# Type II Photoprocesses of Phenyl Ketones. Competitive δ-Hydrogen Abstraction and the Geometry of Intramolecular Hydrogen Atom Transfers

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Abstract: In δ-methoxyvalerophenone (7) the γ C–H bonds are deactivated and the δ C–H bonds activated such that the triplet undergoes roughly 50:50 γ- and δ-hydrogen abstraction, with the formation of cyclopentanols as well as type II products. This result and the 85% maximum quantum yield for products resulting from γ-hydrogen abstraction in nonanophenone-γ,γ-d_2 suggest small amounts of competing δ-hydrogen abstraction in several long-chain ketones. γ,γ-Dimethylvalerophenone (12) photocyclizes to a cyclopentanol and phosphoresces in degassed benzene solution with 40% the intensity displayed by acetophenone. β-Ethoxypropiophenone (14) photocyclizes in 50% quantum efficiency to five-membered ring products but does not eliminate ethanol. The rate of δ-hydrogen abstraction by 14 is not much different from that by 7. Therefore, the lack of normal type II products from β,β-dimethyl β-alkoxy ketones indicates that 3-alkoxy-1-hydroxy 1,4 biradicals preferentially eliminate alcohol. The efficiency of cyclization of the 1,5 biradicals which result from δ-hydrogen abstraction is generally low and is not greatly altered by hydroxylic solvents. α-,β-, and δ-alkyl substitutions cause no steric hindrance to rates of γ-hydrogen abstraction, indicating a strain-free chair-like six-membered cyclic transition state. Geminal dimethyl substitution at the γ position, as in 12, significantly retards δ-hydrogen abstraction, reflecting the torsional strain in a seven-membered cyclic transition state. This ring strain argument is postulated to explain the preference for 1,5- vs. 1,6-hydrogen atom transfers.

I ntramolecular hydrogen atom transfers in acyclic molecules are very specific in that 1,5 transfers generally predominate over 1,6 and other possible modes.[2–4] In particular, irradiation of acyclic ketones

$$X = RCH, \quad O, \quad RN^+$$

$$k_{1,5} \gg k_{1,6}$$
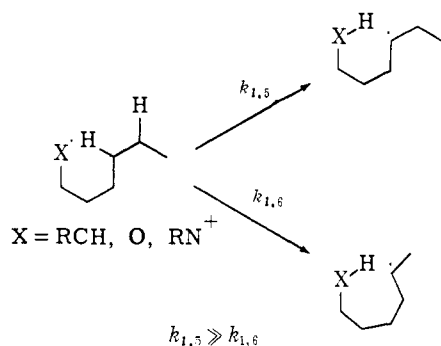
results in reactions arising specifically from γ-hydrogen atom abstraction, i.e., type II elimination and cyclobutanol formation. All evidence indicates that triplet excited ketones abstract γ hydrogens with nearly 100% efficiency.[5,6] We have concluded that triplet ketones behave almost identically with alkoxy radicals.[7] The alkoxy radicals generated from alkyl hypochlorites have been reported to undergo ~15% δ-hydrogen abstraction competitive with γ-hydrogen abstraction especially when the δ carbon bears substituents which weaken its C–H bonds.[8] One might then wonder

whether triplet ketones resemble alkoxy radicals to the point of also undergoing measurable δ-hydrogen atom abstraction. In fact, there are several examples of carbonyl compounds which do yield photoproducts resulting from apparently selective δ-hydrogen abstractions: 5,5-dimethyl-3-hexen-2-one;[9] several β-alkoxy β,β-dimethyl ketones;[10,11] and o-alkoxyphenyl glyoxalate esters.[12] However, there are no reports of cyclopentanols being produced upon irradiation of simple ketones RCO(CH₂)$_n$CH₃.

We have looked very carefully at the photochemistry of several phenyl alkyl ketones which contain δ C–H bonds intrinsically more reactive than their γ C–H bonds and at two phenyl ketones containing δ hydrogens but no γ hydrogens.

Results

Phenyl Alkyl Ketones. Table I lists quantum yields, Stern–Volmer quenching slopes, and rates of triplet reaction of several ketones with varying δ C–H bonds. In the first six ketones, the γ carbon is secondary and bonded to a β-methylene and a δ-alkyl group, such that the γ C–H bond strength should be identical throughout. Likewise, the last three ketones contain only primary γ C–H bonds.

For all ketones, total quantum yields in benzene are low but are enhanced by small concentrations of added *tert*-butyl alcohol.[13] Normally, this same solvent effect manifests itself as increasing type II quantum yields with increasing ketone concentration in ben-

(1) Alfred P. Sloan Fellow, 1968–1972.
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(6) For a review, see P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).
(7) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, 94, 7495 (1972).
(8) C. Walling and A. Padwa, *ibid.*, 85, 1597 (1963).

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Table I. Kinetic Parameters for Type II Photoprocesses of Several Phenyl Alkyl Ketones PhCOR[a]

R		Φ[b]	Φ_{max}[c]	$k_q\tau$, M^{-1}[d]	$k_{\gamma\text{-H}}$, 10^8 sec^{-1}[e]
CH₂CH₂CH₂CH₃		0.40	1.0	40 ± 1	1.25
CH₂CH₂CH₂CH₂CH₃		0.38	0.97	38 ± 1	1.30
CH₂CH₂CH₂CH(CH₃)₂	1	0.33	0.94	27 ± 1	1.74
CH₂CH₂CH₂C(CH₃)₃	2	0.33	0.98	24 ± 0.5	2.10
C(CH₃)₂CH₂CH₂CH₃	3	0.12	>0.5[f]	64 ± 1	0.7[f]
CH₂CH₂CH₂C₅H₁₁[g]	4	0.30	0.97	29 ± 1	1.70
CH₂CH₂CD₂C₅H₁₁[g]	5	0.31	0.85	87 ± 1	0.5[h]
CH₂CH₂CH₃		0.40	1.0	650 ± 10	0.08
CH₂CH(CH₃)₂		0.40	1.0	240 ± 3	0.21 (0.11)[i]
CH₂C(CH₃)₃	6	0.20	>0.7[j]	81 ± 5	0.62 (0.21)[i]

[a] Degassed 0.10 M solutions in benzene irradiated at 313 nm. [b] Total quantum yields for elimination and cyclization in benzene. [c] Maximum total quantum yield obtained upon addition of polar solvent: precision ±0.02. [d] 2,5-Dimethyl-2,4-hexadiene quencher. [e] $k = \Phi_{max}/\tau$; $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$. [f] Reference 14. [g] Reference 5. [h] Uncorrected for incomplete deuteration of ketone. [i] Values in parentheses per methyl group. [j] Reference 13.

zene.[13] Occasionally, the preparation of a ketone introduces a quenching impurity which lowers both Φ and $k_q\tau$ values. This problem can be diagnosed by noting *decreases* in quantum yields with increasing ketone concentration (in any solvent) and can be corrected for by simple extrapolation to zero ketone concentration. None of the ketones studied were subject to any such impurity quenching, with the exception of 5. Therefore, the parallel decreases in Φ and $k_q\tau$ values caused by β- and δ-alkyl substitution are not artifacts. The Φ values reported for 5 are those extrapolated to zero ketone.

Both β,β-dimethylbutyrophenone (6) and α,α-dimethylvalerophenone (3) behave somewhat differently than do the other ketones. For both, total quantum yields of type II processes are unusually low. For both ketones, type II quantum yields increase with added alcohol, but the response is much more gradual than for most other ketones, so that the quantum yields never level off to a constant value and do not reach unity even in neat alcohol.[13] Since acetophenone accounts for >95% of reacted 6, we conclude that $1/\tau$ equals the rate of γ-hydrogen abstraction and that the low quantum yields are due to unusual behavior of the biradical intermediate.

Irradiation of 3 yields a more profuse collection of products, which are described in detail elsewhere.[14] Type II products are accompanied by products of type I cleavage, as expected.[15] Analysis of the behavior of several phenyl *tert*-alkyl ketones[14] indicates triplet state rate constants of 2×10^7 sec^{-1} for α cleavage and that listed in Table I for γ-hydrogen abstraction by 3.

Of the first seven ketones in Table I, only 1 and 5 exhibit maximum type II quantum yields lower than unity (outside experimental error). Both have δ C-H bonds intrinsically more reactive than their γ C-H bonds. The near unit quantum yield of 2 indicates that the lower quantum yield of 1 is not due to any steric effect of the γ-isopropyl group on the biradical. Figure 1 compares the rapid rise in type II quantum yields for 4 and 5 as a function of added *tert*-butyl alcohol. The behavior of 1 is analogous to that of 5. We conclude that another triplet state reaction competes with γ-hydrogen (deuterium) abstraction in these two ketones. Although we suspect δ-hydrogen abstraction, no cyclo-
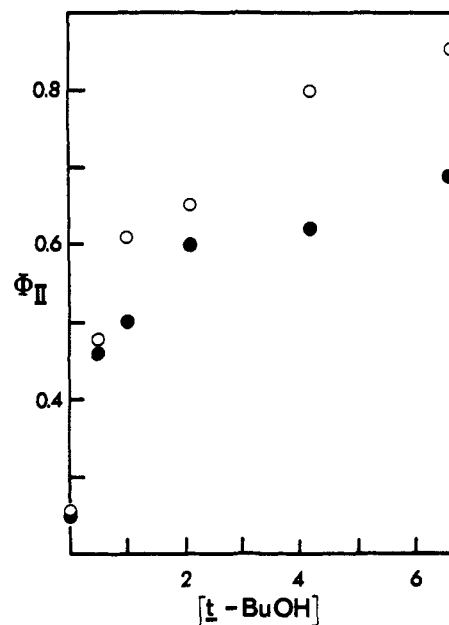
(14) P. J. Wagner and J. M. McGrath, *J. Amer. Chem. Soc.*, 94, 3849 (1972).

(15) (a) N. C. Yang and E. D. Feit, *ibid.*, 90, 504 (1968); (b) F. D. Lewis, *Tetrahedron Lett.*, 1373 (1970); (c) H-G. Heine, *Justus Liebigs Ann. Chem.*, 732, 165 (1970).

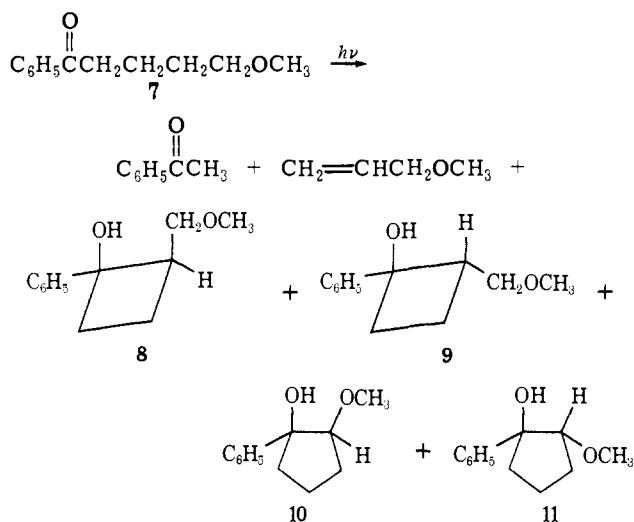Figure 1. Effect of added *tert*-butyl alcohol on quantum yield of acetophenone formation from (O) nonanophenone-γ,γ-h_2 and (●) nonanophenone-γ,γ-d_2.

pentanol products could be detected in the vpc traces of irradiated 1. Vpc traces of irradiated 5 did reveal a small amount (0.5% of reacted ketone) of a photoproduct besides the cyclobutanols. Its retention time was in the region expected for cyclopentanols, but its yield was too small to allow collection and identification.

δ-Methoxyvalerophenone (7) was synthesized and its photochemistry studied for the following reasons. We know that a methoxy group enhances the reactivity of C-H bonds on the carbon to which it is attached by a factor of 5 and we expect the inductive effect of a δ-methoxy group to deactivate γ C-H bonds by another factor of 3.[7] Consequently we expected that the γ and δ C-H bonds of 7 might be of comparable reactivity toward the triplet benzoyl group. As Table II indicates, the maximum quantum yield of products resulting from γ-hydrogen abstraction in triplet 7 rises to only 46% at low alcohol concentrations and does not increase at higher alcohol concentrations. Moreover, *four* products appear with vpc retention times in the regions expected for cyclobutanols and cyclopentanols.

All four of these products were collected from a high conversion run in *tert*-butyl alcohol and proved to be

Table II. Quantum Yields of Product Formation and Ketone Disappearance from Irradiation of δ-Methoxyvalerophenone[a]

| Product	Benzene	t-BuOH
PhCOCH$_3$	0.33	0.37
8	0.10	0.06
9	<0.002[b]	0.03
10	0.019	0.015
11	0.015	0.085
− Ketone	0.47	0.56

[a] 3130-Å irradiation of 0.10 M ketone solutions in the two solvents indicated. [b] None detected.

cyclic alcohols isomeric with the ketone. The major product obtained in benzene displays a concentration-independent hydrogen-bonded O–H stretch in its ir spectrum, prominent M − 28 and m/e 120 peaks in its mass spectrum, and an nmr spectrum consistent with the expected *trans*-cyclobutanol 8. The *cis*-cyclobutanol 9, which is formed in measurable amount only in *tert*-butyl alcohol, has an almost identical mass spectrum and displays a sharp free O–H stretch at 3600 cm^{-1} in its ir spectrum. The other two products have ir, nmr, and mass spectra identical with those of *trans*- and *cis*-2-methoxy-1-phenylcyclopentanol, 10 and 11, which were synthesized unambiguously as described in the Experimental Section. Yields of the various products are listed in Table II.

Quenching studies indicate that triplet 7 decays at a rate of 5.6 × 10^7 sec^{-1}.[7] The solvent effect on the type II quantum yield indicates that only 46% of triplet 7 decay by γ-hydrogen abstraction, with a rate equal to Φ_{max}/τ = 2.7 × 10^7 sec^{-1}, in the range predicted by the inductive effects of other δ substituents.[7] This kinetic analysis of the type II reaction of 7 indicates that its triplet undergoes a competitive reaction with a rate constant on the order of 3 × 10^7 sec^{-1}. Formation of cyclopentanols indicates that the competitive reaction is δ-hydrogen abstraction. Unfortunately, total product formation does not proceed with 100% quantum efficiency. Even though we conclude that triplet 7 undergoes roughly 50% δ-hydrogen abstraction, quantum yields for cyclopentanol formation are only 4% in benzene and 10% in *tert*-butyl alcohol. Therefore, the probability for cyclization of the assumed 1,5-biradical intermediate is only 8% in benzene and rises

to 20% in alcohol. Acetophenone, cyclobutanols, and cyclopentanols account quantitatively for all the reacted ketone in both benzene and *tert*-butyl alcohol.

γ,γ-**Dimethylvalerophenone (12)** was prepared and studied because it has no γ hydrogen but nine δ hydrogens. Irradiation of degassed benzene or *tert*-butyl alcohol solutions of 12 produces, in 60% yield, a product identified by its ir, nmr, and mass spectra as 3,3-dimethyl-1-phenylcyclopentanol, the product expected from δ-hydrogen abstraction.
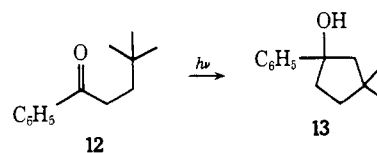
That triplet 12 is quite unreactive is demonstrated by the easily detectable phosphorescence of 12 in degassed benzene solutions. The emission is very similar to that of acetophenone under comparable conditions,[16] with a 0–0 band at 72 kcal and 1700 cm^{-1} spacing between four prominent vibronic bands.

The actual phosphorescence intensity of 0.006 M benzene solutions of 12 is 40% that of comparable acetophenone solutions. Phosphorescence quenching studies with 2,5-dimethyl-2,4-hexadiene yield $k_q\tau$ values of 9,500 and 26,000, respectively, for the two ketones, in fine agreement with the relative emission yields and indicating the same n,π* phosphorescence rate for the two ketones. We estimate a decay rate of 5.3 × 10^5 sec^{-1} for triplet 12, 3.3 × 10^5 sec^{-1} of which must be the rate of δ-hydrogen abstraction, the rest corresponding to the same direct triplet quenching of solvent which accounts for acetophenone's short lifetime.[16]

Distressingly, Stern–Volmer quenching studies (also with 2,5-dimethyl-2,4-hexadiene) of formation of 13 from degassed benzene solutions 0.06 M in 12 yield a $k_q\tau$ value of only 2400 M^{-1} at 2.5% conversion. The quantum yield for formation of 13 under these conditions is 0.040.

We believe that the fourfold discrepancy between the different $k_q\tau$ measurements is due to the formation of a quenching by-product. We observe the very rapid build-up of a strong fluorescer (maximum at 380 nm) while the emission spectra of ketones such as 12 and acetophenone are being recorded. Apparently the reaction of their triplets with benzene produces the fluorescent product. Anything which fluoresces at 380 nm would have a low enough triplet energy to quench the otherwise long-lived ketone triplets very efficiently. We do in fact observe a diminution in the phosphorescence intensity of 12 after its solutions have been irradiated a few minutes in the spectrophotofluorometer. Likewise, at only 0.15% conversion, the quantum yield for formation of 13 is 0.087, the value decreasing at longer irradiation times. Figure 2 shows that the quantum yield extrapolated to zero conversion is on the order of 12%. A plot such as Figure 2 would be linear if a stable quenching product were being formed; consequently we tentatively conclude that a steady-state concentration of the quenching by-product on the order of 3 × 10^{-4} M builds up rapidly, so as to
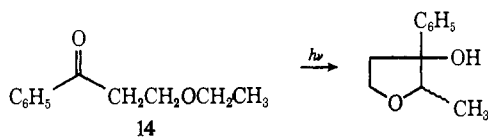
(16) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5411 (1969); J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, M. Wrighton, and J. Winterle, *ibid.*, **92**, 410 (1970).

decrease the triplet lifetime measured at modest conversions.

If our analysis of the less-than-straightforward quenching results is correct, the actual quantum yield for cyclization of unquenched **12** is 12–16%, and since only 60% of triplet **12** abstracts a δ-hydrogen, the cyclization efficiency of the 1,5 biradical is 20–25%.

In both *tert*-butyl alcohol and wet acetonitrile, the phosphorescence of **12** is only 55% as intense as in benzene. At ~2% conversion, quantum yields for formation of **13** are only 0.03 and 0.009, respectively. We have not investigated these solvent effects further.

β-Ethoxypropiophenone (**14**) was prepared and studied

$$
\text{C}_6\text{H}_5 \overset{\text{O}}{\underset{}{\diagup\!\!\diagdown}} \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 \xrightarrow{h\nu} \text{[2-methyl-3-phenyl-3-hydroxytetrahydrofuran]}
$$
14

because of the behavior reported for other β-alkoxy ketones.[12] Upon irradiation, it forms the expected 2-methyl-3-phenyl-3-hydroxytetrahydrofurans quantitatively in quantum yields of 50% (5:1 trans–cis) in benzene and 32% (1:1 trans–cis) in wet acetonitrile. There is no evidence for elimination of ethanol or formation of acrylophenone, such as is found with β-alkoxy ketones containing γ C–H bonds.[10,11]

Quenching of the reaction with 2,5-dimethyl-2,4-hexadiene reveals a $k_q\tau$ value of 360 M^{-1} in benzene, and thus a rate of δ-hydrogen abstraction of 1.4×10^7 sec^{-1}.

Discussion

Rates of δ-Hydrogen Abstraction. Ketone **7** is the cleanest example of competitive γ- and δ-hydrogen abstraction, since products from both processes are formed in good yield. The estimated rate of δ-hydrogen abstraction by triplet **7** can be compared to the 6×10^8 sec^{-1} rate of γ-hydrogen abstraction in triplet γ-methoxybutyrophenone[7] to deduce a γ/δ reactivity ratio of 20 for secondary hydrogens on a carbon bonded to oxygen. The γ/δ reactivity ratio in ketones such as **4** should be similar. The isotope effect on γ abstraction in **5** would lower that ratio to 5. Since triplet **5** does in fact undergo some reaction 15% as rapid as γ-deuterium abstraction, we conclude from the kinetic evidence that that reaction is δ-hydrogen abstraction.

Branching in the alkyl chain apparently decreases the rate of δ-hydrogen abstraction. Comparison of **6** and **12** reveals a γ/δ reactivity ratio of 190 for the primary hydrogens on a *tert*-butyl group. The maximum type II quantum yield of **1** indicates a *maximum* reactivity of a tertiary δ C–H bond relative to two secondary γ C–H bonds of 6.3% and thus 1.6% relative to a tertiary γ C–H bond.[7]

Fate of 1,5 Biradicals. Intramolecular δ-hydrogen abstraction produces a 1,5 biradical which undergoes probably only two further reactions: cyclization and disproportionation back to ground-state ketone. We observe wide variations in this competition depending on substitution, but in no case is cyclization highly efficient. In a straight chain system such as **7**, only ~8% of the biradicals cyclize in benzene. The ratio cyclization/(cyclization + disproportionation) is typically ~10% for 1,4 biradicals,[17] so the two systems do
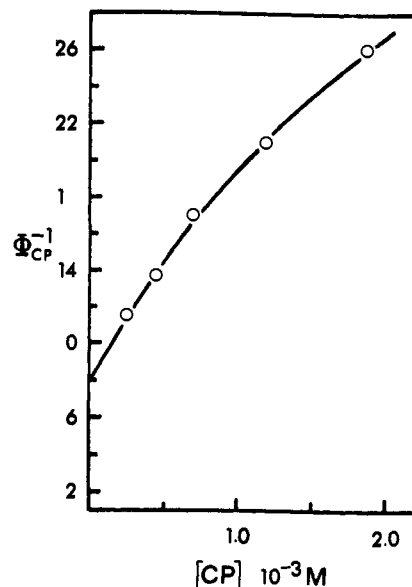

Figure 2. Dependence on conversion of quantum yield of 3,3-dimethyl-1-phenylcyclopentanol (CP) formation from irradiation of γ,γ-dimethylvalerophenone.

not behave all that differently. We presume that comparably low cyclization efficiencies explain the lack of readily observable cyclopentanol formation from **4**, **5**, and especially **1**. Introduction of dimethyl substitution at the γ carbon in **12** raises the percentage cyclization to ~20%, while substitution of an oxygen atom for the γ carbon, as in **14**, increases the per cent cyclization to 50%. Geminal dimethyl substitution often favors cyclizations, while the latter effect parallels that already reported for 1,4 biradicals, α-alkoxyacetophenones producing oxetanols in high yield.[18]

The effects of added polar solvents on the behavior of the 1,5 biradicals vary, causing both quantum yield enhancements and decreases in different compounds. In no case does cyclization become 100% efficient, but cis/trans product ratios are greatly altered. Solvation of these hydroxy biradicals is obviously more complicated than in the case of the type II biradicals and requires further study.

Geometry of Intramolecular Hydrogen Abstractions. The data in Table I reveal that β- and δ-alkyl substitutions produce slight increases in the rate of triplet state γ-hydrogen abstraction while α-dimethyl substitution produces a slight rate decrease. Both effects reflect expected[7,18,19] inductive perturbations. Consequently, we conclude that such substitution produces no *steric hindrance* to γ-hydrogen abstraction. In contrast, alkyl substitution at the γ and δ carbons does seem to hinder δ-hydrogen abstraction significantly.

Steric hindrance in an *intramolecular* reaction reflects extra torsional strain or nonbonded interactions developed during rotation of the molecule into its transition state conformation. In an acyclic system, a transition state geometry which required even partial eclipsing of one C–C bond would make the reaction subject to significant steric effects. Since we find that α, β, and δ substituents produce no steric hindrance to the type II

(17) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, *J. Amer. Chem. Soc.*, 94, 7506 (1972).
(18) N. J. Turro and F. D. Lewis, *ibid.*, 92, 311 (1970).
(19) P. J. Wagner and R. A. Leavitt, *ibid.*, 92, 5806 (1970).

reaction, we can conclude that the conformations of the α,β and β,γ C–C bonds must be totally staggered in the transition state for γ-hydrogen transfer. Staggered conformations about these bonds are, of course, strongly preferred in the ground state, and it is difficult to envision how excitation of the carbonyl group would produce any geometric change in remote bonds.

The well-known order 1,5 > 1,6 ≫ 1,4 in rates of intramolecular hydrogen atom transfers in acyclic systems[2-4,8] was originally thought[2] to reflect a cyclic transition state geometry in which the hydrogen atom lies on a line between the two atoms between which it is being transferred. However, such a linear arrangement of atoms would cause much less angle strain in the transition state for 1,6 transfer than in the transition state for 1,5 transfer. Recent understanding of the torsional strain present in seven-membered and larger cycloalkanes suggests that the great ease of 1,5-hydrogen transfers in acyclic systems reflects primarily a torsion-free, chair-like, six-membered cyclic transition state as exemplified below. Hesse has summarized several examples of intramolecular hydrogen transfers in alkoxy radicals wherein the C–H–O angle must be considerably smaller than 180°.[4]

alkoxy radical   ketone triplet
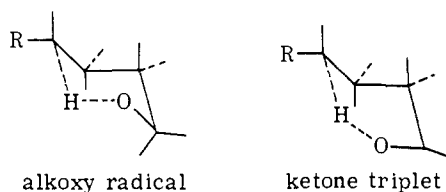
Our results demand such a strain-free transition state for γ-hydrogen transfer by triplet ketones. Torsional strain present in the cycloheptane-like transition state for 1,6-hydrogen transfers[20] explains both the slower rate of δ-hydrogen abstraction in straight chain systems and the retarding effects of alkyl substituents. If the full amount of ring strain present in cycloheptane were present in the transition state for δ-hydrogen abstraction, γ-hydrogen abstraction would be 10^3–10^4 times faster rather than only 20 times faster. The previously unrecognized effect of branching on rates of δ-hydrogen abstraction can be interpreted as reflecting part of the added torsional strain and nonbonded interactions caused by geminal dimethyl substitution in a cycloheptane.

The selective 1,6-hydrogen transfers in esters such as 15[12] represent the exception which proves the rule.

15
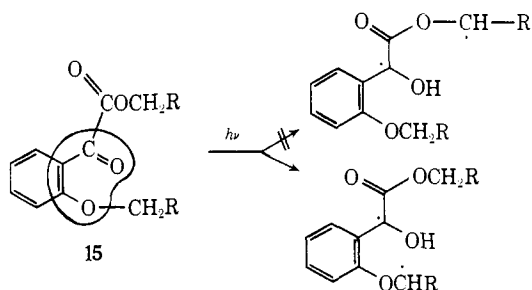
C–H bonds next to an ether oxygen are intrinsically 20–50 times more reactive than those next to an ester oxygen.[1] If 15 were sterically similar to an acyclic

system, a δ/γ ratio of 1–2 would have been expected. That no γ-hydrogen abstraction is observed indicates that the rate of δ-hydrogen abstraction must be enhanced relative to its value in an acyclic system. Since the encircled atoms are almost coplanar in the ground state and even more so in the excited state, there is very little added strain in going to the transition state for δ-hydrogen abstraction in this particular system. The behavior of 15 represents the opposite alteration in normal rates of 1,6-hydrogen transfers from that afforded by 12.

These results extend the usefulness of the alkoxy radical model of n,π^* triplets of ketones, since both species display similar γ/δ reactivity ratios, at least in straight chain systems where they have both been studied. The analogy cannot be perfect, because alkoxy radicals and excited carbonyls do differ in geometry. However, the difference is probably slight. Triplet formaldehyde has long been known to be sp³ hybridized at carbon.[21] More recently it has been ascertained that C–O bond lengths in triplet aldehydes are 0.10 Å longer than in their ground states.[22] That phenyl ketones may undergo similar geometric changes upon excitation is suggested by the similar dipole moments of benzophenone and formaldeyde triplets,[23] which happen to equal the value (1.7 D) characteristic of a C–O single bond.

In the above pictorial comparison of γ-hydrogen abstractions in alkoxy radicals and in ketone triplets, the only real geometric unknowns are the configuration of the carbonyl carbon and the conformation about the carbonyl-α-carbon C–C bond. Consideration of known ground-state conformational preferences limits the uncertainties in the picture of the excited state and provides another expression for the difference between γ- and δ-hydrogen abstraction. Detailed studies[24] of the conformations of carbonyl compounds strongly suggest that the preferred ground-state geometry of phenyl ketones is as pictured below. If excitation does not destroy the planarity of the benzoyl system, the excited state geometry should remain quite similar. Such
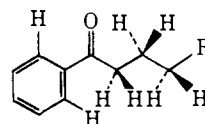
a geometry is ideal for γ-hydrogen transfer, since only one 120° rotation about the α,β C–C bond is required to bring a γ hydrogen near the oxygen. (In the β-alkyl ketones, not even this rotation is necessary.) In fact, in order for a γ hydrogen to be within bonding distance of the oxygen, the α-alkyl group can rotate no more than 30° from the conformation pictured. Such a rotation cannot be required, however, otherwise α-dimethyl substitution would have produced marked steric hindrance—via nonbonded interactions with ortho hydrogens—to γ-hydrogen abstraction.

For δ-hydrogen transfer, rotation about the β,γ C–C bond is also required. Since δ-hydrogen abstraction

(20) See ref 10b for a slightly different, independent statement of this conclusion.

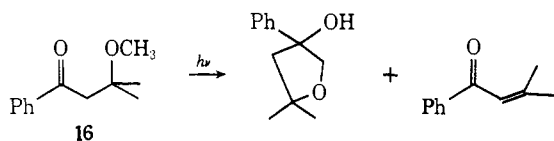(21) J. C. D. Brand and D. G. Wilkinson, Advan. Phys. Org. Chem., 1, 365 (1963).

(22) C. T. Lin and D. C. Moule, J. Mol. Spectrom., 37, 280 (1971); 38, 136 (1971).

(23) R. M. Hochstrasser and T-S. Liu, J. Chem. Phys., 49, 4929 (1968).

(24) For a recent review, see G. J. Karabatsos and D. J. Fenoglio, Top. Stereochem., 5, 167 (1970).

thus involves twice as many frozen rotations in its cyclic transition state as does γ-hydrogen abstraction, part of the rate difference must reflect the differing entropy losses for the two processes.

β-Alkoxy Ketones. The behavior of β-ethoxypropiophenone 14 is very informative as regards the reported behavior of β-alkoxy ketones which also contain γ C–H bonds.[10,11] For example, irradiation of ketone 16 produces both a tetrahydrofuranol and elimination of methanol.[11] Irradiation of 14 produces only cyclization. The rate of δ-hydrogen abstraction by triplet 14 indicates that γ- and δ-hydrogen abstraction would compete 50:50 in triplet 16.[25] Consequently, we con-

clude that the 1,4 biradicals produced from β-alkoxy ketones must react almost exclusively by elimination of alcohol. We cannot tell whether this elimination is a four-centered or six-centered reaction. We are biased toward the latter, because strong intramolecular hydrogen bonding might explain the lack of normal cyclization and type II cleavage of the biradical.[26]

It is interesting that substitution of an oxygen atom for the γ-methylene does not enhance the rate of δ-hydrogen abstraction. One might have expected the lone pairs on oxygen to cause less torsional strain than C–H bonds in the seven-membered ring transition state.

Experimental Section

Chemicals. Solvents, internal standards, and quencher were obtained as usual.[7]

γ,γ-Dimethylvalerophenone was prepared by adding the Grignard reagent from 3,3-dimethyl-1-chlorobutane to benzonitrile, followed by the usual acidic hydrolysis.

δ-Methoxyvalerophenone was prepared by reacting the cyclohexylimine of acetophenone with ethyl magnesium bromide in tetrahydrofuran,[27] followed by addition of 3-methoxy-1-propyl tosylate which had been prepared from 3-methoxy-1-propanol (Pfaltz and Bauer).

β-Ethoxypropiophenone was prepared in very low yield by adding β-ethoxypropionitrile to phenyl magnesium bromide.

β,β-Dimethylbutyrophenone was prepared in 83% yield by treating tert-butylacetyl chloride (Aldrich) in benzene with a 1.1 mole ratio of aluminum chloride. The resulting ketone was distilled, passed through alumina, and redistilled, bp 127–128° (21 Torr).

δ-Methylhexanophenone was prepared in 46% yield by adding benzonitrile in diethyl ether to the Grignard reagent of 1-bromo-4-methylpentane. The reaction mixture was acidified and the aqueous layer heated on a steam bath. The ketone product was distilled, bp 136–137° (8 Torr). The bromide was prepared by treating 4-methyl-1-pentanol (Chemical Samples Co.) with phosphorus tribromide.

δ,δ-Dimethylhexanophenone was prepared similarly, bp 141° (8 Torr). The precursor 4,4-dimethyl-1-pentanol was prepared from 4,4-dimethyl-1-pentene (Chemical Samples Co.). The olefin (0.25 mol) was added dropwise with a syringe to 100 ml of a stirred ice-cold solution of 1.25 M diborane in tetrahydrofuran under a nitrogen atmosphere.[28] The resulting solution was allowed 0.5 hr to come to room temperature, whereupon 36 ml of 3 N sodium hydroxide was added and followed by dropwise addition of 30% hydrogen peroxide. After 1 hr of stirring, the solution was saturated with potassium carbonate and the THF layer was separated

and dried over anhydrous potassium carbonate. Distillation provided the alcohol in 95% yield.

All other ketones discussed were prepared as described in our other papers.[5,7] All ketones were >99% pure as judged by vpc analysis and were identified by their nmr and mass spectra.

Quenching studies and quantum yield measurements were performed as usual.[7]

Products from δ-Methoxyvalerophenone. tert-Butyl alcohol solutions of the ketone were irradiated to complete conversion and the four products were collected by preparative vpc on a column packed with 4% QF-1 and 1.2% Carbowax 20M. (Separations and relative retention times are acutely sensitive to the amount of Carbowax.)

The first eluted product was assigned as the cis-cyclopentanol 10 since it has the same spectral properties as the major product obtained from the addition of phenyl Grignard to 2-methoxycyclopentanone: concentration-independent peak at 3540 cm^{-1} in the ir, indicative of an intramolecularly hydrogen-bonded OH; 70-eV mass spectral peaks at m/e 192 (parent), 174 (P − H$_2$O), 160 (P − CH$_3$OH), 133, 105 (base peak), none at 164 (P − C$_2$H$_4$); nmr (CCl$_4$–TMS) δ 7.35 (m, 1 H, phenyl), 3.9 (m, 1 H, CHO), 3.20 (s, 3 H, OCH$_3$), 2.85 (s, 1 H, OH), 1.8 (br m, 6 H, ring protons).

The third eluted product was assigned as the trans-cyclopentanol 11 since it has the same spectral properties as the major product obtained by methanolysis of 1-phenylcyclopentene epoxide and the minor product obtained upon addition of phenyl Grignard to 2-methoxycyclopentanone: concentration-dependent O–H stretches at 3600 and 3450 cm^{-1}; mass spectrum very similar to that of 10; nmr same as 10 except that the OH peak is concentration dependent, the tertiary proton next to the methoxy group appears at δ 3.5, and methoxy protons appear at δ 2.95.

The second eluted product was assigned as the trans-cyclobutanol 9 on the basis of its spectra: concentration-independent O–H stretch at 3520 cm^{-1}; mass spectral peaks at m/e 192, 174, 164, 160, 120, and 105; nmr δ 7.35 (m, 5 H, phenyl), 3.8 (m, 2 H, CH-CH$_2$O), 3.37 (s, 3 H, OCH$_3$), 2.92 (concentration independent, s, 1 H, OH), 2.8 (m, 1 H, tertiary ring proton), 1.7–2.5 (m, 4 H, ring CH$_2$'s).

The fourth eluted product was assigned as the cis-cyclobutanol 10 because its mass spectrum is very similar to that of 9 while its ir spectrum displays a sharp, free O–H stretch at 3600 cm^{-1}.

Products from β-Ethoxypropiophenone. Vpc analyses of irradiated solutions show only two product peaks whose area accounts quantitatively for the decrease in parent ketone area. On a 4% QF-1, 1.2% Carbowax 20M column, the two product peaks elute after the parent ketone. A benzene solution 0.5 M in ketone was irradiated to partial conversion. The ir spectrum of the photolysate showed free and hydrogen-bonded O–H stretches; the nmr spectrum showed new absorbances at δ 7.3 (characteristic of 1-phenylcycloalkanols), a quartet centered at δ 3.9, a methyl doublet at δ 1.0 (ethoxy group), and a complex multiplet in the δ 2.6–2.0 range. All these peaks are consistent with the expected product 15.

Product from γ,γ-Dimethylvalerophenone. A dilute benzene solution of the ketone was irradiated to 90% conversion through a uranium glass filter (λ > 3400 Å). The solitary volatile product had a vpc retention time slightly shorter than that of the parent ketone. It was collected by preparative vpc and found to be a white solid melting at 68–69° (uncorrected). It was assigned the 3,3-dimethyl-1-phenylcyclopentanol structure on the basis of the following spectral data: ir, OH stretch at 3600 cm^{-1}; mass spectrum, parent peak at m/e 190, base peak (M − H$_2$O) at 172; nmr δ 7.35 (br s, 5 H, phenyl), 1.05 and 1.12 (two sharp s, ~3 H each, methyls), 0.9–2.1 (m, 6 H, ring protons), 1.5 (variable) (s, 1 H, OH). Because this compound undergoes very facile dehydration, another similar photosylate was treated with trimethylsilyl chloride and the silyl ester was collected by preparative vpc. Its nmr spectrum was very similar, showing a phenyl signal at δ 7.35 and the two methyl signals at δ 1.16 and 1.04.

All nmr spectra were taken in CCl$_4$ solutions with tetramethylsilane as internal standard on a Varian T-60. Mass spectra were recorded on a Perkin-Elmer-Hitachi RMU-6E at 70-eV ionizing voltage.

Phosphorescence studies were performed on an Aminco-Bowman spectrophotofluorometer fitted with an off-axis ellipsoidal mirror condensing system, a mercury-xenon lamp, and a side-on potted 1P 21 photomultiplier tube. Spectra were recorded on a Houston Instruments x-y recorder. The sample holder was modified so as to hold 13 × 100 mm Pyrex tubes snugly. These were first degassed, then sealed, and excited with the 313-nm mercury line. In quenching runs, intensities were read directly off the micro-

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(26) Professor Yates has kindly informed us that both α,β- and β,γ-unsaturated products are obtained from phenyl ketones such as 16.

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photometer. A phosphorescence value was determined for each sample by subtracting the emission intensity of the aerated sample from that just recorded for the degassed, sealed sample.
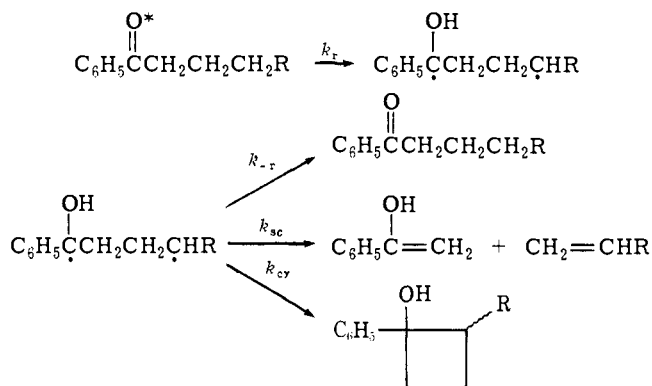
Type II Photoprocesses of Phenyl Ketones. A Glimpse at the Behavior of 1,4 Biradicals

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Abstract: Electron-donating groups on the benzene ring and electron-withdrawing groups at the δ, ε, and even ζ positions enhance quantum yields of type II photoreactions of phenyl alkyl ketones, whereas electron-withdrawing groups on the benzene ring and electron-donating groups at the γ and δ positions have the opposite effect. These effects are interpreted to reflect charge transfer from the γ-alkyl position to the oxygen in the transition state for reverse transfer of hydrogen back to the γ carbon, the major reaction of most 1-hydroxy 1,4 biradicals. Comparison of nonanophenone-γ,γ-h_2 with nonanophenone-γ,γ-d_2 indicates a k_H/k_D value of 1.35 for reverse hydrogen transfer in the biradical. Ring substituents and the length of the alkyl chain have little effect either on relative yields of cyclization and elimination or on cis/trans cyclobutanol ratios except where intramolecular hydrogen bonding can occur. For example, only *trans*-1-phenyl-2-(methoxymethyl)cyclobutanol is obtained from irradiation of δ-methoxyvalerophenone in benzene. In all cases the stereoselectivity of cyclization is lower in alcohol solvent than in benzene. As γ-alkyl substituents increase in size, the cis/trans cyclobutanol ratio surprisingly increases. α-Dimethyl substitution increases the cyclization/elimination ratio by a factor of ten, while β-dimethyl substitution decreases the ratio by a factor of ten. Kinetic analysis suggests that α-dimethyl substitution slows the rate of cleavage of the biradical while β-dimethyl substitution slows the rate of cyclization. These steric effects on biradical behavior are interpreted as reflecting restricted rotation in the biradical, such that cleavage and cyclization occur before rotational equilibrium is established. Pyridine and alcohols apparently do not enhance type II quantum yields in a kinetically controlled process. Rather a rapid equilibrium must be established between solvated and unsolvated biradicals.

For the majority of phenyl alkyl ketones, quantum yields of type II photoelimination and photocyclization are determined solely by the behavior of the 1,4-biradical intermediate.[2,3] In terms of eq 1, $\Phi_{isc} = 1$ and $k_r\tau_t = 1$. The characteristic quantum inefficiency of type II reactions in the gas phase and in hydrocarbon solvents is always partially and sometimes solely due to reverse hydrogen transfer in the biradical.

$$\Phi_{-k} = \Phi_{isc}k_r\tau_tP_p \qquad (1)$$

$$P_p = k_p\tau_{BR} = \frac{k_{sc} + k_{cy}}{k_{sc} + k_{cy} + k_{-r}} \qquad (2)$$

In our other papers in this series, we concerned ourselves primarily with the effects of various structural changes on excited state reactivity; quantum yields were discussed only insofar as their values indicated the absence or presence of other excited state reactions competing with γ-hydrogen abstraction. In this paper we consider structural effects on type II quantum yields and thus on the behavior of 1,4 biradicals. There have been two recent, speculative papers regarding 1,4 biradicals.[4,5] Hopefully a unified presentation of all our results pertaining to 1,4 biradicals will best aid understanding of these species and the many other reactions in which they are thought to intervene.

Results

Our results allow some discussion of substituent effects on the following features of 1,4-biradical behavior: (1) competition between cyclization and cleavage; (2) stereochemistry of cyclization; (3) competition between reverse hydrogen atom transfer and product formation; (4) biradical lifetimes (τ_{BR}).

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