

MISLEADING SIGMAS AND NEGLECTED GEOMETRIES: THE EFFECTS OF METHYL SUBSTITUTION ON RATES OF TRIPLET STATE HYDROGEN ABSTRACTION BY THE BENZOYL GROUP

Peter J. Wagner

Chemistry Department, Michigan State University, East Lansing, Michigan, U. S. A.

Abstract - The effects of ring methyl and polymethyl substitution on rate constants for γ -hydrogen abstraction in triplet phenyl alkyl ketones have been determined. The effect of meta and para methyls is to increase the energetic separation between the reactive n, π^* triplet and the lowest π, π^* triplet and to thus lower the equilibrium concentration of the former. Ortho-methyl groups also introduce a competing enolization reaction which is very rapid in the syn conformer but is limited by the rate of anti \rightarrow syn rotation in the anti conformer.

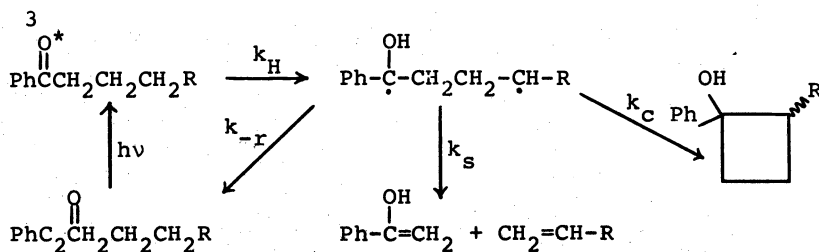
INTRODUCTION

Next to electron transfer, hydrogen atom transfer is the simplest of chemical reactions. Interest in hydrogen abstraction by electronically excited ketones has always been high. Reactivity differences between different excited states has been of particular interest; and it is now well established that ketones with π, π^* lowest triplets are appreciably less reactive than those with n, π^* lowest triplets (1-4). In recent years the most interest has been centered on compounds in which the two lowest triplets lie so close together energetically that they can either equilibrate thermally (5) or mix vibronically (6). Although it has been suggested that vibronic mixing may induce n, π^* -like reactivity in the lowest, most π, π^* triplet (4), we have presented evidence that hydrogen abstraction actually occurs from low equilibrium concentrations of upper n, π^* triplets (7, 8).

Previously we reported the effects of single ring substituents on rate constants for triplet state hydrogen abstraction by valerophenone (9). In this paper we describe the effects of a single substituent, methyl. The paper is divided into two parts: 1) the effects of only meta- and para-methyls, and combinations thereof; and 2) the effects of ortho-methyls, which introduce a competitive photoenolization reaction.

MONITORING SYSTEM

It is now well established that phenyl alkyl ketones undergo Norrish type II photoelimination and cyclization exclusively by γ -hydrogen abstraction (10). The resulting diradical either cleaves, cyclizes, or disproportionates back to ground state ketone. In this latter respect, the reaction is like most other triplet reactions, in that the quantum yield is determined by partitioning of a ground state intermediate (the diradical) as well as by competitive excited state reactions. Unlike most other reactions, however, the reversion of diradical to ground state ketone is suppressed in the presence of Lewis bases (11). What is observed experimentally is an increase in type II quantum yields with added alcohol, pyridine, or dioxane until a maximum value is reached, at which



point it is assumed that all diradicals proceed on to products and any remaining quantum inefficiency arises from competitive excited state reactions (12).

Rate constants k_H for γ -hydrogen abstraction and k_d for any competing triplet reaction are measurable by independent measurements of maximum type II quantum yields (including cyclobutanols), triplet lifetimes, and intersystem crossing yields, according to Eqtns 1-5.

$$\phi_{II} = \phi_{isc} k_H \tau_T k_c (k_c + k_s + k_{-r})^{-1} \quad (1)$$

$$\phi_{II}^{MAX} = \phi_{isc} k_H \tau_T \quad (2)$$

$$1/\tau_T = k_H + k_d \quad (3)$$

$$\alpha \phi_{sens}^{-1} = \phi_{isc}^{-1} (1 + \frac{1}{k_t \tau_T [S]}) \quad (4)$$

$$\phi^O/\phi = 1 + k_t \tau_T [Q] \quad (5)$$

Triplet lifetimes are measured by Stern-Volmer quenching studies (Eqtn 5) with conjugated dienes, for which $k_t = 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° C in benzene (13). Intersystem crossing yields of the ketones are determined by using the ketone to sensitize a well-known triplet reaction such as the cis-to-trans isomerization of 1,3-pentadiene (S), for which reaction the α in Eqtn 4 is 0.55 (14).

RESULTS: META AND PARA METHYLS

Table 1 lists values of k_H for valerophenones with various electron-withdrawing and electron-donating substituents, including polymethyl substitution. All the ketones on the left have n, π^* lowest triplets, as judged by their short (<0.01 sec) phosphorescence lifetimes at 77° K. The ones on the right have longer phosphorescence lifetimes and therefore π, π^* lowest triplets. It is clear that the decreases in reactivity are associated with the reactive n, π^* triplet no longer be lowest in energy. It remains only to find some quantitative correlation of k_H values with structural parameters.

TABLE 1. Rate Constants for Triplet State γ -hydrogen Abstraction by Ring-Substituted Valerophenones

Subst.	$k_H, 10^7 \text{ sec}^{-1}$	Subst.	$k_H, 10^7 \text{ sec}^{-1}$
H	12.5	p-Cl	3.0
m-CF ₃	32	m-CH ₃	3.2
p-CF ₃	28	p-CH ₃	1.8
m-(N)	31	3,5-Me ₂	0.9
p-(N)	68	3,4-Me ₂	0.34
m-F	18	3,4,5-Me ₃	0.034
p-F	15	m-OCH ₃	0.02
m-Cl	16	p-OCH ₃	0.05

A Hammett plot of $\log k_H$ versus σ values for the substituents (or the sum of the σ_m and σ_p values for the di- and trimethyl ketones) is more deceptive than informative. The slight increases in k_H caused by electron-withdrawing groups (with the exception of *p*-Cl) correlate rather well with a ρ value of +0.60. The methyl and *p*-methoxy k_H values also give a good linear correlation with $\rho = +8.5$, although *m*-methoxy does not fit. The sharp increase in slope for electron-donating substituents indicates some change in mechanism which is clearly the inversion of n, π^* and π, π^* triplet levels. It is the purpose of the first part of this paper to demonstrate why any such Hammett-type correlation is coincidental. The fact that *p*-Cl and *m*-OCH₃ both decrease k_H much more than their σ values would suggest is clear evidence that ground-state substituent parameters do not adequately reflect excited state properties.

ANALYSIS OF SUBSTITUENT EFFECTS

As described in our previous paper (9), the observed value of k_H (Eqtn 6) reflects reaction from both triplets. We previously concluded that, for $\Delta E_T \leq 3$ kcal, $k_H^{\pi} \ll \chi_{n, \pi} k_H^n$. The evidence

$$k_H^{\text{obs}} = \chi_{n, \pi} k_H^n + \chi_{\pi, \pi} k_H^{\pi} \quad (6)$$

$$\frac{\chi_{n, \pi}}{\chi_{\pi, \pi}} = \frac{-\Delta E_T / RT}{e} \quad (7)$$

was twofold. First, k_H values were decreased like amounts by electron-withdrawing γ - and δ -substituents for both phenyl (n, π^* lowest) and *p*-methoxyphenyl (π, π^* lowest) ketones (7). This result is required if reaction proceeds from upper n, π^* triplets and seems unlikely if much reaction occurred from the π, π^* triplet, in which the carbonyl is not electron-deficient. Second, temperature effects on the product distribution from 1-benzoyl-4-anisylbutane indicate that triplet excitation is equilibrated between the two nonconjugated chromophores and are consistent with the anisyl group reacting from equilibrium populations of its n, π^* triplet (8).

TABLE 2. Effects of Methyl Substitution on Triplet Energy (kcal) Levels and on Reactivity.

Subst.	$E(^3n, \pi^*)$	$E(^3\pi, \pi^*)$	rel k_N	ΔE_T (Eqtn 6+7)
H	73.4	(75.5)	1	--
<i>m</i> -Me	73.5	73.2	0.30	0.4
<i>p</i> -Me	24.1	73.4	0.14	1.0
3,5-Me ₂	73.6	72.3	0.070	1.5
3,4-Me ₂	24.2	72.2	0.036	1.8
3,4,5-Me ₃	74.3	71.5	0.0055	2.9
<i>p</i> -OCH ₃	74.8	72.0	0.0065	2.8

If, indeed, only the first term on the righthand side of Eqtn 6 is important, k_H values should display a simple Boltzman dependence on ΔE_T , the energy gap between the n, π^* and π, π^* triplets. In Table 2 estimated ΔE_T values for the methylated ketones are listed and compared to observed k_H values. It is apparent that the observed reactivity is well within the uncertainty range for what k_H would be predicted from ΔE_T values. In other words, these results support our original conclusion

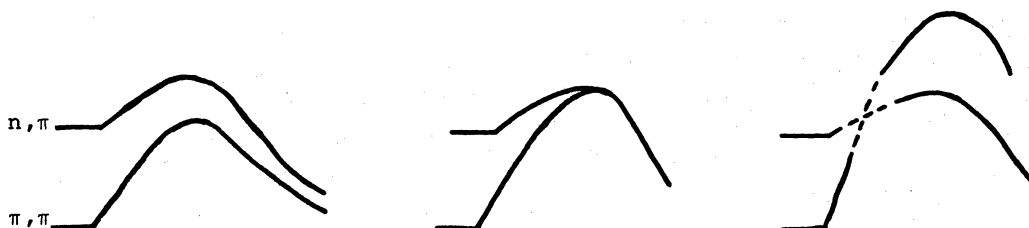
that all triplet state hydrogen abstraction by these ketones with π, π^* lowest triplets slightly lower in energy than their n, π^* triplets occurs from the n, π^* triplets after they have reached thermal equilibrium with the lowest triplet.

It must be pointed out that the $E(\pi, \pi)$ values are measured whereas the $E(n, \pi)$ values are estimated. The estimates are based on substituent effects on the n, π^* triplet energy of benzophenone and on the polarographic reduction potential of acetophenone (15); the accuracy of such estimates is discussed elsewhere (16).

THE MEANING OF THERMAL EQUILIBRATION OF ELECTRONIC STATES

These results and those obtained in our previous studies indicate that hydrogen abstraction by a triplet ketone passes through the same transition state no matter which electronic state is lower. When the π, π^* triplet is lower, it can gain small amounts of energy along coordinates unrelated to the reaction coordinate and thus cross over onto the n, π^* triplet surface. Since hydrogen abstraction by an n, π^* triplet is an activated process, the n, π^* and π, π^* surfaces can equilibrate before any significant irreversible decay sets in.

There apparently has been some confusion generated by the suggestion that an unreactive lower state may cross onto a reactive upper state surface along a reaction coordinate (17). In the present case, n, π^* triplets first gain energy (the activation energy) as the hydrogen begins moving away from carbon and towards oxygen; the normal low reactivity of π, π^* states means that they gain energy even faster along this same reaction coordinate. We have ruled out experimentally the left-hand scheme below. For both states to pass through the same transition state seems unlikely. The right-hand scheme seems most likely, with the π, π^* state crossing the n, π^* before the transition state, in which case the reaction coordinate is just another vibrational mode in which the two states can reach thermal equilibrium.



The dotted lines at the surface crossing indicate the uncertainty about the allowedness of this crossing. If the crossing were strongly forbidden, the situation drawn below would hold, in which the n, π^* triplet itself could not react directly. It is more likely that the n, π^* and π, π^* states remember that they have different electronic symmetries, such that the crossing is only weakly avoided (18).

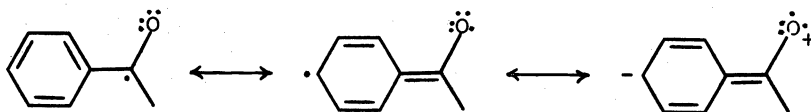


OPPOSITE META/PARA SUBSTITUENT EFFECTS ON n, π^* AND π, π^* TRIPLETS

The fact that a para-methyl is more deactivating than a meta-methyl, as predicted by their σ values, is really coincidental. Inspection of Table 2 reveals that the negligible effect of meta-substitution on n, π^* energies is compensated for by a larger meta than para effect on π, π^* energies.

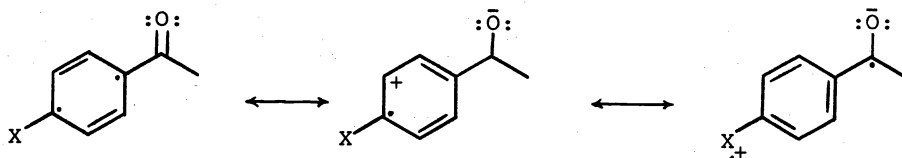
The negligible effects of meta-methyls on both reduction potentials and n, π^* excitation energies of phenyl ketones have a common cause. It is well known from epr studies on radical anions that an electron-withdrawing group destroys the degeneracy of the lowest two π^* orbitals of benzene by

stabilizing the symmetric orbital. Thus benzonitrile radical-anion has negligible spin density at the meta position (19). An n, π^* transition can be considered a one-electron reduction of the π -system, as long as the n -orbital is orthogonal to the π -system. Therefore, the additional electron-density of the benzene ring brought about by n, π^* excitation occupies primarily the 1- and 4- positions, as illustrated below.



It is well known that meta "conjugation" is more important than para "conjugation" in the lowest, L_b singlets of substituted benzenes (20). We had originally thought (9) that energies of the lowest π, π^* triplets, which are L_a (21), would correlate with energies of the L_a second singlet transitions. No such correlation exists, since para-methyl lowers the ${}^1L_{a, \lambda_{max}}$ of acetophenone by 4 kcal, meta-methyl by only 2 kcal (9). It turns out that substituent effects on the excitation energies of the lowest excited states of benzene derivatives (${}^1L_b, {}^3L_a$) are dominated by inductive effects on transition dipoles (21, 22). Vector addition of individual substituent dipoles results in stabilization for 1, 3-grouping of a donor-acceptor combination, and for 1, 4-grouping of two acceptor groups (22). In separate work (23) we have verified that *m*-methyl- and *m*-methoxybenzonitrile each has a lower triplet energy than its para-isomer, whereas *p*-chloro- and *p*-cyanobenzonitrile each has a lower triplet energy than its meta-isomer. Arnold has obtained similar results for substituted benzoate esters (24).

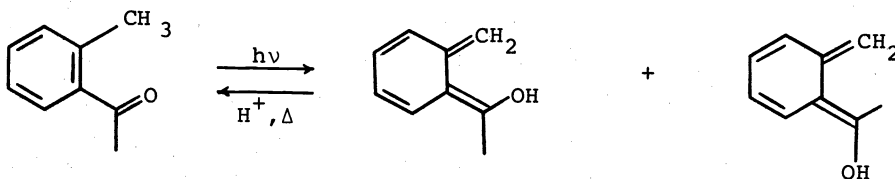
In triplet benzonitrile, which is a model for the π, π^* triplet of acylbenzenes, most of the spin density lies at the para position (25). Inasmuch as zwitterionic forms contribute to the triplet, the positive charge density in the benzene ring must be primarily at the meta position. The three VB forms below can be considered as major contributors to the $L_a \pi, \pi^*$ triplet of phenyl ketones. In fact both meta and para electron-donating substituents stabilize L_a states. The middle form can rationalize any conjugative stabilization afforded by meta substituents. The right-hand form is a



high-energy substituent-to-substituent CT state of the same electronic symmetry as the L_a states (22). It mixes much more with the high-energy 1L_a state than with the low-lying 3L_a state. Therefore the stabilization afforded by para-electron donors is much greater for the singlet state and in fact surpasses the meta > para order caused by transition dipoles. In the triplet, at least for relatively weak donors such as methyl and methoxy, the meta > para order remains.

ORTHO-METHYL KETONES: COMPETITIVE PHOTOENOLIZATION

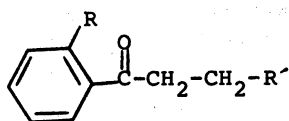
The photoenolization of ortho-alkyl phenyl ketones has been known for some time (26). It has been subjected to flash spectroscopic studies (27, 28) but not to the combination of quenching and sensitization techniques which have provided the basic experimental information about other ketone photo-reactions.



Bergmark showed that *o*-methylvalerophenone does undergo type II photo-elimination in low yield (29); so we undertook a quantitative study of this reaction. Table 3 compares data in benzene and in *t*-butyl alcohol. Rates and quantum yields of type II reaction vary as expected with γ C-H bond strength, the average k_H value being 1/3 as great as for the corresponding ketone without any ring-methyl. Thus *ortho*- and *meta*-methyls have comparable effects of k_H values. Application of Eqtns 2 and 3 to the data reveals a competing reaction, presumably enolization, with a rate constant k_e independent of substitution at the γ -carbon. The value of k_e is only 1/5 as large in alcohol as it is in benzene, in agreement with solvent effects reported for the decay of triplet *o*-methyl-acetophenone (28).

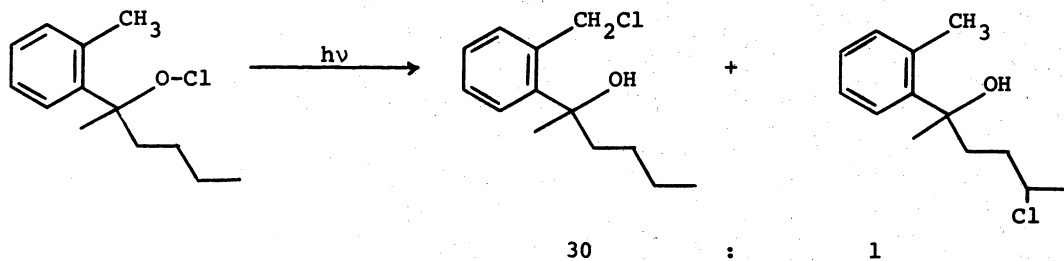
There are two unusual aspects of the data in Table 3. First, the yields of long-lived triplets are low and depend on both solvent and the nature of the *ortho*-substituent. Second, the value of k_e is independent of the *ortho*-alkyl's CH bond strength. This latter fact, together with the low value for k_e , makes it unlikely that hydrogen abstraction is the rate-determining step in enolization. Since Bergmark demonstrated a 30:1 preference for *o*-benzylic: γ -methylene in the corresponding

TABLE 3. Photokinetics of *o*-Alkyl Phenyl Ketones



R	R'	ϕ_{II}^{MAX}	ϕ'_{isc}	10^7 sec^{-1}		
				$1/\tau$	k_H	k_e
in benzene						
CH ₃	CH ₃	0.024	0.21	3.4	0.4	3.0
CH ₃	CH ₂ CH ₃	0.10	0.21	5.6	2.7	2.9
CH ₃	CH(Me) ₂	0.16	0.21	18.0	14.0	4.0
CH ₂ CH ₃	CH ₂ CH ₃	0.07	0.12	5.3	3.0	2.3
in <i>t</i> -BuOH						
CH ₃	CH ₃	0.015	0.11	0.68	0.09	0.6
CH ₃	CH ₂ CH ₃	0.060	0.11	1.5	0.9	0.6
CH ₃	CH(Me) ₂	0.095	0.11	7.9	7.0	0.9
CH ₂ CH ₃	CH ₂ CH ₃	0.048	0.07	2.0	1.3	0.7

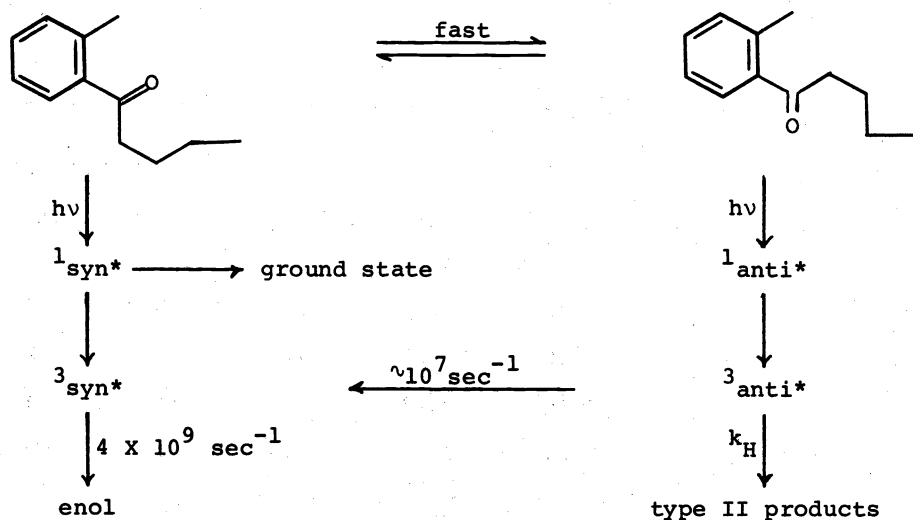
alkoxy radical (29), the rate of *o*-methyl hydrogen abstraction should be at least 10^9 sec^{-1} instead of the 10^7 sec^{-1} found by the flash spectroscopists (27, 28) and by us.



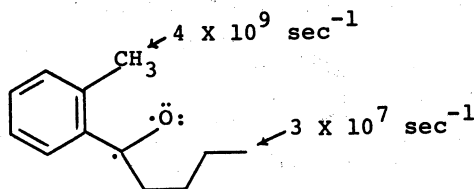
Actually, the alkoxy radical derived from the above hypochlorite is not a perfect model for the excited ketones since the alkoxy radical has a freely rotating aryl group, whereas the excited ketones do not. Population of the π^* orbital enhances the bond order between the benzene ring and the carbonyl carbon and increases the barrier to rotation (30). In the two extreme planar forms, here called syn and anti, only the syn can enolize.



We have already pointed out that k_e probably measures the rate of irreversible anti \rightarrow syn rotation in the triplet manifold and that the ϕ^{isc} values in Table 3 represent the percentage of ground state molecules with conformation closer to anti than to syn (31). (The ground states are somewhat twisted (36)). Thus the enolization which competes with type II reaction of the anti triplet proceeds at a rotation-limited rate. The syn triplet enolizes before it can do anything else.



The validity of the above scheme was demonstrated by triplet counting experiments using *o*-methylacetophenone and 8-methyl-1-tetralone to photo-sensitize the cis \rightarrow trans isomerization of 1,3-pentadiene (31). The tetralone gives a linear plot of $\phi_{\text{c} \rightarrow \text{t}}^{-1}$ vs. $[\text{diene}]^{-1}$, whereas the acetophenone gives a curved plot indicative of both a long-lived and a short-lived triplet. Table 4 lists the lifetimes and intersystem crossing yields obtained from the plots. The long-lived triplet formed from *o*-methylacetophenone is the same one responsible for the type II reactions of the ketones in Table 3. Both ketones have a very short-lived triplet which would be the species which



enolizes at the expected rapid rate. The tetralone, of course, is fixed in a syn structure, so the short-lived triplet in the acyclic ketone is logically a syn conformer. The 100-fold greater reactivity of the o-methyl relative to the γ -methylene is expected on the basis of their intrinsic labilities (33) and the two "frozen rotations" in the former (34).

TABLE 4. Intersystem Crossing Yield Measurements in Benzene

Ketone	Φ_{isc}^{TOTAL}	Φ_{isc}^{LONG}	$1/\tau(\text{short}) - 10^8 \text{sec}^{-1} - 1/\tau(\text{long})$	
	0.28	--	31.	--
	0.52	0.21	50.	0.3
	1.0	0.38	60.	<1.0

The data indicate that some 36-39% of the syn singlets intersystem cross. What the other singlets do is clearly of interest. It has been suggested that they enolize (28), but the following results do not agree with that assessment. Small concentrations of pentadiene (<0.1M) quench 2/3 the deuterium incorporation induced in o-methylacetophenone by irradiation in methanol- o -d. Larger concentrations keep on quenching the process, but with far less efficiency. It appears that over 85% of the deuterium incorporation ($\Phi \sim 0.2$) arises from two triplets, one long-lived ($\tau > 10$ nsec) and one short-lived ($\tau \sim 0.2$ nsec). As Table 4 indicates, o-methylbenzophenone also produces two triplets with a total Φ_{isc} of unity. It undergoes photoinduced deuterium incorporation twice as efficiently as o-methylacetophenone. Provided that deuterium incorporation is a quantitative measure of long-lived enol formation, the low quantum yields of both triplet formation and deuterium incorporation in o-methylacetophenone indicate that the majority of singlet reaction is strictly quenching. It is quite possible that radiationless decay occurs via partial hydrogen abstraction (17, 18).

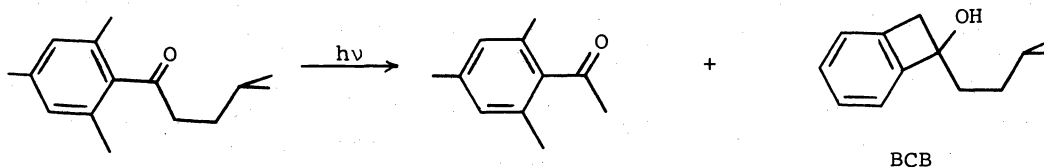
The two triplets observed for o-methylacetophenone remove the possibility that kinetically distinct n, π^* and π, π^* triplets are involved. Such a possibility is very real for the o-tolyl alkyl ketones, but not for the benzophenone since it is well-known that there is a large $n, \pi^* - \pi, \pi^*$ separation in benzophenones (35).

2, 6-DIMETHYL KETONES

2, 6-Disubstituted phenyl ketones are known to be highly twisted in their ground states (32); they cannot have syn and anti conformers. Nonetheless, we find that they seem to form two kinetically distinct triplets. $\gamma, 2, 4, 6$ -Tetramethylvalerophenone undergoes competitive type II elimination and benzocyclobutenol (36) formation, with the kinetic parameters listed in Table 5.

TABLE 5. Photokinetics of  in Benzene

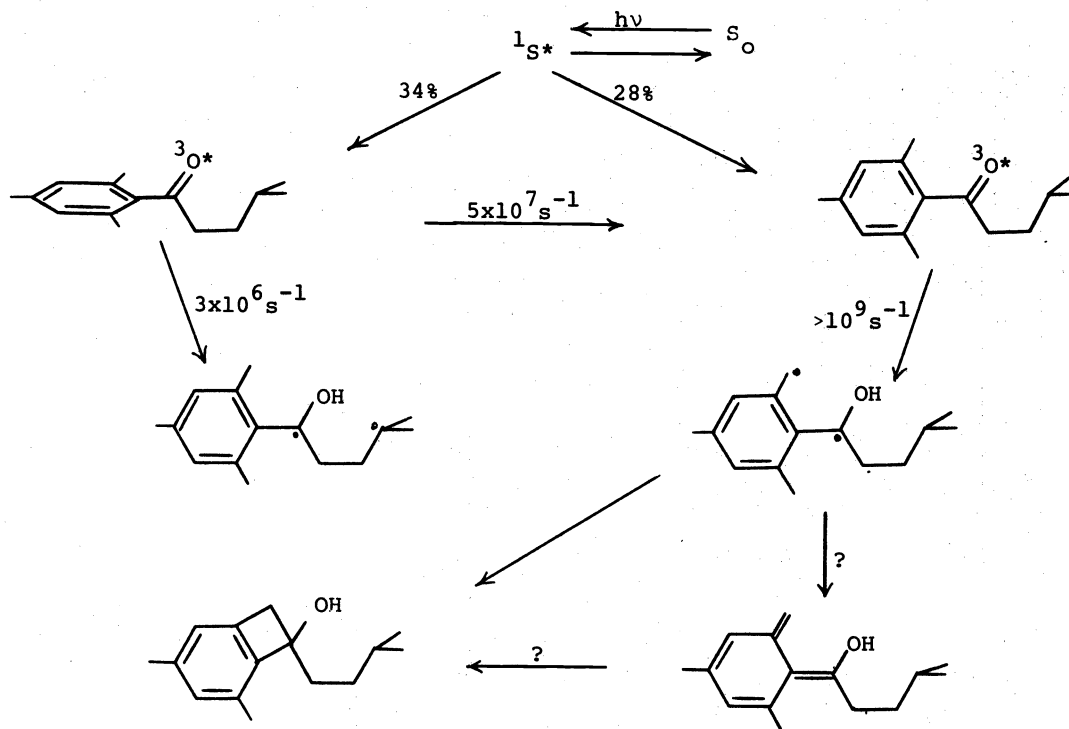
ϕ_{isc}^{TOTAL}	ϕ_{isc}^{LONG}	ϕ_{II}^{MAX}	ϕ_{BCB}	ϕ_{BCB}^{MAX}
0.62	0.34	0.02	0.02	0.21
$10^8/\tau(\text{short}), \text{sec}^{-1}$	$k_q\tau, M^{-1}$	$10^7/\tau(\text{long}), \text{sec}^{-1}$	$k_H - 10^7 \text{sec}^{-1} - k_C$	
12	91	5.3	0.32	5.0



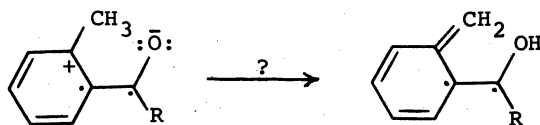
Whereas elimination is readily quenched with dienes, cyclization is not. 3M dioxane increases quantum yields of cyclization ten-fold. Use of the ketone to photosensitize 1,3-pentadiene isomerization reveals a long-lived triplet ($\phi_{isc} = 0.34$) and a short-lived triplet ($\phi_{isc} = 0.28$, $\phi_{isc}^{TOTAL} = 0.62$). The former triplet is the one responsible for type II reaction; the latter with a lifetime of 0.8 nsec, probably produces benzocyclobutenol. High concentrations of dienes do quench cyclization, but do so at least partially by forming an as-yet unidentified cycloadduct with the reactant. The analogous tetralone, 6,8-dimethyl-1-tetralone, produces only one short-lived triplet.

Although the acyclic ketones probably have only one principal ground state conformation, with the phenyl-carbonyl bond twisted some 70° (32), they may well form two triplets with different twist angles. The more planar one can rapidly abstract an ortho-benzylic hydrogen; the more twisted one can undergo γ -hydrogen abstraction or it can rotate with the rate constant k_C (in Table 5) to the more planar form.

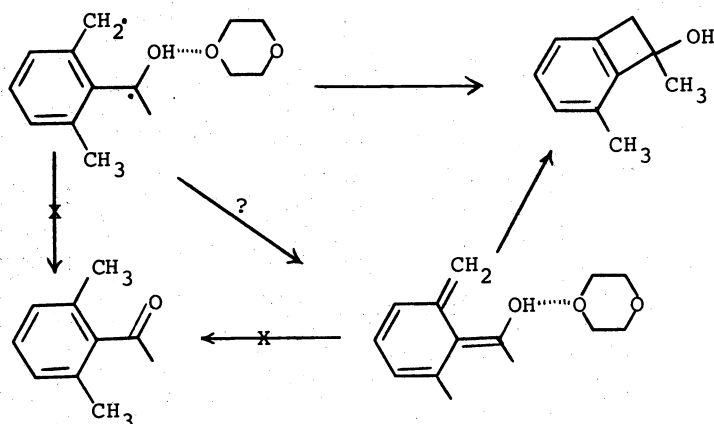
The electronic nature of the two proposed triplets is of some interest. The energy of the π, π^* triplet is more sensitive to the planarity of the benzoyl group than is that of the n, π^* triplet. Therefore, the minimum on the n, π^* surface may well occur at a larger twist than that on the π, π^* surface. It is unlikely, however, that the two distinct triplets are a fairly planar π, π^* state and a twisted n, π^* state. The rate constant for γ -hydrogen abstraction is too slow for an n, π^* triplet and is close to what would be predicted from the $n, \pi^* - \pi, \pi^*$ equilibrium model



discussed earlier, with the π, π^* state some 3 kcal lower. The rate constant for benzylic hydrogen abstraction seems too high for a π, π^* state. Although it is conceivable that the partial zwitterionic character of the π, π^* state aids enolization, the reaction certainly usually happens from n, π^* triplets.



At this stage of our studies, the photokinetics of 2,6-dialkyl ketones remain as uninterpretable as ever (27, 28, 37). The very large solvent effect on benzocyclobutenol formation adds one further piece of information about the puzzling competition between cyclobutenol and dienol formation (37). The intermediate which leads to cyclobutenol, like the hydroxydiradical in type II reactions, is prevented by a Lewis base from reverting to ground state reactant. A similar hydroxydiradical may well be involved here. It is also possible that the normally rapid thermal reversion of Z-dienol to ketone is slowed down by hydrogen bonding.



Acknowledgement - I would like to thank Eugene Harris and Mary May, who did the work on *m*- and *p*-methyl substitution; Andy Chen, who is doing all the work on *o*-alkyl ketones; and the National Science Foundation (U. S. A.) for financial support.

REFERENCES

- G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).
- G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).
- J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).
- (a) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, **89**, 5466 (1967).
(b) N. C. Yang and R. Dusenbery, *J. Am. Chem. Soc.*, **90**, 5899 (1968).
- (a) P. J. Wagner, M. J. May, A. Haug, D. R. Graber, *J. Am. Chem. Soc.*, **92**, 5269 (1970).
(b) E. Migirdicyan, *Chem. Phys. Lett.*, **12**, 473 (1972).
(c) M. E. Long and E. C. Lim, *ibid.*, **20**, 413 (1973).
(d) R. O. Loutfy and J. M. Morris, *ibid.*, **22**, 584 (1973).
- (a) T. H. Li and E. C. Lim, *Chem. Phys. Lett.*, **2**, 15 (1970).
(b) L. Goodman and M. Koyanagi, *Mol. Photochem.*, **4**, 369 (1972).
- P. J. Wagner, A. E. Kempainen, and H. N. Schott, *J. Am. Chem. Soc.*, **92**, 5280 (1970).
- P. J. Wagner and T. Nakahira, *J. Am. Chem. Soc.*, **95**, 8474 (1973).
- P. J. Wagner, A. E. Kempainen, and H. E. Schott, *J. Am. Chem. Soc.*, **95**, 5604 (1973).
- P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 7480 (1972).
- P. J. Wagner, I. Kochevar, and A. E. Kempainen, *J. Am. Chem. Soc.*, **94**, 7489 (1972).
- P. J. Wagner and H. E. Schott, *J. Am. Chem. Soc.*, **91**, 5383 (1969).
- (a) P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).
(b) W. D. K. Clark, A. D. Litt, and C. Steel, *ibid.*, **91**, 5412 (1969).
(c) G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A.*, **315**, 163 (1970).
- A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
- R. O. Loutfy and R. O. Loutfy, *Tetrahedron*, **29**, 2251 (1973).
- P. J. Wagner, M. J. Thomas, and E. Harris, *J. Am. Chem. Soc.*, in press.
- L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).
- L. Salem, C. Leforestier, G. Segal, R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975).
- P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).
- (a) R. Grinter and E. Heilbronner, *Helv. Chim. Acta*, **45**, 2496 (1962).
(b) E. Havinga, R. O. deJongh, and W. Dorst, *Rec. Trav. Chim.*, **75**, 378 (1956).
(c) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 922 (1963).
- D. R. Kearns, *J. Chem. Phys.*, **36**, 1608 (1962).
- (a) J. Petruska, *J. Chem. Phys.*, **34**, 1120 (1961).
(b) P. E. Stevenson, *J. Chem. Educ.*, **41**, 234 (1964).
- M. J. May, Ph.D. Thesis, Michigan State University, (1976).
- D. R. Arnold, J. R. Bolton, and J. A. Pedersen, *J. Am. Chem. Soc.*, **94**, 2872 (1972) and private communication of unpublished results.
- P. J. Wagner and M. J. May, *Chem. Phys. Lett.*, **39**, 350 (1976).

26. (a) E. F. Zwicker, L. J. Grossweiner, and N. C. Yang, J. Am. Chem. Soc., **85**, 2671 (1963).
(b) K. R. Huffman, M. Loy, and E. F. Ullman, ibid., **87**, 5417 (1965).
27. G. Porter and M. Tahir, J. Chem. Soc. (A), 3772 (1971).
28. H. Lutz, E. Breheret, and L. Lindqvist, J. Chem. Soc., Faraday Trans. 1, 2096 (1973).
29. W. R. Bergmark, B. Beckmann, and W. Lindenberger, Tetrahedron Lett., 2259 (1971).
30. R. Hoffmann and J. R. Swenson, J. Phys. Chem., **64**, 415 (1970).
31. P. J. Wagner and C. P. Chen, J. Am. Chem. Soc., **98**, 239 (1976).
32. (a) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N. Y., (1965), p. 438ff.
(b) A. G. Pinkus and H. C. Custard, Jr., J. Phys. Chem., **74**, 1042 (1970).
(c) D. Liebfriz, Chem. Ber., **108**, 3014 (1975).
33. C. Walling and M. J. Gibian, J. Am. Chem. Soc., **87**, 3361 (1965).
34. F. D. Lewis, R. W. Johnson, and D. R. Kory, J. Am. Chem. Soc., **96**, 6100 (1974).
35. D. R. Kearns and W. A. Case, J. Am. Chem. Soc., **88**, 5087 (1966).
36. T. Matsuura and T. Kitaura, Tetrahedron, **25**, 4487 (1969).
37. P. G. Sammes, Tetrahedron, **32**, 405 (1976).