Quenching of benzaldehyde formation from **1** by 1,3-pentadiene gave a Stern–Volmer plot with upward curvature. Curved Stern–Volmer plots (Φ_0/Φ *vs.* quencher) were also observed for 1,3-pentadiene quenching of benzaldehyde formation from α,α-dimethyl-

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, the Research Corporation, and the Merck Foundation for support of this research.

(2) NDEA Fellow, 1970–present.

(3) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, p 204.

(4) (a) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 1271 (1968); (b) *ibid.*, **36**, 1095 (1971); (c) *Chem. Commun.*, 204 (1969); (d) A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969).

(5) (a) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, **89**, 5466 (1967); (b) N. C. Yang and R. L. Dusenbery, *ibid.*, **90**, 5899 (1968); (c) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

(6) F. D. Lewis, *J. Phys. Chem.*, **74**, 3332 (1970), and references cited therein.

(7) For a preliminary report of a portion of this work, see F. D. Lewis, *Tetrahedron Lett.*, 1373 (1970).

(8) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

(9) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(10) D. I. Schuster, R. G. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4304 (1971).

(11) T. Matsuura and Y. Kitaura, *Tetrahedron*, **25**, 4487 (1969).

(12) H.-G. Heine, *Justus Liebigs Ann. Chem.*, **732**, 165 (1970).

(13) F. D. Lewis and T. A. Hillard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970).

(14) F. D. Lewis and T. A. Hillard, *ibid.*, **94**, 3852 (1972).

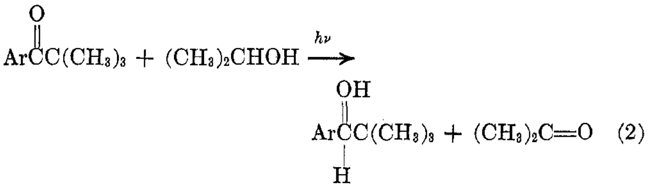
(15) J. Kenyon, A. Rassoul, and G. Soliman, *J. Chem. Soc.*, 1774 (1956).

(16) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(17) F. D. Lewis and D. R. Kory, unpublished results.

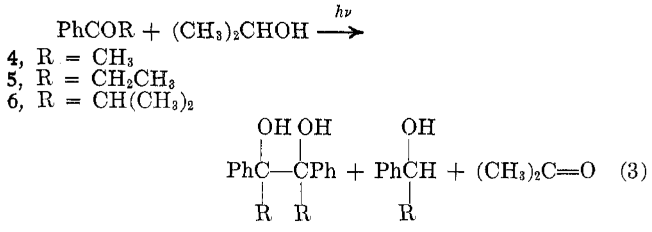
butyrophenone and α,α-dimethylvalerophenone.[14] The curvature presumably is due to scavenging of benzoyl radicals by the diene. Imposition of a linear least-squares fit on the 1,3-pentadiene quenching data for ketone **1** gave a slope of 220, in reasonable agreement with that recently reported by Heine[12] ($k_q\tau = 160$). Quenching of benzaldehyde formation from **1–3** with 2×10^{-4} to 3×10^{-3} *M* naphthalene ($E_T \cong 61$ kcal/mol[18]) using 365-nm irradiation to avoid competitive absorption led to the linear Stern–Volmer plots shown in Figure 1. The slopes of the Stern–Volmer plots are equal to $k_q\tau$ (Table I), where k_q is the rate constant for quenching of the ketone triplet state by naphthalene and τ is the ketone triplet lifetime. Assumption of the value $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for k_q[19] allows calculation of τ or $1/\tau$ (Table I).

Photoreduction.—Irradiation of ketones **1** and **2** in degassed 2-propanol–benzene solution results in formation of the corresponding carbinols and acetone (eq 2)



$$\text{Ar}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{C(CH}_3)_3 + (\text{CH}_3)_2\text{CHOH} \xrightarrow{h\nu} \text{Ar}\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\text{C(CH}_3)_3 + (\text{CH}_3)_2\text{C{=}O} \quad (2)$$

as well as the products of α cleavage (eq 1). The absence of pinacol formation from photoreduction of ketone **1** has previously been noted.[7,12] Irradiation of alkyl phenyl ketones **4–6** in 2-propanol solution under nitrogen resulted in the formation of acetone, a mixture of *dl* and meso pinacols, and the corresponding carbinol (eq 3). No mixed pinacols of the type observed by Weiner[20] for benzophenone photoreduction by 2-propanol were detected; however, the possibility of their presence in small amounts cannot be eliminated. Carbinol products were isolated by silica gel chromatography and were identical with authentic samples. In view of the small percentage of carbinol in the product mixture from acetophenone (**4**), it is not surprising that previous reports of acetophenone photoreduction[4-6] do not mention carbinol formation. Mixtures of the diastereomeric pinacols were obtained by fractional distillation of the photolysis products. No attempt was made to separate the *dl* and meso isomers; however the nmr and ir spectra of the mixtures were consistent with the assigned structures and literature reports.[5,21,22]



$$\text{PhCOR} + (\text{CH}_3)_2\text{CHOH} \xrightarrow{h\nu}$$

4, R = CH_3
5, R = CH_2CH_3
6, R = $CH(CH_3)_2$

$$\text{Ph}\underset{\text{R}}{\overset{\text{OH}}{\text{C}}}\text{—}\underset{\text{R}}{\overset{\text{OH}}{\text{C}}}\text{Ph} + \text{Ph}\underset{\text{R}}{\overset{\text{OH}}{\text{C}}}\text{H} + (\text{CH}_3)_2\text{C{=}O} \quad (3)$$

Irradiation of isobutyrophenone (**6**) in $(CH_3)_2CHOD$ followed by silica gel chromatography gave a mixture of deuterated and undeuterated carbinols.

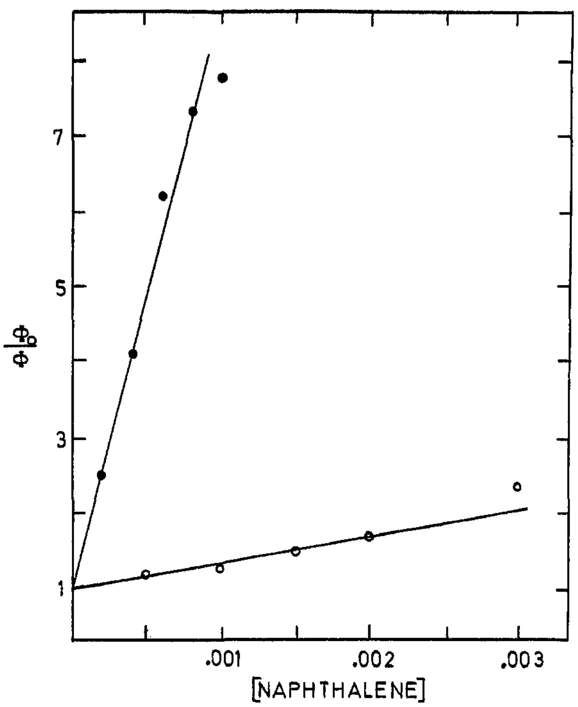
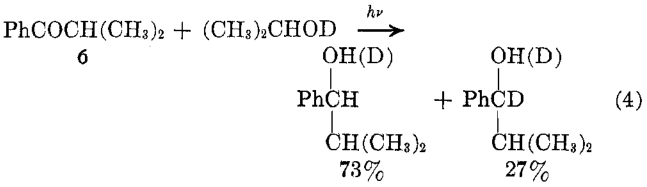


Figure 1.—Stern–Volmer plots for quenching of benzaldehyde formation from pivalophenone (○) and *p*-methoxypivalophenone (●).

Nmr analysis of this mixture showed 27 ± 3% C–D incorporation (eq 4).



$$\underset{\mathbf{6}}{\text{PhCOCH(CH}_3)_2} + (\text{CH}_3)_2\text{CHOD} \xrightarrow{h\nu} \underset{73\%}{\text{Ph}\underset{\text{CH(CH}_3)_2}{\overset{\text{OH(D)}}{\text{C}}}\text{H}} + \underset{27\%}{\text{Ph}\underset{\text{CH(CH}_3)_2}{\overset{\text{OH(D)}}{\text{C}}}\text{D}} \quad (4)$$

Quantum yields for product formation were determined for degassed 0.1 *M* solutions of ketones **4–6** in 2.0 *M* 2-propanol–benzene solution using 313-nm irradiation. Products were analyzed on calibrated vpc columns after <10% conversion of starting ketone.[23] The results are given in Table II. In all cases $\Phi_{\text{acetone}} \approx \Phi_{\text{pinacol}} + \Phi_{\text{carbinol}}$.[6,7] Quantum yields for carbinol formation from ketones **1** and **2** were measured as a function of 2-propanol concentration (0.5–4.0 *M*) in benzene solution. Values are given in Table II for 4.0 *M* 2-propanol–benzene solution. The low quantum yields combined with the necessity of analysis at low

TABLE II

QUANTUM YIELDS FOR PHOTOREDUCTION OF ARYL ALKYL KETONES

Ketone	Solvent,[a] *M*	Φ_{pinacol}	Φ_{carbinol}
$PhCOC(CH_3)_3$ (**1**)	4.0	<0.001	0.0099
p-$CH_3OPhCOC(CH_3)_3$ (**2**)	4.0	<0.001	0.011
p-$PhPhCOC(CH_3)_3$ (**3**)	4.0	<0.001	<0.001
$PhCOCH_3$ (**4**)	2.0	0.37	0.007
$PhCOCH_2CH_3$ (**5**)	2.0	0.19	0.033
$PhCOCH(CH_3)_2$ (**6**)	2.0	0.071	0.049

[a] Concentration of 2-propanol in benzene.

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[18] P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971).

[19] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2332 (1968).

[20] S. A. Weiner, *ibid.*, **93**, 425 (1971).

[21] H. Agahigian, J. F. Moraveck, and H. Gauther, *Can. J. Chem.*, **41**, 194 (1963).

[22] W. A. Mosher and N. D. Heindel, *J. Org. Chem.*, **28**, 2154 (1963).

[23] Quantum yields for acetophenone photoreduction decrease for conversions over 10%.[6]

conversion resulted in fairly large errors for these measurements (±20%).

Plots of $1/\Phi$ for carbinol formation from ketones **1** and **2** *vs.* 1/[2-propanol] had intercepts near unity and slopes equal to $(\tau k_r)^{-1}$, where k_r is the rate constant for intermolecular hydrogen abstraction. Values of $(\tau k_r)^{-1}$ are given in Table III along with k_r values calculated using the τ values from Table I. The rate constants for intermolecular hydrogen abstraction (k_r) and nonradiative decay (k_d) of the carbonyl triplet states of **4–6** in 0.1 *M* 2-propanol–benzene solvent[6] were determined by standard Stern–Volmer analysis of the variation of $1/\Phi$ for acetone formation with quencher (piperylene) concentration (eq 5). The values of

TABLE III

KINETIC DATA FOR PHOTOREDUCTION OF ARYL ALKYL KETONES[a]

Ketone	$(\tau k_r)^{-1}$	$\tau \times 10^6$, sec	$k_d \times 10^5$, sec^{-1}	$k_r \times 10^5$, M^{-1} sec^{-1}
1	460	0.09		0.24
2	192	1.5		0.035
4[b]		2.4	3.4	6.8
5		2.7	3.2	4.4
6		2.9	3.4	0.9

[a] Limits of error for kinetic data = ±10% for **4**, ±20% for **1**, **2**, **5**, and **6**. [b] Values from ref 6.

$$\frac{1}{\Phi} = \frac{k_r[\mathrm{RH}] + k_d}{k_r[\mathrm{RH}]} + \frac{k_q[\mathrm{Q}]}{k_r[\mathrm{RH}]} \tag{5}$$

k_r obtained from the slopes of linear Stern–Volmer plots assuming $k_q = 5 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ [19] decrease with increasing α substitution (Table III). The k_d values obtained from the intercepts of the Stern–Volmer plots in 0.1 *M* 2-propanol–benzene are the same for **4–6** within the experimental error and are in good agreement with values for acetophenone obtained by phosphorescence decay measurements.[24] The calculated values for τ, the triplet lifetime [$\tau = (k_r[\mathrm{RH}] + k_d)^{-1}$] increase slightly for the series **4–6**. Since the triplet lifetimes of **1** and **2** in benzene solution are determined by α cleavage as well as by nonradiative decay, no value of k_d for **1** or **2** is included in Table III.

Discussion

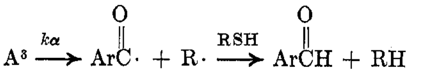
α Cleavage and Photoreduction.—The yields and efficiencies of photochemical α-cleavage reactions of carbonyl compounds have frequently been observed to depend on the stability of the pair of radicals or biradical that is formed.[25] This dependence reflects the balance between the carbonyl excited state energy and the heat of reaction. The calculated heat of reaction for α cleavage of *tert*-alkyl phenyl ketones is comparable to the carbonyl triplet energy (73 ± 1 kcal/mol).[14] Thus it is not surprising that *tert*-alkyl[11–14] and benzyl phenyl ketones[15] undergo α cleavage, but primary and secondary alkyl phenyl ketones do so inefficiently, if at all.

The photochemical α-cleavage reactions of a *tert*-alkyl aryl ketone (A) can be described by the following simplified mechanism, where Q is the triplet quencher naphthalene and RSH is the radical scavenger 1-dodecanethiol. In benzene solution photoreduction does not compete with α cleavage. Hence the quantum yield for benzaldehyde formation in the absence and presence of naphthalene is given by eq 10 and 11, respectively, where β is the probability that the initially formed benzoyl-*tert*-alkyl radical pair will lead to benzaldehyde formation. Addition of 1-dodecanethiol increases β (and Φ_0) by providing a source of readily abstractable hydrogens for the benzoyl radical.[26] Values of Φ_0 less than unity for ketones **1** and **2** are due at least in part to cage recombination of the initially formed radical pair.[27] Assuming that the triplet quencher naphthalene does not alter β,[29] the Stern–Volmer equation (eq 12) can be obtained from eq 10 and 11. The $1/\tau$ values in Table I equal the sum of the rate constants for α cleavage (k_α) and nonradiative decay (k_d). Values of $k_d \sim 3 \times 10^5\ \mathrm{sec}^{-1}$ have been reported by ourselves[6,7] and others[24] for a number of aryl ketones, including **4–6**, in benzene solution. Such values are small compared to $1/\tau$ for ketone **1**, indicating that $k_\alpha \approx 1/\tau$. However, $1/\tau$ for ketone **2** is not much greater than k_d, so that $k_\alpha \leq 1/\tau$. Thus part of the inefficiency of benzaldehyde formation from ketone **2** may be due to competition of nonradiative decay with α cleavage.

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}^1 \xrightarrow{k_{\mathrm{ST}}} \mathrm{A}^3 \tag{6}$$

$$\mathrm{A}^3 \xrightarrow{k_d} \mathrm{A} \tag{7}$$

$$\mathrm{A}^3 + \mathrm{Q} \xrightarrow{k_q} \mathrm{A} + \mathrm{Q}^3 \tag{8}$$



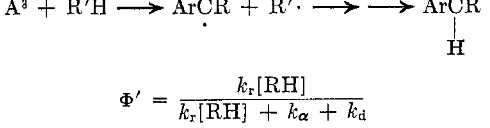
$$\mathrm{A}^3 \xrightarrow{k\alpha} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot + \mathrm{R}\cdot \xrightarrow{\mathrm{RSH}} \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} + \mathrm{RH} \tag{9}$$

$$\Phi_0 = \left(\frac{k_\alpha}{k_\alpha + k_d}\right)\beta \tag{10}$$

$$\Phi = \left(\frac{k_\alpha}{k_\alpha + k_d + k_q[\mathrm{Q}]}\right)\beta \tag{11}$$

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q[\mathrm{Q}]}{k_\alpha + k_d} = 1 + k_q\tau[\mathrm{Q}] \tag{12}$$

In 2-propanol–benzene solution photoreduction (eq 13) competes with α cleavage. The quantum yield for formation of carbinol (Φ') in the absence of quencher is given by eq 14. From plots of $1/\Phi'$ *vs.* 1/[RH] (eq 15) and the values of $1/\tau$ in Table I, the rate constants



$$\mathrm{A}^3 + \mathrm{R'H} \xrightarrow{k_r} \mathrm{Ar}\overset{\mathrm{OH}}{\overset{|}{\underset{\cdot}{\mathrm{C}}}}\mathrm{R} + \mathrm{R'}\cdot \longrightarrow\longrightarrow \mathrm{Ar}\overset{\mathrm{OH}}{\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}}}\mathrm{R} \tag{13}$$

$$\Phi' = \frac{k_r[\mathrm{RH}]}{k_r[\mathrm{RH}] + k_\alpha + k_d} \tag{14}$$

$$\frac{1}{\Phi'} = 1 + \frac{k_\alpha + k_d}{k_r[\mathrm{RH}]} = 1 + \frac{1}{\tau k_r[\mathrm{RH}]} \tag{15}$$

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(24) (a) W. C. K. Clark, A. D. Litt, and C. Steel, *Chem. Commun.*, 1087 (1969); (b) H. Lutz and L. Lindquist, *ibid.*, 493 (1971).

(25) (a) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970); (b) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966); (c) H. Küntzel, H. Wolf, and K. Schaffner, *Helv. Chim. Acta*, **54**, 868 (1971).

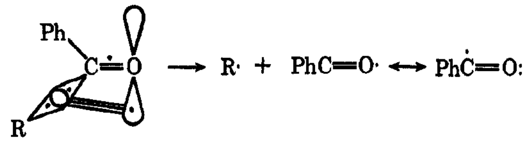
(26) The resulting thiyl radicals do not react with benzaldehyde: R. M. Kellog, "Methods in Free Radical Chemistry," Vol. II, E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969, p 107.

(27) Fractions of cage recombination >0.2 have been observed for pairs of ketyl radicals.[28]

(28) S. A. Weiner, *J. Amer. Chem. Soc.*, **93**, 6978 (1971).

(29) Naphthalene is an inefficient scavenger even for reactive radicals such as methyl radical, which adds to dienes 300 times more rapidly than to naphthalene: W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 221.

for hydrogen abstraction (k_r) in Table III were obtained. The bimolecular rate constants for hydrogen abstraction (k_r) for ketones **1** and **2** are much smaller than the rate constants for α cleavage. However, both primary processes show similar substituent effects, with *p*-methoxy substitution (**2**) resulting in a large decrease in rate constant and *p*-phenyl substitution (**3**) resulting in total lack of reactivity. Similar substituent effects on the efficiency of phenyl ketone intra-[30,31] and intermolecular[5] hydrogen abstraction have been observed. Decreased excited state reactivity results from lowered energy of the unreactive $^3(\pi,\pi^*)$ state relative to that of the reactive $^3(n,\pi^*)$ state upon substitution with electron-releasing groups. The residual reactivity of some such ketones has been attributed by Yang[5] to mixing of an upper $^3(n,\pi^*)$ state with a lowest $^3(\pi,\pi^*)$ state, and, recently, by Wagner[32] to abstraction from an equilibrium concentration of an upper $^3(n,\pi^*)$ state. In either case, the similarity of the substituent effects indicates that α cleavage, like hydrogen abstraction, occurs more efficiently from a $^3(n,\pi^*)$ state than from a $^3(\pi,\pi^*)$ state. The half-vacant nonbonding orbital on oxygen of the n,π^* excited state can overlap with the bond undergoing homolysis (eq 16).[9,10] No such overlap is possible for a π,π^* excited state.



(16)

Steric Effects on Photoreduction.—With the measurement of the rate constant for intermolecular hydrogen abstraction (k_r) by pivalophenone (**1**), comparison of the complete series of α-methyl-substituted acetophenones (**1**, **4**, **5**, and **6**, Table III) becomes possible. The rate constant for hydrogen abstraction by propiophenone (**5**) is only slightly smaller than that for acetophenone (**4**); however, much larger decreases are observed for isobutyrophenone (**6**) and pivalophenone (**1**). It is unlikely that the decrease in k_r with α-methyl substitution is due to a change in triplet energy or the n,π^* character of the lowest triplet state. Phosphorescence lifetime measurements indicate that the n,π^* triplet is of lower energy than the π,π^* triplet for ketones **1** and **4** in nonpolar media.[33] α-Methyl substituents cause no decrease in the rate constants for intramolecular γ-hydrogen abstraction by butyrophenone or valerophenone.[14] Furthermore, CNDO-2 calculations by Blanchi[34] show that there is no change in the excited state charge density on oxygen with α substitution for **4**–**6**.

The observed effect of α-methyl substitution is consistent with increased steric hindrance of intramolecular hydrogen abstraction. Additional evidence for a steric requirement for hydrogen abstraction by alkyl phenyl ketones has been provided by using 2,4-dimethyl-3-heptanol in place of 2-propanol as the hydrogen donor for ketones **4**–**6**.[7] The increased steric requirements of the secondary alcohol resulted in decreased values of k_r.[7]

Two possible cases of a steric effect on benzophenone photoreduction by secondary alcohols have been reported;[35] however, in neither case have quantitative excited state reactivity data been presented. Steric effects are reported to be unimportant for hydrogen abstraction by excited uranyl ion from secondary alcohols.[36] However, the steric requirements for hydrogen abstraction *via* an intermolecular collision are clearly smaller for the uranyl ion than for aryl alkyl ketones. Steric hindrance of triplet energy transfer has been postulated in several instances.[37] Our results would at first seem to be in agreement with those of Hammond[37a] for triplet energy transfer from ortho alkyl benzophenones to stilbenes. However, photoenolization and possibly undetected competing reactions[11,38] greatly complicate interpretation of Hammond's results. Wagner[39] recently compared the rate constants for energy transfer from valerophenone and α,α-dimethylvalerophenone and found no evidence for steric hindrance. Since Wagner's system is quite similar to ours, it seems reasonable to conclude for aryl alkyl ketones that steric effects are considerably more important for intermolecular hydrogen transfer than for energy transfer.

The effects of substituents on photochemical reduction can be compared with results for ground-state reductions of alkyl phenyl ketones. Brown and Ichikawa[40] attributed the decrease in relative rates of sodium borohydride reduction for ketones **4** (1.0), **5** (0.56), and **6** (0.52) to a combination of inductive and steric effects. The large increase in relative rate for **1** (18.1) was attributed to partial deconjugation of the phenyl and carbonyl groups due to the interaction of the phenyl and *tert*-butyl groups.[40] The increase in relative rate of hydrogenation on palladium for ketones **4** (1.0), **5** (1.34), **6** (1.55), and **1** (2.84) was similarly attributed to acceleration of hydrogenation due to release of steric strain in a transition state with considerable tetrahedral character.[41] It seems likely that the transition state for photochemical hydrogen abstraction is more reactantlike, thus explaining the absence of steric acceleration for ketone **1**.

Ketyl Radical Disproportionation and Combination.—In addition to their effect on the rate of intermolecular hydrogen abstraction, α-methyl substituents influence the quantum yields for pinacol and carbinol formation (Table II). Pinacol formation is known to occur by combination of two ketyl radicals (eq 17).

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[30] E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **88**, 2652 (1966).

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

[32] P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.*, **92**, 5806 (1970).

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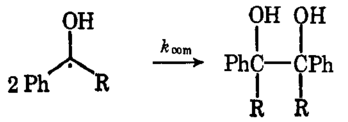
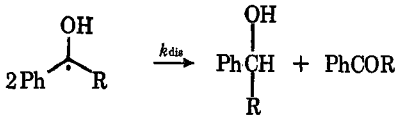
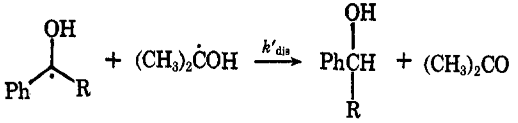
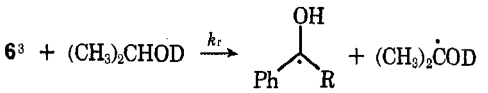
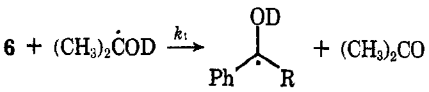

(17)


(18)


(19)

Carbinol formation could conceivably occur either by disproportionation of two ketyl radicals (eq 18) or by disproportionation of the nonsymmetrical radical pair (eq 19). The reduction of **6** in $(CH_3)_2CHOD$ was studied in order to differentiate between these possibilities (eq 20–23). Disproportionation of the nonsymmetrical radical pair (eq 23) requires carbinol formation with 100% C–D incorporation. Ketyl radical disproportionation (eq 21, 22) should lead to ≤50% C–D incorporation with the exact value depending on the size of the isotope effect on disproportionation. The experimental value was 27 ± 3% C–D incorporation. Although a small amount of nonsymmetric radical disproportionation (eq 23) cannot be ruled out, this result is in accord with ketyl radical disproportionation (eq 21, 22) having a primary kinetic isotope effect of $k_H/k_D = 2.7$. This isotope effect is somewhat larger than that obtained by Gibian and Corley[42] by comparing the disproportionation/combination ratios of $Ph\dot{C}HCH_3$ and $Ph\dot{C}HCD_3$ $[(k_{dis}/k_{com})(H)/(k_{dis}/k_{com})\cdot(D) = 1.87]$. The isotope effect is indicative of a small activation energy for free-radical disproportionation in solution.[43]


(20)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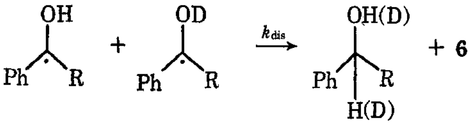
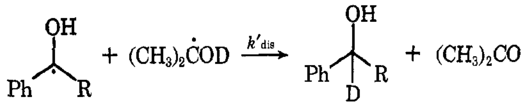
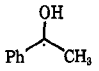
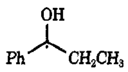
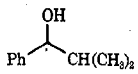
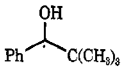

(22)


(23)

Since pinacol and carbinol formation are the result of ketyl radical disproportionation and combination, the ratio of rate constants (k_{dis}/k_{com}) can be obtained from the quantum yields in Table II. The results are given in Table IV along with selected values for other free radicals. The value of k_{dis}/k_{com} for acetophenone ketyl radical is much lower than those for the hydroxyl radicals formed upon pulse radiolysis of ethanol[44] and cyclohexanol.[45] Low values of k_{dis}/k_{com} are characteristic of benzyl type radicals and apparently are the result of enhanced combination rate constants for radical pairs in which the odd electron is highly delocalized.[28,46] The k_{dis}/k_{com} ratio is observed to increase by over a factor of 500 in going from acetophenone ketyl radical to pivalophenone ketyl radical.[47] The effect of β substituents on acetophenone ketyl radicals is thus far greater than the effect of α-methyl substituents on simple alkyl radical gas phase k_{dis}/k_{com} ratios (Table II).[48–50] Whereas α-substituent effects on k_{dis}/k_{com} have been extensively studied for alkyl radicals, less is known about β-substituent effects. Small increases in k_{dis}/k_{com} are observed for ethyl *vs.* 1-propyl and 2-propyl *vs.* 2-butyl radicals (Table IV). The larger increase in k_{dis}/k_{com} for cumyl *vs.* 2-phenyl-3-methyl-2-butyl radical has been attributed with trepidation to simple steric hindrance.[46c] A comparable but larger increase is observed for acetophenone *vs.* isobutyrophenone ketyl radical. The very large increase in k_{dis}/k_{com} between isobutyrophenone and pivalophenone ketyl radicals is similar to that observed for S_N2 rate constants for isobutyl and neo-

TABLE IV

DISPROPORTIONATION/COMBINATION RATIOS FOR RADICAL PAIRS

Radical pair	k_{dis}/k_{com}	Ref
	0.02	*a*
	0.17	*a*
	0.69	*a*
	>10	*a*
α-Hydroxyethyl	0.25	*b*
α-Hydroxycyclohexyl	2.0	*c*
Methyl + ethyl	0.036	*d*
Ethyl	0.134	*d*
1-Propyl	0.154	*d*
2-Propyl	0.694	*d*
2-Butyl	1.2	*e*
tert-Butyl	2.32	*d*
Cumyl	0.054	*f*
2-Phenyl-3-methyl-2-butyl	0.3	*g*

[a] This work. [b] Reference 44. [c] Reference 45. [d] Reference 48. [e] Reference 49. [f] Reference 46a. [g] Reference 46b.

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[42] M. J. Gibian and R. C. Corley, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. 0-140.

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[44] I. D. Taub and L. M. Dorfman, *J. Amer. Chem. Soc.*, **84**, 4953 (1962).

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[46] (a) S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966); (b) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967); (c) S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969); (d) R. C. Neuman, Jr., and E. S. Alhadeff, *J. Org. Chem.*, **35**, 3401 (1970); (e) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Amer. Chem. Soc.*, **90**, 354 (1968); (f) G. S. Hammond and S. A. Weiner, *Intra-Sci. Chem. Rep.*, **3**, 241 (1969).

[47] Since disproportionation of ketyl radicals involves hydroxyl hydrogen transfer, there is no need to normalize these results for the number of abstractable β hydrogens.

[48] (a) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2327 (1967); (b) *ibid.*, **46**, 664 (1968).

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pentyl substrates.[51] The k_{dis}/k_{com} results for ketyl radicals are consistent with a steric hindrance argument. The magnitude of the β-substituent effect is clearly greater than would have been predicted on the basis of previous free-radical literature. Generalization of these results should be treated with caution in view of the complex nature of the interactions of such large and delocalized free radicals in solution.[46f]

Summary.—The rate constant for acetophenone photoreduction decreases with increasing α-methyl substitution. This trend is attributed to increasing steric hindrance of the primary photoprocess, intermolecular hydrogen abstraction. In contrast to the continuous decrease in rate constant for photoreduction with α-methyl substitution, photochemical α cleavage occurs efficiently only for *tert*-alkyl aryl ketones. Quantitative comparison of the competition between photoreduction and α cleavage requires kinetic data for both processes. The similar effects of aromatic substituents on the rate constants for photoreduction and α cleavage indicates that both processes occur from a $^3(n,\pi^*)$ state. Deuterium labeling establishes that carbinol formation is the result of ketyl radical disproportionation. The marked increase in the ratio of disproportionation to combination rate constants with methyl substitution is due to a large steric effect on ketyl radical termination.

Experimental Section

Materials and Solvents.—Acetophenone (Eastman) and propiophenone (MCB) were purified by recrystallization from ethanol–water and from petroleum ether (bp 30–60°) at 10° and then distilled. Isobutyrophenone (Aldrich) was distilled and the middle fraction was retained. The *tert*-butyl aryl ketones **1–3** were prepared by the method of Peterson.[52] The physical constants of **1**[52] and **2**[53] were in agreement with literature values. Ketone **3** was obtained as a colorless solid, mp 92–93°, nmr (CCl_4) δ 1.35 (s, 9 H), 7.2–7.8 (m, 9 H). The carbinols prepared by reduction of ketones **1–4**[54] and **5**[53] with lithium aluminum hydride all had physical constants in agreement with literature values. Benzaldehyde, anisaldehyde (Eastman), and 4-biphenylcarboxaldehyde (Aldrich) were commercial samples. Benzene and 2-propanol were purified as previously described. 2-Propanol-*O-d* was prepared by treatment of purified 2-propanol with a 50-fold excess of D_2O followed by extraction with benzene. *n*-Dodecanethiol (Aldrich) was used as received.

Product Studies.—Carbinol products from ketones **1**, **2**, and **4–6** and aldehydes from **1** and **2** were isolated by chromatography of large-scale photolysis mixtures on silica gel with benzene–ethyl acetate solvent. The isolated carbinols and aldehydes had nmr and ir spectra and vpc retention times identical with those of authentic samples. The extent of C–D incorporation in the carbinol from irradiation of ketone **6** (0.8 g) in 20 ml of 3 *M* 2-propanol-*O-d*–benzene was determined by comparison of the integrated methine and hydroxyl regions of the nmr spectrum with those for an undeuterated authentic sample. Mixtures of *dl* and meso pinacols from ketones **4–6** were obtained by distillation of large-scale photolysis mixtures at 0.2 mm. The fractions with bp >120° were recrystallized from hexane and had melting points (for pinacols from **4**,[22] **5**,[22] and **6**[55]), ir spectra (pinacols from **4**[22] and **5**[22]), and nmr spectra (pinacol from **4**[21]) in accord with literature data. Propiophenone pinacol nmr follows (CCl_4): *dl*, δ 0.55 (t, J = 7.5 Hz, CH_3), 2.42 (s, OH); meso, δ 0.52 (t, J = 7.5 Hz, CH_3), 1.98 (s, OH). Isobutyrophenone pinacol nmr follows (CCl_4): *dl*, δ 0.77 (q_{ab}, J = 6.5 Hz, Δ_{ab} = 42 Hz, CH_3), 1.75 (septet, J = 6.5 Hz, CH), 2.71 (s, OH); meso, δ 0.67 (d, J = 6.9 Hz, CH_3), 2.28 (septet, J = 6.9 Hz, CH), 2.08 (s, OH). Infrared spectra were recorded on a Beckman IR-10 spectrometer and nmr spectra on a Varian A-60 spectrometer.

Quantum Yields and Rate Constants.—The yields of benzaldehyde and/or carbinol from ketones 1 and 2 were determined by vpc analysis on a calibrated 7 ft × 0.125 in. column of 10% FFAP on DMSC-treated Chromosorb G. Yields of acetone, pinacol, and carbinol from ketones **4–6** were determined as previously described. Actinometry, isolation of 313-nm irradiation, and determination of rate constants were as previously described.[6,7] Corning filters 7-54 and 0-52 were used to isolate the 365-nm mercury line.

Registry No.—**1**, 938-16-9; **2**, 2040-26-8; **3**, 34546-86-6; **4**, 98-86-2; **5**, 93-55-0; **6**, 611-70-1; *meso*-propiophenone pinacol, 16020-86-3; (±)-propiophenone pinacol, 16020-87-4; *meso*-isobutyrophenone pinacol, 22210-57-7; (±)-isobutyrophenone pinacol, 22210-56-6.

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