Type II Photoprocesses of Phenyl Ketones. Triplet State Reactivity as a Function of γ and δ Substitution

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Abstract: An extensive study has been made of the effects of γ and δ substituents on rates of γ-hydrogen abstraction by triplet states of phenyl alkyl ketones. Two ϵ substituents and the ζ-cyano substituent have also been studied. A Hammett plot of relative rates *vs.* σ_I parameters yields a ρ of -1.85 for δ substituents, indicating the highly electrophilic nature of the triplet benzoyl group. Each additional insulating methylene group lowers ρ by the normal factor of 0.43. This observation suggests a ρ value for γ substituents of -4.3, from which inductive effects of the various γ substituents can be calculated. After such correction for inductive effects, a γ-carbomethoxy group is seen to afford little rate enhancement; γ-vinyl, -phenyl, and -cyano groups enhance the rate by a factor of ten, and γ-alkoxy groups enhance the rate by factors of $\sim$50, presumably reflecting charge transfer stabilization of the transition state for hydrogen abstraction. There is a remarkable parallel between the triplet benzoyl group and the *tert*-butoxy radical in selectivities of hydrogen atom abstraction, as regards both C–H bond strengths and inductive effects of substituents. There is absolutely no correlation between quantum yields of type II reactions and triplet state reactivities. This observation provides kinetic evidence for the intermediacy of a 1,4 biradical.

Since triplet state type II reactions of ketones proceed *via* intramolecular abstraction of a γ-hydrogen atom by the carbonyl oxygen,[2] the dependence of triplet state reactivity on γ C–H bond strength is of obvious interest. In their study of intermolecular hydrogen abstraction by triplet benzophenone, Walling and Gibian found that the ketone triplet behaves as an electrophilic species.[3] This electrophilicity must also affect intramolecular reactions. Since γ substituents can thus have inductive effects on reactivity separate from their effects on C–H bond strength, quantitative knowledge of pure inductive effects is necessary for complete understanding of the effects of γ substituents.

We have studied the photochemistry of various γ-substituted butyrophenones and δ-substituted valerophenones in order to separate inductive effects from bond energy effects. Our results, reported in this paper, provide an extensive quantitative correlation of rates of triplet state hydrogen abstraction as a function of C–H bond strength and provide further evidence for the highly electrophilic nature of n,π^* ketone triplets.

Results

The ketones which we have studied are listed in Tables I and II. For each ketone quantum yields of acetophenone formation and triplet state lifetimes in benzene were determined. Quantum yields of cyclization and of ketone disappearance, together with the effect of added *tert*-butyl alcohol on quantum yields, were also determined for most ketones. Maximum type II quantum yields are listed in the tables. In all experiments, irradiations were performed at 3130 Å on degassed solutions contained in sealed Pyrex tubes. The samples were held in a water bath, in which the temperature varied from 23 to 26°.

Triplet state lifetimes of the ketones were determined by the usual Stern–Volmer quenching studies, with 2,5-dimethyl-2,4-hexadiene as quencher. Relative quantum yields of acetophenone formation at conversions $<5\%$ were measured by glpc analysis. Stern–Volmer plots of reciprocal relative quantum yields *vs.* diene concentration were in all cases linear, with the slopes listed as $k_q\tau$ values in the tables. Lifetimes were determined on the basis that $k_q = 5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in benzene at 25°.[4]

Type II quantum yields of several ketones including valerophenone were determined very carefully relative to the acetophenone-sensitized cis–trans isomerization of 1,3-pentadiene.[5] A 0.10 *M* benzene solution of valerophenone was then used as an actinometer for all the other phenyl ketone studies.

Several of the γ-substituted ketones display conversion-dependent quantum yields and triplet lifetimes. The values in Table I were obtained by extrapolation to zero conversion.[6]

The quantum yields and triplet lifetimes which we have measured agree quite well with those reported by Pitts, for the few compounds we both have studied,[7,8] with the possible exception of butyrophenone. We experience difficulty in obtaining reproducible data for this compound and find that it is very sensitive to trace impurities formed by oxidation of the ketone or present in added solvents. We report our highest Φ and $k_q\tau$ values. We did not search for the 1% side product reported by Pitts.[7a] Our $k_q\tau$ value for γ-vinylbutyrophenone, however, is considerably smaller than that measured by Padwa and Eastman;[9] moreover, their calculation of k_r did not take biradical revertibility

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[1] Alfred P. Sloan Fellow, 1968–1972.

[2] P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 7480 (1972), and references therein.

[3] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965); see also A. Padwa, *Tetrahedron Lett.*, 3465 (1964).

(4) (a) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968); (b) W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5413 (1969); (c) G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

(5) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(6) P. J. Wagner, I. Kochevar, and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **94**, 7489 (1972).

(7) (a) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966); (b) J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5900 (1968).

(8) It should be noted that our first reported $k_q\tau$ values for butyrophenone and valerophenone were a factor of 2.5 too high, apparently because of a miscalculation of quencher concentration: P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(9) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

Table I. Triplet State Kinetic Parameters for γ-Substituted Butyrophenones, $C_6H_5COCH_2CH_2CHR_1R_2$[a]

R_1	R_2	Φ_{II}[b]	Φ_{CB}[c]	Φ_{max}[d]	$k_q\tau$, M^{-1}[e]	k_r, 10^7 sec^{-1}
H	H	0.35	0.03	1.0	660 ± 20	0.76
CH_3	H	0.33	0.07	1.0	40 ± 2	12.5
CH_3	CH_3	0.25	0.03	1.0	10 ± 0.5	50.0
C_6H_5[g]	H	0.50	0.06	1.0	13 ± 0.5	38.5
$CH_2{=}CH$[g]	H	0.26	0.04		11	45.5
OC_6H_5	H	0.32			23	22
OH	H	0.31		1.0	13 ± 0.8	38.5
OCH_3	H	0.23	0.09	1.0	8 ± 0.5	62.5
OCH_3	CH_3	0.20	0.05	1.0	10.5 ± 0.5	47.5
Cl	H	0.11	0.003	0.18	180 ± 4	1.0–2.8[f]
$OCOCH_3$	H	0.48			400	1.25
CO_2CH_3[g]	H	0.50			490	1.0
CN[g]	H	0.32			1300	0.39

[a] 0.10 *M* ketone solutions irradiated at 3130 Å. [b] Quantum yield of acetophenone formation in benzene. [c] Quantum yield of cyclization in benzene; no value means cyclobutanols not looked for. [d] Maximum quantum yield for elimination plus cyclization obtained by addition of *tert*-butyl alcohol (ref 6). [e] Stern–Volmer slopes in benzene, averages of duplicate runs with precision indicated. [f] Uncertainty due to 35% material balance. [g] All values extrapolated to zero conversion.

Table II. Triplet State Kinetic Parameters for δ-Substituted Valerophenones, $C_6H_5COCH_2CH_2CH_2X$[a]

X	Φ_{II}	Φ_{CB}	Φ_{max}	$k_q\tau$, M^{-1}	k_r, 10^7 sec^{-1}
$C(CH_3)_3$	0.24	0.09	1.0	24 ± 0.1	21.0
$CH(CH_3)_2$	0.25	0.08	0.94	27 ± 1	17.5
$(CH_2)_4CH_3$	0.24	0.06	0.98	29 ± 1	17.0
$(CH_2)_{10}CH_3$	0.26	0.03		28	17.5
CH_2CH_3	0.30	0.07	1.0	38 ± 1	13.0
CH_3	0.33	0.07	1.0	40 ± 2	12.5
CH_2COOCH_3	0.61	0.18	1.0	131 ± 3	3.8
CH_2COOH	0.56			189 ± 2	2.6
CH_2OCH_3	0.33	0.10	0.47	90	2.6
CH_2Cl	0.58	0.08	0.80	230 ± 5	1.8
CH_2CN	0.48	0.05	1.0	516 ± 14	1.0
CH_2CH_2Cl	0.44			89	5.6
CH_2CH_2CN[b]	0.45			110	4.5
$CH_2CH_2CH_2CN$[b]	0.37			63	8.0

[a] Generally 0.10 *M* ketone solutions irradiated at 3130 Å. All symbols the same as in Table I. [b] 0.02 *M* ketone solutions.

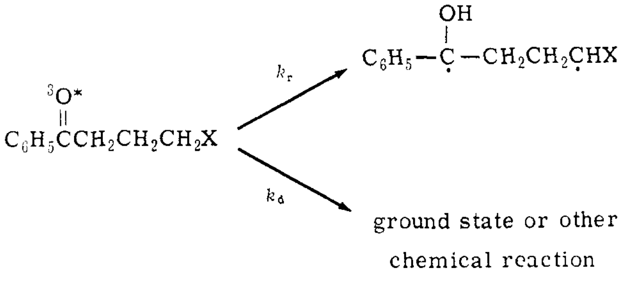
into account. Since a Stern–Volmer plot of their quenching experiment is not linear, we feel that it probably is not reliable, particularly since it was run to moderately high conversion in order to measure ketone disappearance.

For most of the ketones studied, total type II quantum yields approach unity in *tert*-butyl alcohol as solvent and quantum yields in benzene increase with increasing ketone concentration in the usual fashion,[6] thus demonstrating the absence of impurity quenching. In the particular cases of the δ-chloro-[6] and δ-methoxyvalerophenones, quantum yields reach maximum values appreciably lower than unity at high concentrations of *tert*-butyl alcohol. We conclude that the triplets of these two ketones undergo some process competitive with γ-hydrogen abstraction, presumably δ-hydrogen abstraction[10] for the δ-methoxy compound. Rate constants for γ-hydrogen abstraction are estimated by multiplying $1/\tau$ by Φ_{max}.

For most of the ketones studied, only two or three product peaks appear in vpc traces of reaction mixtures: one corresponding to acetophenone, one or two corresponding to cyclobutanols, and their sum accounting for all the reacted ketone. In all cases both acetophenone formation and cyclobutanol formation are quenched to the same degree by a given concentration of added quencher. δ-Methoxyvalerophenone also gives a small amount of cyclopentanol product;[10] γ-vinylbutyrophenone also yields 1-phenyl-3-cyclohexen-1-ol and 1-phenyl-4-hexen-1-one.[9] γ-Chlorobutyrophenone is exceptional in that it furnishes only a 35% yield of type II cyclization and elimination products. Irradiated solutions turn yellow and a large amount of a product with a vpc retention time double that of the parent ketone is formed. We suspect that a homolytic C–Cl cleavage occurs in this compound and may well be occurring to a smaller extent in δ-chlorovalerophenone. We are currently studying the γ-chloro ketone further to characterize the reaction and in particular to determine whether the unknown reaction occurs from the triplet state competitive with γ-hydrogen abstraction or from the biradical intermediate.

Discussion

We are interested in the rates of triplet state reactions of the ketones. In particular, the value of k_r can be calculated from measured triplet lifetimes and maximum quantum yields of type II products, according to eq 1.[2,6] For most of the ketones reported in this paper,



$$k_r = \frac{\Phi_{max}}{\tau} \tag{1}$$

$\Phi_{max} = 1$ so that $k_r = 1/\tau$. The exceptions were noted above.

Inductive Effects. All the ketones listed in Table II contain at their γ positions a methylene group bonded to two other methylene groups. Therefore, the γ C–H bond strengths of all these ketones should be the same and any differences in reactivity must reflect inductive

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(10) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, and R. G. Zepp, *ibid.*, 94, 7500 (1972).

effects of remote substituents. We have shown separately that any steric effects on reactivity are negligibly small.[10]

The triplet benzoyl group is obviously quite electrophilic in intramolecular hydrogen abstraction reactions, since electron-withdrawing groups in the δ position produce large decreases in the rate of γ-hydrogen abstraction. The rate suppression is smaller for ϵ substituents and smaller yet—though still appreciable—in ω-cyanoheptanophenone. We have reported separately that complete methyl substitution at the β and δ carbons enhances reactivity by factors of 1.5–2.0,[10] the kind of effect expected for the weak ($\sigma_I = -0.05$) electron donating ability of methyl groups.

Figure 1 displays a Hammett plot of log (k_r/k_r^0) *vs.* σ_I,[11] where k_r^0 is $1/\tau$ for valerophenone. For the δ substituents the plot has a slope of -1.85. The σ_I value for the carboxyl group should be similar to that for carbomethoxy. Obviously the triplet benzoyl group senses differences between them. The reactivities of the δ-alkylated valerophenones fit well in the plot, in accord with our conclusion[10] that γ substituents produce no steric hindrance to γ-hydrogen transfer.

The two points for ϵ substituents indicate a ρ value of -0.76, which is 41% of the ρ toward δ substituents. The one ζ substituent suggests a ρ value of -0.34 (45% of -0.76) for substituents three carbons removed from the γ carbon. The inductive effects of the remote substituents are revealing because intervening methylenes insulate the triplet benzoyl group against the inductive effect of substituents in exactly the same way they do for ground state reactions, that is by a factor of 0.43.[12] This fact is indicated in Figure 1 by the good fit of ϵ- and ζ-substituent effects when plotted against 0.43 and $(0.43)^2$, their respective σ_I values.

Quantitative studies of inductive effects on free-radical hydrogen abstraction reactions have generally been restricted to benzylic systems. Thus, attack of the *tert*-butoxy radical on substituted toluenes displays a ρ of -0.35 to -0.40.[13] Walling and Gibian estimated a ρ of -1.1 for triplet benzophenone and concluded that the triplet ketone is more electrophilic than the radical.[3] Their conclusion may be unreliable for the following reasons. We have found that the maximum quantum yield for photoreduction of acetophenone by toluene is 47%.[14] Presumably half of the radicals formed in benzene disproportionate back to reactants. Therefore, the relative quantum yields of substituted toluene disappearance reflect substituent effects both on excited state reactivity and on radical behavior. Until a more quantitative analysis of photoreduction is undertaken, the relationship between quantum yields and excited state reactivity can be considered only semiquantitative.

γ **substituents** produce just the rate effects one might expect for hydrogen abstraction by an electrophilic species. The dependence on bond dissociation energies is revealed by tertiary–secondary–primary C–H bond reactivities being in the order 200:25:1 and by benzylic and allylic C–H bonds being some three–four times more reactive than simple secondary C–H bonds. Hydrogens on carbons attached to ether oxygen are also very reactive, while hydrogens on carbons bonded to strong electron-withdrawing groups are severely deactivated (by factors of 5, 10, 12, and 30 for chloro, acetoxy, carbomethoxy, and cyano, respectively). Of course all substituents stabilize a radical at the γ position, which stabilization is reflected in the transition state for hydrogen abstraction. The inductive effects of the γ substituents must be very strong and in most cases oppose the radical stabilizing effects. The two effects can be separated as follows. It is possible to estimate a ρ value of -4.3 for γ substituents by dividing -1.85 by 0.43 (which corresponds to removing the final insulating methylene group). Inductive deactivations of γ C–H bonds can then be calculated and are listed in the third column of Table III. The ability of γ substituents to enhance rates of hydrogen abstraction through their radical stabilizing abilities is then isolated by dividing the observed rate constants by those predicted for inductive effects.

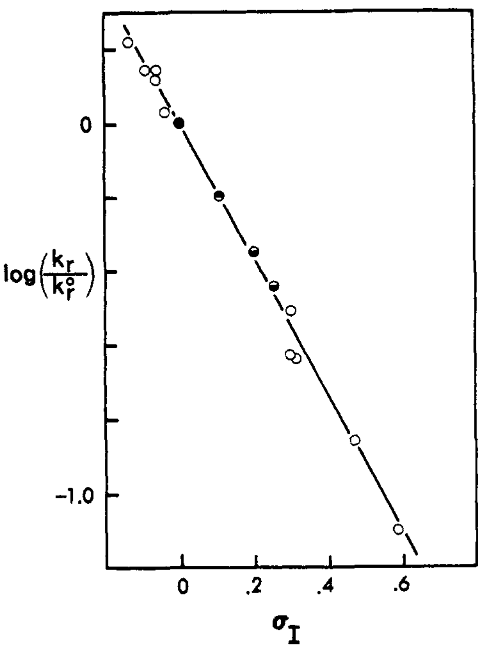

Figure 1. Hammett plot of relative rates of triplet state γ-hydrogen abstraction: ○, δ-subsituted valerophenones; ◒, ϵ-substituted hexanophenones; ◓, ω-cyanoheptanophenone; ●, valerophenone itself.

The following conclusions are suggested. The radical-stabilizing effect of the carbonyl group is very small, in agreement with recent findings.[15] Phenyl, vinyl, and cyano substituents apparently stabilize the incipient γ-radical site by an equivalent amount. Weak electron withdrawal by the phenyl group partially neutralizes its resonance effect, while strong electron withdrawal by the cyano group completely offsets its resonance effect.

Perhaps most interesting is the observation that chlorine stabilizes the incipient radical site as well as do the π systems, while oxygen is almost an order of magnitude better. Obviously the nonbonding electrons on these elements help stabilize the radical site, but

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(11) Compiled from consideration of both: (a) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 376; and (b) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 415.

(12) Reference 11a, p 366.

(13) H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1967).

(14) P. J. Wagner and R. A. Leavitt, *ibid.*, **92**, 5806 (1970).

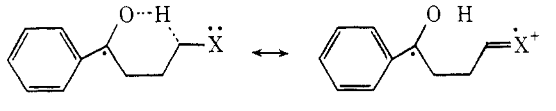
(15) (a) G. A. Russell and J. Lokensgard, *ibid.*, **89**, 5059 (1967); (b) K. D. King, D. M. Golden, and S. W. Benson, *ibid.*, **92**, 5541 (1970).

Table III. Separation of Inductive and Resonance Effects for γ-Substituted Butyrophenones, $C_6H_5COCH_2CH_2CH_2X$

X	σ_I[a]	$10^{-4.3\sigma_I}$[b]	k/k_0[c]	Resonance stabilization factor	$D(\mathrm{C-H})$[d]
CH_3			1.0	1.0	94.5
C_6H_5	0.10	0.37	3.1	8.4	~82
$CH{=}CH_2$	0.09[e]	0.41	3.6	8.8	~82
OH	0.25	0.085	3.1	37	~93
OCH_3	0.30[f]	0.051	5.0	98	~93
$OCOCH_3$	0.39[g]	0.021	0.10	4.8	~94
$COOCH_3$	0.30	0.051	0.08	1.6	~96
Cl	0.47	0.010	0.08–0.23[h]	8–23[h]	~98
CN	0.59	0.0029	0.031	10.7	~83

[a] Reference 11. [b] Relative reactivities predicted for pure inductive effects. [c] Observed relative reactivities. [d] J. A. Kerr, *Chem. Rev.*, **66,** 456 (1966). [e] From pK_a of vinylacetic acid: M. L. Dondon and M. T. Paris, *J. Chim. Phys.*, **58,** 222 (1961). [f] From pK_a values of methoxyacetic acid and 4-methoxybicyclo[2.2.2]-octane-1-carboxylic acid: H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86,** 5188 (1964). [g] P. R. Wells, *Chem. Rev.*, **63,** 171 (1963). [h] Uncertainty introduced by 35% chemical yield of normal products from γ-hydrogen abstraction.

they do not lower bond dissociation energies anywhere near as much as they enhance rates of hydrogen abstraction. Another effect must be operative, namely charge transfer stabilization *specifically* of the transition state for hydrogen transfer.[16] This resonance effect of



the heteroatoms opposes their inductive effect in the same way observed when they are para substituents on benzylic systems. The amount of charge transfer stabilization of the transition state for hydrogen transfer apparently is greater than that in the free radical (if the relative dissociation energies of C–H bonds are any criterion) and therefore must depend strongly on the electron demand of the attacking reagent. A large amount of charge transfer in the transition state for abstraction of a hydrogen next to oxygen also explains the low deuterium isotope effects observed for such systems (1.7–2.8) compared with pure alkyl systems (4.8–7).[2]

The strong deactivating effect of the γ-acetoxy substituent indicates that the ester oxygen does not stabilize the transition state for hydrogen abstraction very well. This effect is understandable in terms of the nonbonding electrons on oxygen being delocalized onto the carbonyl group. We estimate that the acetoxy group stabilizes the transition state by resonance by a factor of only five relative to methyl, an order of magnitude decrease compared to the alkoxy groups.

Table IV. Relative Reactivities of C–H Bonds

C–H bond	Benzoyl[3]* (type II)	t-BuO[a]	$(C_6H_5)_2CO^*$[b]
CH_3	0.04	0.07	0.02
CH_2CH_3	1	1	1
$\mathit{CH}(CH_3)_2$	8	5.4	6
$\mathit{CH}_2C_6H_5$	3	3.5	5–9
$\mathit{CH}_2CH{=}CH_2$	3.6	4.6	
CH_2OCH_3	5.0	6.2	
$\mathit{CH}(CH_3)OCH_3$	7.0	6.9	36[e]
$\mathit{CH}_2OC_6H_5$	1.8	3.1	
CH_2OCOCH_3	0.1	0.2[d]	
CH_2Cl	0.1–0.25	0.38	
CH_2CN	0.036	0.054	
CH_2CH_2COOH	0.20	0.28[c]	
CH_2CH_2Cl	0.16	0.35[d]	
CH_2CH_2CN	0.05	0.11[d]	
$\mathit{CH}_2CH_2CH_2Cl$	0.40	0.70[d]	

[a] Average values at 40° taken from ref 21, with a few values taken from other work. [b] From ref 3. [c] N. C. Deno, R. Fishbein, and J. C. Wyckoff, *J. Amer. Chem. Soc.*, **92,** 5274 (1970). [d] C. Walling and B. B. Jacknow, *ibid.*, **82,** 6113 (1960). [e] Isopropyl alcohol.

Comparison of Triplet Benzoyl with Alkoxy Radicals. It has been noted many times that a ketone n,π^* excited state resembles an alkoxy radical.[3,17] Table IV compares the relative reactivities of γ C–H bonds in type II processes to the relative reactivities of analogous C–H bonds toward the *tert*-butoxy radicals. The parallel is remarkable. Obviously the alkoxy radical is a very good model for the triplet benzoyl group, at least as regards hydrogen abstraction. The ketone triplet appears to be slightly more selective than the alkoxy radical as regards both C–H bond strength and inductive effects of nearby substituents. However, the differences between the two reactants are not as great as suggested by the work of Walling and Gibian.[3] In particular, primary aliphatic C–H bonds have significant reactivity, as evidenced by the ability of *tert*-butyl alcohol to reduce triplet ketones.[18]

As already noted for alkoxy radicals,[19] the effects of γ-alkoxy groups reflect the availability of the nonbonding electrons on oxygen: $CH_3O > HO > C_6H_5O \gg CH_3COO$. Moreover, the slightly greater reactivity of a tertiary relative to a secondary C–H next to oxygen is not enough to offset the greater number of hydrogens in the latter case, so that triplet γ-methoxyvalerophenone is slightly less reactive than triplet γ-methoxybutyrophenone. The same effect has been noted for alkoxy radicals[19] and for α-alkoxyacetophenones.[20] It is interesting that triplet benzophenone is three times more reactive toward isopropyl alcohol than is triplet acetophenone.[21] Presumably triplet benzophenone is more electrophilic than triplet phenyl alkyl ketones[22] and is thus more susceptible to charge transfer stabilization during hydrogen abstraction such as discussed above.

We observe that a γ-acetoxy group deactivates γ hydrogens by an order of magnitude. Expressed another way, acetylation of γ-hydroxybutyrophenone decreases the rate of triplet state γ-hydrogen abstraction by a factor of 1/30. This effect obviously reflects the decreased availability of the nonbonding electrons on oxygen because of delocalization into the carbonyl group. The deactivating effect of acyloxy substituents does not seem to be generally recognized, despite its observation for a wide number of radicals.[23]

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(16) *E.g.*, S. G. Cohen and J. I. Cohen, *J. Amer. Chem. Soc.*, **89,** 164 (1967).

(17) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5,** 93 (1968).

(18) (a) D. S. Kendall and P. A. Leermakers, *J. Amer. Chem. Soc.*, **88,** 2766 (1966); (b) W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87,** 1947 (1965); (c) S. G. Cohen and S. Aktipis, *Tetrahedron Lett.*, 579 (1965).

(19) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89,** 1515 (1967).

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

(21) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1,** 159 (1969).

(22) I. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, **92,** 5742 (1970).

(23) (a) Alkoxy, ref 19; (b) phenyl, R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85,** 3754 (1963); (c) trichloromethyl, E. S. Huyser

Nature of Triplet State Hydrogen Abstraction. Our quantum yield and lifetime measurements indicate that the triplet benzoyl group attacks γ C–H bonds with almost the same selectivity and electrophilicity displayed by *tert*-butoxy radicals in bimolecular reactions. These extensive kinetic results corroborate our conclusions that the type II reactions of phenyl ketones proceed *via* 1,4-biradical intermediates.[2,8,24] A glance at Tables I and II reveals absolutely no correlation between quantum yields and triplet state reactivity, a fact which demands formation of an intermediate which can revert to ground state as well as yield stable product.

All effects of γ and δ substituents are readily explicable in terms of ground state chemical concepts. Hammond has suggested that chemical reactions of excited states should be treated in terms of radiationless decay theory instead of in normal kinetic terms.[25] Heller has specifically applied this reasoning to hydrogen abstraction reactions by suggesting that electronic excitation energy is first converted into vibrational energy of a C–H bond after which homolytic cleavage occurs.[26]

Qualms about the spin forbiddenness of a triplet undergoing such electronic–vibronic energy transfer aside, our results indicate quite clearly that intramolecular hydrogen transfer to triplet benzoyl groups is not adequately described by radiationless decay theory. Rates vary with bond strength and inductive effects of substituents exactly as expected for free-radical hydrogen abstraction reactions and do not in any way correlate with C–H stretching frequencies. In particular, a normal deuterium isotope effect is observed in type II reactions.[2,10] It seems highly unlikely that the inductive effects of remote substituents can be ascribed to changes in the anharmonicity of γ C–H stretching modes,[26] and protic solvents with high frequency O–H stretching modes, far from quenching ketone triplets, enhance the quantum yields of their reactions. Hydrogen abstraction by ketone triplets seems to behave kinetically like a typical low activation energy process.

Experimental Section

Chemicals. Benzene, tetradecane, 2,5-dimethyl-2,4-hexadiene, and *tert*-butyl alcohol were purified as usual.[2,6]

The following ketones were commercial samples purified by a combination of distillation, recrystallization from hexane, and chromatography on alumina: butyrophenone, valerophenone, isovalerophenone, hexanophenone, nonanophenone, pentadecanophenone, γ-phenylbutyrophenone, δ-benzoylbenzoic acid.

The following ketones were prepared by addition of benzonitrile to alkyl Grignard reagents, followed by hydrolysis of the resulting imine, distillation, and recrystallization: δ-methylhexanophenone, bp 136–137° (9 mm) from 4-methyl-1-bromopentane, bp 95–98° (146 mm) prepared by treatment of 4-methyl-1-pentanol (Chemical Samples Co.) with phosphorus tribromide (PBr_3); δ,δ-dimethylhexanophenone, bp 141° (8 mm) from 4,4-dimethyl-1-bromopentane prepared from 4,4-dimethyl-1-pentene;[11] γ-methoxybutyrophenone, bp 103–104° (1 mm) from 3-methoxy-1-bromopropane prepared from 3-methoxy-1-propanol (Pfaltz and Bauer); γ-methoxyvalerophenone, bp 138° (9 mm) from 3-methoxy-1-bromobutane prepared from 3-methoxy-1-butanol (Metheson Coleman and Bell); γ-vinylbutyrophenone, bp 122° (8 mm) from 5-bromo-1-pentene (Chemical Samples Co.).

The following ketones were prepared by addition of phenyl magnesium bromide to aliphatic nitriles, followed by the usual work-up: γ-chlorobutyrophenone, bp 110–111° (2.5 mm) from γ-chlorobutyronitrile (Aldrich); δ-chlorovalerophenone (mp 49–51°) from δ-chlorovaleronitrile (Aldrich); ε-chlorohexanophenone (mp 31°) from ε-chlorohexanonitrile (Columbia Organic); ω(ζ)-cyanoheptanophenone (mp 30°) in 2% yield from 1,6-dicyanohexane (Eastman); γ-phenoxybutyrophenone (mp 62.5–63.5°) from γ-phenoxybutyronitrile (Aldrich).

γ-Methylvalerophenone, bp 122° (10 mm), was prepared both from the addition of phenyl Grignard to γ-methylvaleronitrile and by Friedel–Crafts acylation of benzene with γ-methylvaleryl chloride (Eastman) in the presence of a slight mole excess of aluminum chloride.

γ-Cyanobutyrophenone (mp 39°) was prepared by adding the ethylene glycol ketal of γ-chlorobutyrophenone to a dimethyl sulfoxide solution of sodium cyanide at 90°. The reaction mixture was diluted with water and extracted several times with ether. The ketal recovered from the washed ether extracts was then hydrolyzed, distilled, and recrystallized from an ethanol–petroleum ether mixture. Attempted displacement directly on the chloro ketone failed to yield any cyano ketone.

δ-Cyanovalerophenone (mp 69–71°) and ε-cyanohexanophenone (mp 33.5–34°) were both prepared by straight displacement on the chloro ketone with cyanide in DMSO. The δ-cyano ketone was also prepared by a somewhat longer procedure. Adipic acid monomethyl ester (Aldrich) was stirred in cold, concentrated ammonium hydroxide at 5° for 2 hr, yielding the ammonium salt of the monoamide. Upon acidification with dilute hydrochloric acid, the half acid–half amide crystallized out. The crystals were dried in a dessicator and then treated with excess thionyl chloride in refluxing benzene for 24 hr. Solvent was distilled off and δ-cyanovaleryl chloride, bp 133° (10 mm), collected by distillation. Diphenylcadmium was prepared by addition of a slight excess of anhydrous cadmium chloride to phenyl magnesium bromide in ether. After replacement of ether with benzene, addition of the cyanovaleryl chloride, and a brief reflux, the ketone collected after acid work-up was dried, distilled, recrystallized from ethanol–petroleum ether, and then sublimed.

γ-Hydroxybutyrophenone (mp 28–30°) was prepared beginning with β-benzoylpropionic acid made by Friedel–Crafts acylation of benzene with succinic anhydride. The acid was converted to the ethyl ester by refluxing for 24 hr in ethanol containing a pinch of *p*-toluenesulfonic acid. The ethylene glycol ketal was then prepared and reduced with lithium aluminum hydride. Up to this point, the procedure followed was that reported by Ward.[27] When the reduced ketal was worked up with hydrochloric acid, γ-chlorobutyrophenone was obtained in high yield. Work-up with 6 M sodium bisulfate followed by hydrolysis in 1% sulfuric acid produced a good yield of the hydroxy ketone which was purified by recrystallization from carbon tetrachloride.

γ-Acetoxybutyrophenone, bp 147° (3 mm), was prepared by acetylation of the γ-hydroxy ketone with acetyl chloride, followed by distillation and recrystallization from a cold hexane–ethanol mixture.

γ-Carbomethoxybutyrophenone, bp 137° (2 mm), and δ-carbomethoxyvalerophenone (mp 35–36°) were prepared by treatment of the corresponding ω-benzoyl acids (Aldrich) with diazomethane.

All ketones were 99% pure by glpc analysis. Their identities were confirmed by ir, nmr, and mass spectra.

Procedures. Quantum yield determinations and quenching studies were performed as described in the accompanying papers.[2] In particular, most solutions contained 0.004 M tetradecane as internal standard for analysis of acetophenone formation.

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and K. L. Johnson, *J. Org. Chem.*, **33**, 3972 (1968); (d) methyl and trifluoromethyl, K. C. Ferguson and J. T. Pearson, *Trans. Faraday Soc.*, **66**, 910 (1970); (e) Br and I, R. K. Solly and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 509 (1971).

(24) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

(25) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

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

(27) H. P. Ward and P. D. Sherman, *J. Amer. Chem. Soc.*, **90**, 3816 (1968).