by para substituents, *e.g.*, CF_3, CN, and NO_2 (*cf.* Tables I–VIII), could have some small (secondary) π-delocalization effect contributions (R effects) as well as the predominant polar effect contributions (I effects). However, the previously reported equal solvent sensitivity for the "completely twisted" and the "coplanar" NO_2 substituents does not appear at first sight to support this possibility. However, unpublished results of Mr. Imuta appear to invalidate this evidence.[19]

Fourthly, for structure I type systems, the ρ_R effects may be apparent from the resonance polar effects[12] of the substituents. Such a result would be expected, however, to lead to $\lambda \equiv \rho_R/\rho_I$ = constant, independent of solvent. Only the G = $HC(C_6H_5)$ data set gives this result (*cf.* Table I).

Acknowledgment. We are pleased to acknowledge helpful discussions with Dr. James L. Lyle and Professor C. S. Giam regarding their correlations of F nmr shifts with the E_T solvent polarity parameters. Constructive comments of Dr. R. T. C. Brownlee are acknowledged too. We are also indebted to Dr. R. G. Pews for preparation of the diphenyl ether and sulfide samples and for preliminary measurements. The shift measurements of Dr. P. D. Heffley on the diphenyl sulfide series in CH_2Cl_2 solutions are also gratefully acknowledged.

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[19] Unpublished results of Mr. M. Imuta. With both 4-nitro-3,5-dimethylfluorobenzene and 4-cyano-3,5-dimethylfluorobenzene, Mr. Imuta has found significantly greater shift sensitivity to polar aprotic solvents than for the corresponding para-substituted fluorobenzene. Consequently, it appears very probable that the equality of 4-nitro-3,5-di-*tert*-butylfluorobenzene and *p*-nitrofluorobenzene solvent shifts is coincidental. The 3,5-di-*tert*-butyl groups probably play two additional roles besides giving rise to "complete twisting." There is steric hindrance to solvation of the "completely twisted" NO_2 which reduces the solvent induced electron-withdrawing polar effect compared with the "coplanar" *p*-NO_2 of the fluorobenzene. This reduction, however, is probably totally compensated by the lower effective dielectric constant applicable for the former, which gives rise to greater effective transmission of the reduced substituent solvation effect—thus a coincidental stand-off.

Effects of Ring Substituents on the Type II Photoreactions of Phenyl Ketones. How Interactions between Nearby Excited Triplets Affect Chemical Reactivity

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Abstract: The effects of various ring substituents on the type II reactions, phosphorescence, and uv and epr spectra of phenyl alkyl ketones have been determined. Phenyl, methoxy, methyl, *o*-chloro, and *p*-chloro substituents decrease the chemical reactivity of the ketone triplets; trifluoromethyl substituents double reactivity; fluoro and *m*-chloro substituents produce little change; and *p*-hydroxy, *p*-bromo, and *p*-thiomethoxy substitution completely suppresses type II reaction. All ring substituents which affect triplet reactivity lower the O–O phosphorescence band energies of phenyl alkyl ketones. With phenyl-, methoxy-, thiomethoxy-, and methyl-substituted ketones, the observations of $\Delta M = 2$ epr signals and phosphorescence lifetimes greater than 0.1 sec indicate π,π^* lowest triplets. The spectroscopic behavior of the *p*-chloro ketone suggests virtually isoenergetic n,π^* and π,π^* triplet levels. The fluoro-, trifluoromethyl-, *m*- and *o*-chloro-substituted ketones retain n,π^* lowest triplets. The decreased reactivity of the *o*-chloro ketone probably reflects a steric effect. The increased reactivity of the trifluoromethyl ketones probably reflects a weak inductive effect. The triplet-state reactivity of ketones with π,π^* lowest triplets decreases as the energy gap ΔE_T between the π,π^* and n,π^* triplets increases. This effect is produced as substituents become more electron donating ($CH_3S > CH_3O > CH_3 > Cl$) and as the solvent is changed from benzene to methanol. Observed rates of triplet state γ-hydrogen abstraction respond identically with changes in C–H bond strength and to inductive effects of γ and δ substituents for both *p*-methoxy and unsubstituted phenyl ketones. This behavior suggests that the *p*-methoxy ketones react primarily from equilibrium concentrations of upper n,π^* triplets, with a ΔE_T of 2.8 kcal in benzene and 4.2 kcal in methanol. Intersystem crossing yields of the methoxy ketones are nearly unity in polar and nonpolar solvents. Consideration of the spectroscopy and the low triplet-state reactivity of naphthyl and biphenylyl ketones suggests that vibronic mixing of n,π^* and π,π^* triplets is very ineffective at promoting chemical reactivity when $\Delta E_T > 2$ kcal. With the methyl- and *p*-chloro-substituted phenyl ketones, $\Delta E_T < 2$ kcal and the two triplets may be strongly mixed. If they are, reaction may take place from equilibrium populations of both states.

Correlation of the effects of substituents on the reactivity of benzene derivatives is one of the principal weapons of physical and mechanistic organic chemistry. Determination of the effects of ring substituents on the photochemistry of phenyl ketones[2-4] has turned out to be a very complicated business. Any effect of substituents on the reactivity

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[1] (a) Alfred P. Sloan Fellow, 1968–1972; (b) NDEA Title IV Fellow, 1968–1970.

[2] (a) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2051 (1963); (b) G. Porter and P. Suppan, *ibid.*, **61**, 1664 (1965).

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

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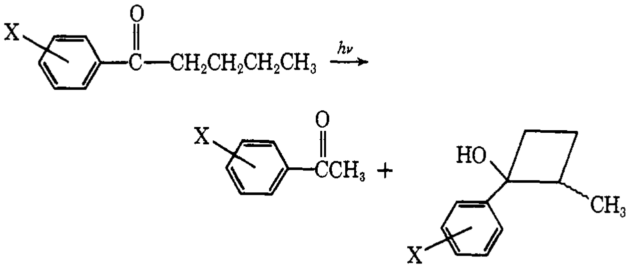
of individual states is normally overshadowed by their effects on the relative energy levels of the lowest excited states.[2-4] A general view has developed that π,π^* triplets of ketones are substantially less reactive than n,π^* triplets in radical-like reactions. In this regard, the energetic proximity of n,π^* and π,π^* triplets[2-9] makes interpretation of triplet ketone reactivities unusually challenging, especially since spectroscopists have just begun[10] to describe the interactions between such energetically proximate states.

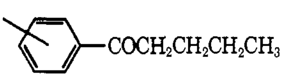
Type II photoelimination of phenyl ketones is an ideal reaction to monitor substituent effects on triplet-state reactivity since it is now clearly understood to involve rapid triplet state γ-hydrogen atom abstraction,[11] rates of which are largely solvent independent.[12] Therefore, we have carefully examined the effects of various ring substituents on the spectroscopy[13] and triplet-state reactivity[14] of valerophenone. We also have looked in detail at several *p*-methoxy-substituted ketones[15] in order to determine the mechanism whereby ketones with π,π^* lowest triplets display n,π^* reactivity. We report here in full our results, some of which have been published in preliminary form.[13-16]



Results

Substituted Valerophenones. In general, degassed benzene solutions 0.1 *M* in ketone were irradiated at 3130 Å to conversions of 5% or lower. Quantum yields of substituted acetophenone formation were determined relative to valerophenone itself. Quenching studies were performed with 2,5-dimethyl-2,4-hexadiene; linear Stern–Volmer plots were obtained in the Φ_0/Φ region of 1–3 for all ketones, from which $k_q\tau$ values were obtained. In all cases that we checked, Stern–Volmer plots remain linear out to large Φ_0/Φ values. Table I lists quantum yields,[17] $k_q\tau$ values, and triplet lifetimes for all the valerophenones in benzene and for the *p*-methyl and *p*-methoxy ketones in methanol.

Table I. Quenching Kinetics[a] for Ring-Substituted Valerophenones



Substituent	Φ_{11}[b]	$k_q\tau$, M^{-1}	$1/\tau$, 10^7 sec^{-1} [c]
None	0.33	40 ± 1	12.5
o-CF_3	0.20	38 ± 0.4	13
m-CF_3	0.23	16 ± 0.1	32
p-CF_3	0.26	18 ± 1	28
o-(N)[d]	0.14	27	19
m-(N)[d]	0.16	16	31
p-(N)[d]	0.22	7	68
o-F	0.33	35 ± 0.3	14
m-F	0.27	28 ± 3	18
p-F	0.36	34 ± 1	15
o-Cl	0.45	141 ± 9	3.5
m-Cl	0.33	32 ± 2	16
p-Cl	0.29	135 ± 3	3.7
m-CH_3	0.34	128 ± 4	3.9
p-CH_3	0.39	272 ± 1	1.8
p-CH_3[e]	0.88	2000	0.37[f]
o-OCH_3	0.20	350 ± 50[g]	~1.4
m-OCH_3	0.013	350 ± 100[g]	~1.4
p-OCH_3	0.14	2250 ± 50	0.22
p-OCH_3[e]	0.09	13,000 ± 300	0.06[f]
p-Phenyl[h]	0.0002		
p-OH	<0.001		
p-SCH_3	<0.001		
p-Br	<0.001		

[a] 0.10 *M* ketone in benzene, irradiated at 313 nm. [b] Quantum yield for acetophenone formation. [c] $k_q = 5 \times 10^9$ M^{-1} sec^{-1}. [d] P. J. Wagner and G. Capen, *Mol. Photochem.*, **1**, 173 (1969). [e] In methanol. [f] $k_q = 7.5 \times 10^9$ M^{-1} sec^{-1}. [g] Values highly variable. [h] γ-Methylvalerophenone.

Effect of Added Lewis Bases on Quantum Yields. The effect of added *tert*-butyl alcohol[12] on type II quantum yields was determined for several of the substituted valerophenones.[16] As for valerophenone, total quantum yields rise to unity for the ketones substituted with *p*-methyl[18] and electron-withdrawing groups, indicating that their triplet lifetimes are determined solely by rates of γ-hydrogen atom abstraction.[12] For the methoxyvalerophenones quantum yields rise slightly in the presence of small concentrations of *tert*-butyl alcohol, methanol, or pyridine; reach maximum values at moderate (~0.5 *M*) alcohol concentrations; and then gradually decrease at high alcohol concentrations. For *p*-chlorovalerophenone,[18] the maximum quantum yield leveled off at 80%.

***p*-Methoxy Ketones.** Several *p*-methoxy phenyl ketones with varying substitution about the γ carbon were prepared and studied. Table II lists quantum yields in benzene, maximum quantum yields obtained upon addition of *tert*-butyl alcohol,[16] and $k_q\tau$ values obtained from Stern–Volmer quenching studies in benzene. Triplet lifetimes were divided into rate constants for γ-hydrogen abstraction, k_r, and for triplet decay, k_d, according to eq 1.[12] The similar k_d

$$\Phi_{\mathrm{MAX}} = k_r\tau = k_r(k_r + k_d)^{-1} \qquad (1)$$

values, which should be a function only of the *p*-anisyl chromophore, for the different ketones are a good measure of the internal consistency of our results.

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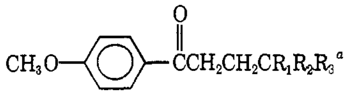
(18) Our original Φ values[16] for *p*-methylvalerophenone were too low because of impurity quenching, which we suspect to be involved in *p*-chlorovalerophenone also.

Table II. Photokinetic Parameters for *p*-Anisyl Ketones


$CH_3O-C_6H_4-C(=O)CH_2CH_2CR_1R_2R_3$[a]

R_1	R_2	R_3	Φ_{II}[b]	Φ_{TOT}^{MAX}[c]	$k_q\tau$, M^{-1}	k_r, 10^6 sec^{-1}	k_d, 10^6 sec^{-1}
H	H	H	0.012	0.04	3300	0.06	1.5
H	H	CH_3	0.145	0.26	2300	0.56	1.6
H	CH_3	CH_3	0.22	0.67	1100	3.0	1.5
H	H	CO_2CH_3[d]	0.008	0.019	830	0.025	6.0
H	H	CH_2CN	0.009	0.015	2650	0.03	1.7
H	H	$CH_2CO_2C_2H_5$[e]	0.10	0.14	2500	0.28	1.7

[a] First three ketones 0.10 *M* in benzene; last three 0.05 *M*; irradiation at 313 nm. [b] Acetophenone formation in benzene. [c] Sum of acetophenone and cyclobutanol; maximum value reached upon addition of *tert*-butyl alcohol. [d] Values all decrease with increasing conversion; ones listed are at 6% conversion. [e] In ref 15, this compound was incorrectly listed as a methyl ester.

Our k_d value is higher, and our Φ lower, than that found for *p*-methoxybutyrophenone by other investigators.[3,19] Probably our solvent contained an impurity more completely removed by others. The Φ and $k_q\tau$ values for the γ-carbomethoxy ketone decrease with conversion because of quenching by the acrylate product.[17] The high k_d value reflects this phenomenon.

Intersystem Crossing Yields of Anisyl Ketones. The relative efficiencies with which acetophenone, *o*-methoxyacetophenone, *p*-methoxyacetophenone, and *m*-methoxyacetophenone sensitize the cis–trans isomerization of 0.2 *M* 1,3-pentadiene[20] were measured at 3130 Å. The Φ_{ISC} values so determined are 1 (assumed), 0.98, 0.98, and 0.96, respectively, in benzene. Methoxy substitution does produce a slight decrease in intersystem crossing, but surely not enough to account for the low quantum yields in type II reactions of the various methoxy-substituted ketones. The Φ_{ISC} value for *p*-methoxyacetophenone was also measured in methanol and acetonitrile and found to be 0.96 and 0.98, respectively. Consequently, the low quantum yield for type II reaction of *p*-methoxyvalerophenone in methanol is not due to decreased intersystem crossing, as has been found to occur in fluorenone[21] and *p*-aminobenzophenone.[22]

Table III. Phosphorescence (77°K) of Ring-Substituted Valerophenones[a]

Substituent	Solvent	E_T, kcal[b]	τ_p^{short}, msec[c]	τ_p^{long}, msec[d]	D^* [e]
None	2-MP[f]	74.3	6.4	27 (2)	N.O.
	IP[g]	72.0	5.3	20 (18)	
	EtOH[h]	74.5	34	260 (6)	0.1347
o-CF_3	IP	72.0	8.5		
m-CF_3	IP	72.0	2.7		
p-CF_3	IP	71.0	5.2		
o-(N)	IP	70.0	1.8		
	EtOH	72.5	4.1		
m-(N)	IP	72.0	2.6		
	EtOH	74.0	6.9		
p-(N)	IP	71.0	2.0		
	EtOH	71.5			
o-F	IP	72.0	5.0		
	EtOH	75.3	13	200 (2)	N.O.
m-F	IP	70.6	8.0	132 (12)	
p-F	IP	72.4	39	127 (19)	
o-Cl	IP	70.4	1.9		
	EtOH	73.0	7.0	32 (4)	N.O.
m-Cl	IP	70.6	6.0	20 (37)	
	EtOH	73.6	41	175 (8)	N.O.
p-Cl	IP	70.5	4.7	75 (7)	
	EtOH	72.3	40	99 (50)	N.O.
m-CH_3	2-MP	72.5	200		
	EtOH	~72	90	290 (36)	0.1365
p-CH_3	2-MP	~73	130		
	EtOH	~73	175	940 (6)	0.1269
o-OCH_3	2-MP	72.5	300		
	EtOH	72.7	122	400 (42)	0.1331
m-OCH_3	2-MP	~70.0	440		
	EtOH	~70.0	230	700 (50)	0.1429
p-OCH_3	2-MP	~71	450		
	EtOH	~71	208	520 (68)	0.1178
p-SCH_3	2-MP	64.2	120		
	EtOH	65.0	320		0.1114
p-phenyl	2-MP	60.9	320		
	EtOH	60.9	370		0.0987

[a] Although quantum yields were not measured directly, all ketones studied emitted with comparable intensities, so that $\Phi_p > 0.5$ (see N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenberg, *J. Amer. Chem. Soc.*, **89**, 5466 (1967)). [b] O–O band of phosphorescence. [c] Shorter lived component. [d] Long-lived component, percentage of total intensity in parentheses (measured at O–O band). [e] From H_{min} for $\Delta M = 2$ epr transition at 9.24 GHz. [f] 2-Methylpentane. [g] Isopentane. [h] Same lifetime values obtained in a 1:1 ethanol–iodoethane glass.

Phosphorescence spectra and lifetimes of the various ketones were determined at 77°K in various glassy matrices.[13] In agreement with other workers,[6,23] we find that most of the ketones (exceptions: pyridyl and biphenylyl ketones) display nonexponential phosphorescence decay, which can be analyzed as the sum of two exponential decays. Table III lists for each ketone the energy of the highest energy (O–O) band and the lifetime of the major decay component. The minor decay component is always longer lived than the major component; its cause or causes are not yet understood.[13,23] For the methyl, methoxy, and thiomethoxy-substituted ketones, the actual phosphorescence spectra were so broad that no sharp O–O bands were evident. The E_T values were assigned from the energies of the highest energy shoulder in each spectrum and are thus less accurate than the other values.

Triplet epr absorption[24] was also evident for several of the ketones, although $\Delta M = 1$ lines could be observed only for the biphenylyl ketone. The D^* values obtained are listed in Table III.

Uv spectra of the various ketones in heptane solution were also recorded. The λ_{max} values and extinction coefficients for the second benzene transitions ($^1A \rightarrow {}^1B_{1u}$ or ^1L_a) are listed in Table IV. Each ketone also showed normal n → π* absorption in the 300–370-nm range and a moderate $^1A \rightarrow {}^1B_{2u}$ (^1L_b) band just below 300 nm. In the *p*-fluoro, chloro, methyl, methoxy, and thiomethoxy ketones, this band was mostly or completely buried under the more intense ^1L_a band.

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Table IV. Substituent Effects on $S_0 \rightarrow {}^1L_a$ Transitions of Benzene and Acylbenzenes

	Valerophenone[a]		Benzene[b]
Substituent	λ_{max}, nm	$-\Delta\nu$, kcal/mol	$-\Delta\nu$, kcal/mol
H	238 (14,000)	0	0
o-CF_3	218 (4400)[c]	−11.0	
m-CF_3	234 (9600)	−2.1	
p-CF_3	234 (13,000)	−2.1	
o-(N)	226 (10,000)[d]	−6.4	
m-(N)	227 (11,000)[d]	−6.0	−4.6
p-(N)	221 (10,000)[d]	−9.3	
o-F	233 (11,000)	−2.6	
m-F	236 (11,000)	−1.1	0.6
p-F	240 (11,000)	1.0	
o-Cl	234 (4800)	−2.1	
m-Cl	239 (10,000)	0.4	7.1
p-Cl	249 (18,500)	5.0	
m-CH_3	242 (11,000)	1.9	4.0
p-CH_3	247 (15,500)	4.2	
o-OCH_3	243 (7800)	2.3	
m-OCH_3	246 (7800)	3.9	9.7
p-OCH_3	264 (17,000)	11.8	
p-SCH_3	304 (23,000)	26.0	22.3[e]

[a] In heptane; molar extinction coefficients in parentheses. [b] From ref 25. [c] Shoulder. [d] P. J. Wagner and G. Capen, *Mol. Photochem.*, **1**, 173 (1969). [e] For SH.

In the *o*-pyridyl and *o*-trifluoromethyl ketones, the ${}^1L_a$ band is a shoulder on the ${}^1A \rightarrow {}^1E$ transition.

Discussion

As indicated in the introduction, substituent effects on triplet reactivity involve several factors. Our discussion of these factors follows the following logical order: (1) what the spectroscopic results indicate about the nature of the lowest triplet; (2) correlation of observed triplet reactivities with the nature of each ketone's *lowest* triplet; (3) an examination of possible sources of n,π^*-like reactivity for ketones with π,π^* lowest triplets; (4) why the behavior of the *p*-methoxy ketones suggests reaction from equilibrium levels of upper n,π^* triplets; (5) a critical analysis of how much chemical reactivity vibronic mixing of states may produce. Finally, we note the exceptional behavior of several individual ketones.

Spectroscopy. Recent spectroscopic studies of phenyl alkyl ketones[5–9,23] indicate that their n,π^* and π,π^* triplets lie in energetic proximity[5–7] and are coupled vibronically.[8,9] It is well known that the $\pi \rightarrow \pi^*$ excitation energies of benzene are strongly influenced by substituents.[25] Consequently, before any discussion of how individual ring substituents affect the chemical reactivity of triplet valerophenone is possible, the effects of each substituent on the actual energy levels of the n,π^* and π,π^* triplets must be determined. It is simplest to begin by temporarily ignoring mixing of the two states.

Although it is generally believed that the lowest triplet of phenyl alkyl ketones is n,π^* in hydrocarbon glasses,[5–7] while the lowest triplet of *p*-methoxyphenyl alkyl ketones is π,π^*,[5,9] spectroscopists do not agree on which is the lowest triplet for the corresponding *p*-methyl[5,9,26] and *p*-chloro[5,9,27] ketones. Therefore, it is desirable to look separately at substituent effects on n $\rightarrow$ π^* and $\pi \rightarrow \pi^*$ transitions in systems clearly displaying only one or the other.

In benzophenone, the n,π^* triplet is far enough below the lowest π,π^* triplet that the substituents which we are considering do not invert triplet levels.[28] It has been found that the triplet excitation energies of substituted benzophenones correlate with the common Hammett σ values of substituents.[29] We assume that the n,π^* triplet levels of phenyl alkyl ketones are similarly affected by substituents.

Porter and Suppan[2] have suggested that there might be parallel substituent effects on $\pi \rightarrow \pi^*$ triplet energies of phenyl ketones and on $\pi \rightarrow \pi^*$ uv transition energies. We have already pointed out[30] that the best chance for such a parallel exists for the *second* singlet $\pi \rightarrow \pi^*$ transition (${}^1S_0 \rightarrow {}^1L_a$), to which the lowest $\pi \rightarrow \pi^*$ triplet transitions of simply substituted benzenes correspond. Table IV compares $S_0 \rightarrow {}^1L_a$ λ_{max} values for the substituted valerophenones to those for monosubstituted benzenes. The inductive and conjugative effects of substituents on the $\pi \rightarrow \pi^*$ transitions of benzene do not exactly parallel their effects on ground-state reactivities.[31] In particular, chlorine and the higher halogens are stronger electron donors than are alkyl groups. With the exception of fluorine, which perturbs benzene's $S_0 \rightarrow {}^1L_a$ transition only weakly, the conjugative effects of most substituents far outweigh their inductive effects, such that both electron donors and electron acceptors stabilize $\pi \rightarrow \pi^*$ transitions. Only aza and trifluoromethyl substituents, which cannot extend π conjugation, destabilize the ${}^1L_a$ state.

The acyl group itself produces one of the strongest stabilizations of excited benzene, lowering the S $\rightarrow$ ${}^1L_a$ band by 20 kcal and the S $\rightarrow$ ${}^3L_a$ band by $\sim$9 kcal. When both the acyl group and an electron-donating group are attached to the benzene ring, the two groups reinforce each other in stabilizing the ${}^1L_a$ state. However, the effects of the two groups are additive only for 1,4 substitution. *m*-Methoxy, methyl, and chloro substituents stabilize the S $\rightarrow$ ${}^1L_a$ transition of valerophenone only slightly.

The strongly electron-withdrawing CF_3 and aza substituents tend to counter the effect of the acyl group, such that these substituents increase the $S_0 \rightarrow {}^1L_a$ transition energy of phenyl ketones. The much larger hypsochromic shift for the *o*-CF_3 ketone relative to the *o*-pyridyl ketone can be attributed to some steric hindrance by the CF_3 group toward formation of a planar benzoyl system.[32] The slight destabilizations caused by *o*-chlorine and *o*-fluorine presumably reflect similar steric hindrance.

The effects of substituents on "pure" ^{3}n,π^* and ${}^1L_a$ π,π^* states suggest a general scheme (Scheme I) for substituent effects on the excitation energies of the lowest triplets of phenyl alkyl ketones, before any mixing of states is considered.

Since, in terms of changes in dipole moment, the

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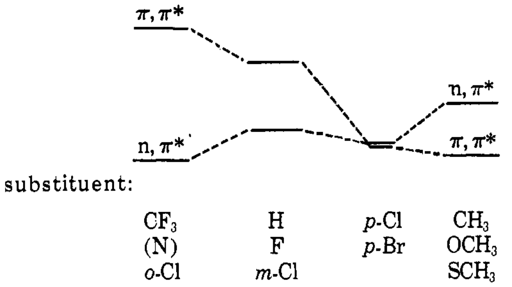
(29) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(30) P. J. Wagner and G. S. Hammond, *ibid.*, **5**, 101 (1968).

(31) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen and Co., Ltd., London, 1963, pp 206, 227.

(32) H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 613 (1960).

Scheme I



L_a state is more polar and the n,π* state less polar than the ground state, polar solvents such as alcohols are expected and have been observed[6,7,9] to produce the same triplet state inversion as do electron-donating groups.

Our phosphorescence results summarized in Table III are completely consistent with the above diagram. Unsubstituted valerophenone displays in hydrocarbon glasses the typically short-lived, high quantum yield phosphorescence characteristic of ketones with n,π* lowest triplets. The most prominent vibrational progression corresponds to the ground-state carbonyl stretch. In the very polar ethanol glass, however, valerophenone's phosphorescence lifetime is considerably longer, its spectrum is less structured, and triplet epr absorption is observed. We do not yet know the identity of the minor emission component observed for valerophenone and most of its derivatives. Several mechanisms apparently can be responsible for the isolation in rigid media of geometrically distinct emitting isomers.[23c,d] Since this matter is still somewhat controversial, we shall attempt no interpretation here.

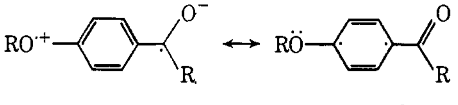
Strong electron-withdrawing groups such as trifluoromethyl and the nitrogen of pyridyl ketones stabilize the n,π* triplets slightly, as indicated by the lower energy O–O bands and very short lifetimes, even in ethanol glasses. It has already been demonstrated that such substitution increases the energy of L_a π → π* transitions.[33–35]

The electron-donating methyl, methoxy, and thiomethoxy substituents obviously invert the triplet levels, since O–O bands are at lower energies than for valerophenone itself, but phosphorescence lifetimes exceed 0.1 sec and $\Delta M = 2$ epr signals are readily observed. The *p*-thiomethoxy group produces a much larger stabilization of the π,π* triplet than does the methoxy group. This behavior is markedly different from their relative effects (σ values)[36] on ground-state reactions and reflects the charge-transfer nature of L_a excited states.[37]

The biphenylyl ketone, *p*-phenyl-γ-methylvalerophenone, clearly has a π,π* lowest triplet, as evidenced by its long-lived, structureless phosphorescence. Its triplet epr spectrum indicates D and E values of 0.0978 and 0.0074 cm^{-1}, considerably different from the 0.1096 and 0.0036 cm^{-1} values we measure for biphenyl itself.[38] The actual E_T value for this acylbiphenyl is probably around 65 kcal, because of the large geometric difference between triplet and ground states.[39] The E_T value for biphenyl itself has been estimated to be ~70 kcal;[39] the lower estimate for this acylbiphenyl is consistent with the difference in triplet state zero field parameters, which indicate the expected additional conjugation.

The situation with the halosubstituted ketones is less clear. The small effects of fluorine substitution on phosphorescence parallel the small effects on $S_0 \rightarrow {}^1L_a$ transitions. Chlorine substitution lowers triplet excitation energy but produces little change, relative to valerophenone itself, in phosphorescence lifetimes. This behavior is consistent with the prediction that chlorine's electron-withdrawing inductive effect should stabilize the n,π* state while its electron-donating resonance effect should stabilize the L_a π,π* states. We have already suggested,[13] on the basis of the intermediate lifetime of the major phosphorescing component, the n,π* polarization of the highest energy phosphorescence band,[27] and the pronounced heavy-atom effect on the lowest energy S → T* band,[5] that in polar solvents the π,π* triplet of *p*-chloro ketones lies only ~100 cm^{-1} below the n,π* triplet so that the major phosphorescence component arises from both, but principally from the faster emitting n,π* state. That is, the two states may equilibrate thermally before emitting. (In that case, the longer-lived minor emission component must represent a geometrically isolated conformer of one state.) If this explanation of various spectroscopic observations is true, the polar solvent effect on valerophenone's phosphorescence lifetime would have a like cause. Even though the π,π* triplet lies slightly lower, the n,π* triplet is responsible for 90% of the emission, so that there is no heavy atom effect (see Table III) on the phosphorescence lifetime. Li and Lim[9] have suggested that the intermediate lifetimes and other phosphorescence properties of *p*-methyl- and *p*-chloroacetophenones are due to strong mixing of n,π* and π,π* triplets. We say more about this phenonemon below, but note here that mixed states may also be close enough energetically to equilibrate before emitting.

At this point we should note that there indeed are parallel substituent effects on the energies of the $S \rightarrow {}^1L_a$ and $S \rightarrow {}^3L_a$ transitions of acylbenzenes.[2] The parallel is not exact, however. The $S_0 \rightarrow {}^1L_a$ bands of *p*-methoxy and *p*-methyl ketones and benzonitriles[25,40] occur at lower energy than those of the meta and ortho derivatives, presumably because the ${}^1L_a$ state can mix strongly with the somewhat higher energy charge-transfer state.[25,37] (It is this kind of charge-transfer state which Porter and Suppan suggested becomes the lowest excited state in *p*-amino ketones.[2]) However, because of the huge singlet–triplet splitting of L_a states, the ${}^3L_a$ state cannot couple so strongly to the charge-transfer state,[41] so that the meta-substituted ketones seem to have slightly lower



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[33] N. C. Yang and R. Dusenbery, *J. Amer. Chem. Soc.*, **90**, 5899 (1968).

[34] N. C. Yang and R. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

[35] P. J. Wagner and G. Capen, *ibid.*, **1**, 173 (1969).

[36] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[37] S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

[38] See also, J. Mispelter, *Chem. Phys. Lett.*, **10**, 539 (1971).

[39] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967).

[40] P. J. Wagner, unpublished results.

[41] Reference 31, p 302.

E_T values than do the para-substituted derivatives.[40] This latter pattern is predicted for any benzene π,π^* state in the absence of strong charge transfer[25] and is well known to profoundly affect the chemical reactivity of the lowest singlets (^1L_b) of substituted benzenes.[42] Apart from the differing amounts of charge-transfer character in ^1L_a and ^3L_a states, however, substituent effects on the two states apparently are quite similar.

Triplet Epr. With the exception of *p*-chlorovalerophenone, all the ketones thought to possess π,π^* lowest triplets display $\Delta M = 2$ epr signals, detection of which is better than just consistent with the π,π^* assignment. Even though D for the n,π^* triplet of benzophenone[43] has an absolute value very similar to the D^* values of these substituted valerophenones, all phenyl alkyl ketones with lowest n,π^* triplets display considerably larger values of D (0.24–0.44 cm^{-1}).[44] Our D^* value for valerophenone itself in ethanol agrees closely with both the D and D^* values (E is quite small) recently reported for benzonitrile[44c] and methyl benzoate.[45] (Both the cyano and the carboxy groups closely mimic the acyl group in their effects on π,π^* transitions of benzene,[25] without introducing low-lying n,π^* transitions.) The variation in D^* values for the isomeric methoxyvalerophenones is not yet readily interpretable.[45]

Chemical Reactivity. Table V compares the triplet reactivity of the substituted valerophenones with the energy levels of their two triplets, which energies were estimated[46] from the spectroscopic data. Unfortunately, it is impossible to determine ΔE_T values any more accurately, surely not within ±1 kcal. Phosphorescence excitation techniques[5] have provided estimates of such ΔE_T values for ketones in polar glasses at 77°K. However, it is now known that n → π^* triplet excitation energies of ketones are ~2 kcal lower in solution than in rigid media.[47,48] Moreover, there is a 1–2 kcal Stokes shift between the O–O bands of ketone S → T n,π^* emission and absorption.[5] In any event, only the trend in ΔE_T values, not their exact values, is important. Given the trends noted in Table V, we can discuss the differing effects of electron-withdrawing and electron-donating substituents on the reactivity of triplet phenyl alkyl ketones.

Table V. Substituent Effects on Triplets of Substituted Valerophenones

Substituent	k_r^{obsd}, 10^7 sec$^{-1\,a}$	$E_{n,\pi}{}^b$	$E_{\pi,\pi}{}^b$	$\Delta E_T{}^{b,c}$
H	12.5	72.0	~75	3
o-CF$_3$	13	72.0	~78	6
m-CF$_3$	32	72.0	~76	4
p-CF$_3$	28	71.0	~76	5
o-(N)	19	70.0	~77	7
m-(N)	31	72.0	~76	4
p-(N)	68	71.0	~78	7
o-F	14	72.0	~76	4
m-F	18	70.6	~75	4.4
p-F	15	72.4	~75	2.6
o-Cl	3.5	70.4	~76	5.6
m-Cl	16	70.6	~74	3.4
p-Cl	3.0^d	70.5	~71.5	~1.0
m-CH$_3$	3.9	~72.5	72.5	<0^e
p-CH$_3$	1.8	~73	73	<0^e
o-OCH$_3$	~0.3^{d,f}	~73.5	72.5	−1
m-OCH$_3$	~0.02^{d,f}	~73	70	−3
p-OCH$_3$	0.05^d	~74	71	−3
p-C$_6$H$_5$	~0.0001^g	~71	~65	−6
p-SCH$_3$	<0.0001^g	~74	64	−10

^{a} $k_r = 1/\tau$, unless otherwise indicated. ^{b} Kcal/mol. ^{c} $E_{\pi,\pi} - E_{n,\pi}$. ^{d} $\Phi_{\max}/\tau$. ^{e} On the basis of long phosphorescence lifetimes. ^{f} See text. ^{g} On the assumption that $k_d = 10^6$ sec^{-1}.

Fluorine and *m*-chloro substituents produce little change in the energy levels of the excited states and no change in the reactivity of the triplet ketone.

Both trifluoromethyl and aza substituents increase the energy gap between the two triplet levels and enhance reactivity by factors of 2–3. This small rate effect, identical with that reported for triplet benzophenone,[34] is probably a simple inductive effect on the reactivity of the electrophilic n,π^* state and is noteworthy only for its smallness; in terms of Hammett σ–ρ correlations, a ρ value of +0.5 is suggested. We do not understand the tenfold increase in reactivity of triplet acetophenone reported to be caused by a *p*-CF$_3$ group.[33]

Those ketones with π,π^* lowest triplets show considerably reduced triplet state reactivity relative to those with n,π^* lowest triplets, the reduction in reactivity being roughly proportional to ΔE_T. The reduction caused by a *p*-methyl is the same as that reported for the acetophenone system.[33] If the lowest triplets of the methyl and methoxy-substituted ketones remained n,π^*, there would be at most a twofold inductive change in reactivity relative to that of triplet valerophenone, comparable to the effects actually observed for substituted benzophenones.[34] The much larger decreases in reactivity observed here parallel the inversion of triplet levels indicated by spectroscopy. As mentioned above, spectroscopists do not all agree on the configuration of the lowest triplets of methyl and *p*-chloro-substituted acetophenones. Our rough estimates of triplet energy levels merely indicate that the two states are almost isoenergetic. The majority of spectroscopic evidence does suggest that the lowest triplets of these ketones possess much π,π^* character.[9,43] Their lowered triplet reactivities surely support such a conclusion. With the *p*-phenyl and *p*-thiomethoxy ketones, which have the lowest lying π,π^* triplets of the ketones we have studied, photoreactivity is slight.

Reactivity of Ketones with π,π^* Lowest Triplets. It remains to be determined whence ketones with π,π^* lowest triplets derive their chemical reactivity. The greatly reduced reactivity in hydrogen abstraction reactions of carbonyl compounds such as naphthyl and

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(42) (a) H. Havinga, R. O. de Jongh, and W. Dorst, *Recl. Trav. Chim. Pays-Bas*, **75**, 378 (1956); (b) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).

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

(44) (a) A. M. Nishimura and J. S. Vincent, *Chem. Phys. Lett.*, **13**, 89 (1972); (b) A. M. Nishimura and D. S. Tinti, *ibid.*, **13**, 278 (1972); (c) S. W. Mao, T. C. Wong, and N. Hirota, *ibid.*, **13**, 199 (1972); (d) T. H. Cheng and N. Hirota, *ibid.*, **14**, 415 (1972).

(45) D. R. Arnold, J. R. Bolton, and J. A. Pedersen, *J. Amer. Chem. Soc.*, **94**, 2872 (1972).

(46) Key assumptions: that electron-donating substituents increase ^{3}n,π^* energies just as they do in benzophenone;[29] and that electron-withdrawing substituents increase $^3\pi,\pi^*$ energies in a manner proportional to their effects on the $^1S_0$ → ^1L_a transitions.

(47) J. Saltiel, *et al.*, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

(48) P. J. Wagner, A. Haug, and M. May, *Chem. Phys. Lett.*, **13**, 545 (1972).

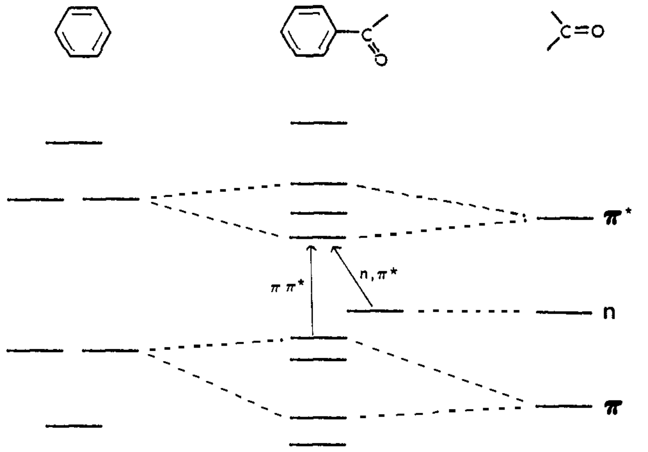
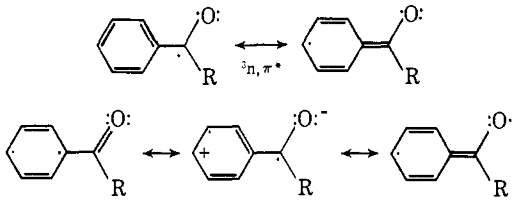


Figure 1. Mixing of π orbitals in benzoyl system.

biphenylyl ketones, which possess π,π* triplets well below their n,π* triplets, has long been associated with the fundamental difference in electron distribution between the two kinds of triplets.[2,3,49,50] It is well established that n → π* excitation of carbonyl compounds produces an alkoxy-radical-like excited state, in which the electron deficiency at the oxygen induces typical radical reactivity in the molecule.[11,51] The nature of the "pure" L_a triplet of the benzoyl group is not altogether clear. It is alternatively viewed as (1) having its excitation largely localized on the benzene ring, with the carbonyl providing a strong energetic perturbation,[31] or (2) as a charge-transfer state.[37] It is most likely a mixture and in any case should be electron rich rather than electron poor at the carbonyl oxygen and would not be expected to react like an electrophilic radical. Below are some valence bond representations of the two triplets.



$^3\pi,\pi^*$ (L_a)

In fact, aryl ketones with π,π* lowest triplets are not totally unreactive in hydrogen abstraction processes. Benzoylbiphenyl photoreduces handily,[2] while naphthyl ketone triplets[49] are 10^{-3} as reactive toward tributylstannane as are the n,π* triplets of aliphatic[52] and phenyl[53] ketones. We thus need to understand two separate aspects of π,π* reactivity: (1) whether there is any radical-like reactivity intrinsic to a $^3\pi,\pi^*$ state; and (2) how the proximity of a ^{3}n,π* state enhances reactivity.

The benzoyl group is an 8-π-electron system, so that there is some mixing of the carbonyl π and π* orbitals with the benzene orbitals as long as the two π systems are not perpendicular. Figure 1 depicts the probable orbital correlation.[37] The highest occupied π orbital is mostly benzene-like with a little carbonyl character, while the lowest π* orbital resides primarily on the carbonyl and only a little on benzene. Therefore, although the middle and left-hand resonance forms above must predominate in the L_a states, there is a finite possibility that the π electron promoted to the π* orbital comes from oxygen, as represented by the right-hand biradical form. The measurable reactivity of triplet naphthyl ketones and of excited benzoate esters[54] may thus be simply intrinsic to π,π* states of acyl aromatics. In this regard, triplet epr results are interesting. The lowered *D* values for triplet phenyl ketones relative to toluene (D = 0.17 cm^{-1})[55] presumably reflect the delocalization of free spin onto the carbonyl group but do not demonstrate equivocally much free electron spin at oxygen. Most of the decrease in *D* may involve the middle, charge-transfer resonance form, which involves little free spin at oxygen. The sharp decreases in *D* caused by para substituents which can stabilize the charge transfer form attest to its predominance.

It is also possible that the radical-like reactivity of π,π* triplets involves the mixing in of n,π* character.[30,33] With the alkyl group of these phenones necessarily impeding planarity of the benzoyl group,[32] the n and π orbitals of these compounds are not cleanly orthogonal, leading to "configurational" mixing of n,π* character into π,π* states.[28] This phenomenon may explain the meager triplet-state reactivity of naphthyl ketones and of benzoate esters. However, this kind of mixing should not vary much from one benzoyl system to another, so some other form of mixing is required to explain the widely varying π,π* reactivities reported in this paper and in acetophenone photoreductions.[33]

This problem brings us to a very important phenomenon which our discussion has so far ignored. Whenever two electronic states are as close as the n,π* and π,π* triplets of these phenyl ketones, they can mix vibronically.[10] The wave function Ψ of the lowest triplet is thus represented as a linear combination of the two unperturbed wave functions ψ, with the mixing coefficients *a* and *b* being dependent on the energy gap between the two "pure" states and on the availability and efficacy of mixing vibrations of the proper symmetry.[10] This vibronic coupling is in-

$$\Psi_{T_1} = a\psi(\pi,\pi^*) + b\psi(n,\pi^*) \qquad (2)$$

voked to explain the structure of both absorption[8,28] and emission[5,6,9,56] spectra, although no quantitative evaluations of the values of *a* and *b* have been attempted for any specific ketone. Our results and those of Yang and coworkers involving the photoreduction of acetophenones[33,57] indicate that the photoreactivity of aryl alkyl ketones decreases as the energy gap between their n,π* and π,π* triplets increases. As just de-

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(49) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962).

(50) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(51) (a) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965); (b) A. Padwa, *Tetrahedron Lett.*, 3465 (1964).

(52) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2503 (1967).

(53) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *ibid.*, **94**, 7480 (1972).

(54) J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. B*, 251 (1971).

(55) M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *Mol. Phys.*, 10, 91 (1965).

(56) (a) R. J. Zwarick and L. Goodman, *Chem. Phys. Lett.*, **7**, 609 (1970); (b) M. Koyanagi, R. Zwarich, and L. Goodman, *ibid.*, **9**, 73 (1971); (c) M. Koyanagi and L. Goodman, *J. Chem. Phys.*, **55**, 2959 (1971).

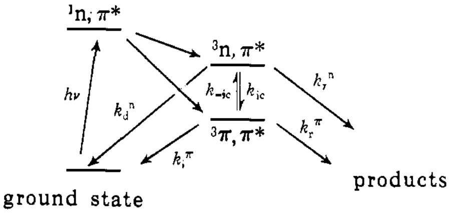
(57) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Amer. Chem. Soc.*, **89**, 5466 (1967).

scribed, vibronic mixing coefficients are inversely proportional to ΔE,[10] so that it has been suggested that the slight, vibronically induced n,π^* character of these ketones' lowest triplet is responsible for their observed photoreactivity.[33] Spin-orbit coupling introduces some singlet n,π^* character into the π,π^* triplet. However, the amount must be much too small to account for the observed photoreactivity.

The postulate of strong mixing of nearly isoenergetic n,π^* and π,π^* triplets demands that the second lowest triplet, which is mostly n,π^* in nature, lie within a few kilocalories of the lowest triplet. If the intrinsic decay rates of the individual triplets are slower than rates of thermal interconversion of triplets, as is generally assumed,[58] the two triplets will equilibrate before decaying or reacting. Since the upper, mostly n,π^* triplet *must* be photochemically reactive, the photoreactivity of ketones with very close-lying triplets can arise partially from equilibrium concentrations of the upper n,π^* triplet. Thus we are faced with the problem of distinguishing which of the two mechanisms, vibronic mixing or equilibration, is primarily responsible for the photoreactivity of ketones with π,π^* lowest triplets.

The following scheme (Scheme II) outlines the kinetic possibilities. The lowest singlet, n,π^* in all cases, crosses over probably to both triplets,[58] which are assumed to be mixed vibronically. The ^{3}n,π^* state can either react at its normal rate k_r^n or decay to the $^3\pi,\pi^*$ state, the latter reaction presumably being much the faster. In general, the possibility exists for direct decay of the n,π^* triplet to ground-state ketone, but for most simple ketones $k_r^n \gg k_d^n$.[11] The π,π^* triplet can decay (mechanism both unspecified and unknown) to ground state, return thermally to the n,π^* triplet, or possibly react slowly because of its partial n,π^* character. Any k_d extracted from application of eq 1 to the lifetime data in Tables I, II, and V must be k_i^π.

Scheme II



Equations 3 and 4 are kinetic definitions of product quantum yield and triplet lifetime under equilibrium conditions [$k_{ic} > (k_r^n + k_d^n)$; $k_{-ic} > (k_r^\pi + k_i^\pi)$], with P_p being the probability that metastable primary photoproducts (here 1,4-biradicals) proceed on to stable product(s) rather than reverting to ground-state reactant. Equation 6 is the limiting Stern-Volmer equation at low enough quencher concentration that equilibration of states is not upset. At large [Q], a Stern-Volmer plot should bend.[59]

$$\Phi_P^{EQUIL} = (\chi_{n,\pi} k_r^n + \chi_{\pi,\pi} k_r^\pi) P_p \tau_{eq} = k_r^{obsd} P_p \tau_{eq} \quad (3)$$

$$1/\tau_{eq} = \chi_{n,\pi}(k_r^n + k_d^n) + \chi_{\pi,\pi}(k_r^\pi + k_i^\pi) \quad (4)$$

$$\chi_{n,\pi} = 1 - \chi_{\pi,\pi} = \frac{k_{-ic}}{k_{-ic} + k_{ic}} \quad (5)$$

$$\Phi_0/\Phi \approx 1 + k_q[Q]\tau_{eq} \quad (6)$$

Equations 7 and 8 point out the expected dependence

$$^3\text{n},\pi^* \text{ reacts: } k_r^{obsd} = \chi_{n,\pi} k_r^n \propto e^{-(\Delta E_T + E_a)/RT} \quad (7)$$

$$^3\pi,\pi^* \text{ reacts: } k_r^{obsd} = \chi_{\pi,\pi} k_r^\pi \propto b^2 \propto \frac{e^{-E_a'/RT}}{\Delta E_0^2} \quad (8)$$

of observed rate constants k_r on the ^{3}n,π^*–$^3\pi,\pi^*$ energy gap (ΔE_T is the actual energy gap between real mixed states, ΔE_0 is the hypothetical energy gap between "pure" states before mixing) for the two extreme situations, where reaction comes only from equilibration or only from vibronic mixing. Both equations are simply limiting cases of eq 3. Equation 7 expresses the Boltzman dependence of $X_{n,\pi}$ on ΔE_T, while eq 8 postulates a direct proportionality between the degree of n,π^* reactivity induced by vibronic mixing and the amount of mixing as described by eq 2.

There are several obvious ways of varying parameters upon which the two extreme mechanisms depend differently. Temperature effects would be easy to obtain experimentally but hard to interpret. It would be easy enough to measure separate triplet-state activation energies for valerophenone and for a substituted valerophenone and to then try to equate any difference with ΔE_T. However, there is no easy way of estimating how the activation energy E_a' for hydrogen abstraction by a largely π,π^* triplet would compare with the normal E_a for hydrogen abstraction by a n,π^* triplet.

Determination of k_r^{obsd} values as a function of varying ring substituents and therefore varying ΔE_T values is hampered by the difficulty of determining ΔE_T values accurately, as described above.

A third test, the one we have employed,[15] is based on the following reasoning. If most reaction comes from equilibrium levels of an n,π^* triplet, k_r^{obsd} values for a ketone with a π,π^* lowest triplet should vary with substitution *at the C–H bond being attacked* in a manner exactly parallel to the variation in k_r^n values measured for a ketone with a n,π^* lowest triplet. If, however, reactivity comes from the lowest, mostly π,π^*, intrinsically less reactive triplet, then k_r^{obsd} values should not vary like k_r^n values. Selectivity toward C–H bond strength should increase as k_r decreases. Even more crucial, a few per cent of n,π^* character would not be expected to be enough to make the π,π^* triplet electrophilic, so that the inductive effect of substituents near the C–H bond being attacked should differ dramatically for k_r^n and k_r^π.

This expectation of differing substituent effects on k_r^n and k_r^π is based on the following interpretation of inductive effects. $\Delta G^{\ddagger}$ for hydrogen atom transfers consists of two terms. One is based on differences in bond energies. The inductive effects of substituents can be considered an electrostatic contribution to $\Delta G^{\ddagger}$, in this case an interaction between the electron affinity of oxygen and the electron density of the γ C–H bond. Since the electron density about the oxygen must differ considerably for n,π^* and π,π^* states,

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[58] For example, M. A. El-Sayed, *Accounts Chem. Res.*, 4, 23 (1971).

[59] P. J. Wagner, *Mol. Photochem.*, 3, 23 (1971); "Creation and Detection of the Excited State," Vol. 1A, A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971, p 173.

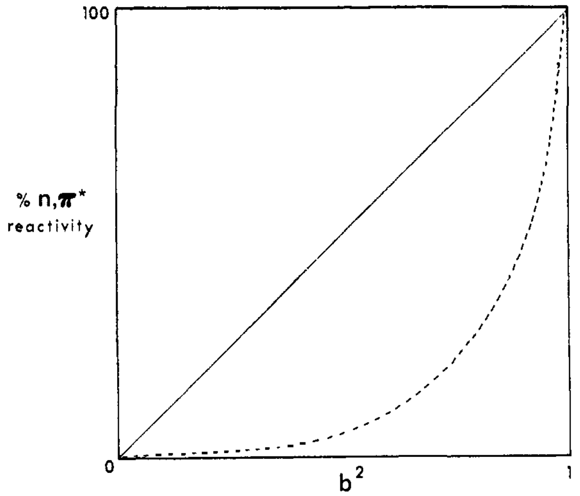

Figure 2. Dependence of k_r^{obsd} on vibronic mixing (eq 8).

as described above, the electrostatic interaction with a C–H bond must differ also and could conceivably even change from attractive to repulsive.

As Table VI indicates, k_r^{obsd} values for p-methoxy ketones, which clearly have π,π^* lowest triplets, vary with γ C–H bond strength and with the inductive effect of δ substituents exactly as do k_r^n values for simple phenyl ketones which clearly have n,π^* lowest triplets. It is important to point out that there is no spectroscopic evidence that γ or δ substitution in any way affects the triplet benzoyl or anisoyl groups. Consequently, we conclude from the evidence in Table VI that, at least in p-methoxyphenyl alkyl ketones, photoreactivity arises from equilibrium populations of the upper n,π^* triplet. Furthermore, since k_r^{obsd} averages 0.5% k_r^n and a p-methoxy substituent should roughly halve k_r^n, eq 7 indicates that $\chi_{n,\pi}$ is 0.01; ΔE_T must therefore equal 2.8 kcal (1000 cm^{-1}).

Table VI. Effects of γ Substitution on Triplet-State Reactivities of $ArCOCH_2CH_2R$ in Benzene[a]

R	Ar = C_6H_5[b] $10^{-7}k_r^n$	Ar = p-$CH_3OC_6H_4$[c] $10^{-7}k_r^{obsd}$
CH_3	0.8 (0.04)	0.006 (0.06)
CH_2CH_3	12.5 (10)	0.056 (10)
$CH(CH_3)_2$	48 (80)	0.30 (110)
$CH_2CO_2CH_3$	1.0 (0.085)	0.0025 (0.045)
$CH_2CH_2CO_2C_2H_5$	4.0 (0.32)	0.028 (0.50)
CH_2CH_2CN	1.0 (0.085)	0.003 (0.054)

[a] Values in parentheses are relative k_r values *per C–H bond* for the six ketones in that column, with the n-butyl ketones being assigned the value of 10 in each case. [b] Reference 11. [c] Table II.

Solvent Effects. Spectroscopic evidence clearly indicates that polar solvents stabilize π,π^* states relative to n,π^* states.[6,7,9] We find that the triplet lifetimes of both p-methoxy- and p-methylvalerophenone are longer in methanol than in benzene, as summarized in Table VII. The lowered reactivity of the triplets is reflected in a lowered quantum yield for the p-methoxy ketone and explains the gradual decreases in Φ_{max} values observed at increasing alcohol concentrations >0.5 M.[16] For both substituents lowered k_r^{obsd} values are best interpreted as reflecting larger ΔE_T values. We calculate (eq 7) $\chi_{n,\pi}$ and ΔE_T values of 10^{-3} and 4.2 kcal for p-methoxy ketones and 0.03 and 2.1 kcal for p-methyl ketones in methanol. These ΔE_T values are slightly lower than those measured by phosphorescence excitation techniques[5,33] for the correspondingly substituted acetophenones in polar glasses at 77°K. For reasons stated above, the solution ΔE_T values most likely are lower than those in rigid media.

Table VII. Solvent Effects on Triplet-State Reactivity of Para-Substituted Valerophenones

Ketone	Solvent	k_r^{obsd}, 10^6 sec^{-1}	k_d^π, 10^6 sec^{-1}
p-CH_3	Benzene	18	<0.1
p-CH_3	Methanol	3.7	<0.1
p-OCH_3	Benzene	0.56	1.6
p-OCH_3	Methanol	0.06	0.6
p-H	Benzene	125	<0.1
p-H	Methanol	75	<0.1

Frozen ethanol, in which we have concluded that the lowest triplet of valerophenone is π,π^*, has a considerably higher dielectric constant than does liquid methanol, so that the n,π^* and π,π^* triplets are probably almost isoenergetic in the latter medium. In that case, the two states would be approximately equally populated at room temperature, so that k_r^{obsd} would equal $^1/_2k_r^n$. Such is indeed the case (Table VII) if the correct k_q value has been chosen for methanol (see Table I). Under such conditions maximum mixing of states would also be expected, so that the lower, mostly π,π^* state should have a maximum amount of n,π^* character. Unfortunately, we cannot predict either the actual extent of mixing or how much reactivity the mixing would promote.

Reactivity Induced by Vibronic Mixing. Since we have concluded that, in terms of eq 3, $\chi_{n,\pi}k_r^n \gg \chi_{\pi,\pi}k_r^\pi$ for p-methoxy ketones, we can provide no evidence about the ability of vibronic mixing to promote chemical reactivity. Vibronic mixing of n,π^* and π,π^* triplets has been suggested as the cause of both the total reactivity of π,π^* lowest triplets[33] and the reduced reactivity of n,π^* lowest triplets.[30,34,35] In fact, these two interpretations probably are contradictory. In the absence of any theoretical or experimental evidence on the topic, one can only hope that the n,π^*-like reactivity of a mixed state will be linearly proportional to the mixing coefficient b^2 (eq 2), as suggested by eq 8 and described by the straight line in Figure 2. If the smidgeon of π,π^* character in the lowest n,π^* triplet of phenyl alkyl ketones does cut their reactivity in half, as was once suggested,[33–35] then the actual plot would look more like the dotted line (provided that no unusual discontinuity exists in this particular segment of nature) and one would have to presume very little vibronically induced reactivity in the π,π^* lowest triplets. It may be that the π,π^* contribution to these mixed triplets imparts "negative" reactivity, but it seems at least as reasonable to assume an approximate linear relationship between k_r^π and b^2 and to assign the greater k_r^{obsd} values of pyridyl- and trifluoromethyl-substituted ketones[33–35] solely to a small inductive effect.

A comparison of the spectroscopy and triplet-state reactivity of the p-phenyl and the p-methoxy ketones actually suggests that little chemical reactivity is induced by vibronic mixing. Both kinds of ketones display phosphorescence lifetimes on the order of 0.4 sec, whereas τ_p is 4 sec for biphenyl[60] and 2–4 sec for methoxybenzonitriles.[61] In the case of biphenyl, addition of an acyl group and, in the case of the nitriles, replacement of a cyano group with an acyl group produce low-lying n,π^* triplets not present in the parents. Since phosphorescence quantum yields of the ketones are high, their shorter lifetimes indicate faster phosphorescence rates, which in turn must be associated with the slight n,π^* character induced in the lowest triplet by vibronic and spin–orbit coupling. It probably is not possible to separate the two effects, otherwise a value for b in eq 2 could be calculated. However, the similar phosphorescence lifetimes of the two ketones do indicate that the lowest triplet of the p-methoxyphenyl ketone contains little more n,π^* character than does the lowest triplet of the biphenylyl ketone. Therefore, we might expect similar vibronically induced reactivity in both ketones. Nonetheless, the k_r^{obsd} value for p-methoxy-γ-methylvalerophenone must be at least 100 times larger than that for the corresponding biphenylyl ketone, since there is no reason to suspect that the k_i^{π} value for the latter ketone is any higher than those for other ketones. Of course, thermal equilibration with the n,π^* triplet provides an alternate mechanism for the enhanced reactivity of the p-methoxy ketones.

In the case of the methyl and p-chloro ketones, the "pure" triplets are so close together (Table V) that they could mix quite strongly.[9,10] Although the requirement of a small ΔE_T is met, it is not yet known how many vibrational modes can *efficiently* couple the two states. If there is strong mixing and if such mixing does induce reactivity, it is very possible that reaction comes from equilibrium concentrations of *both* triplet levels. Further experimental work and some quantitative theoretical forays into the chemical effects of vibronic coupling are required for any further understanding of the problem.

Specific Substituent Effects. Table I contains many results which, in light of the foregoing discussion, are only partially explicable. Our quantum yield values agree quite well with those reported for substituted butyrophenones.[62] However, substituent effects on quantum yields reflect primarily effects on biradicals[63] and are discussed as such elsewhere.[64] Only in the case of methoxy substitution does direct triplet decay compete with γ-hydrogen abstraction so that variations in quantum yields reflect variations in triplet-state reactivity.[15] The same is true for the unreactive ketones, except that k_r^{obsd} values are unobtainable.

Although it is possible to discuss the effects of most substituents on triplet-state reactivity in terms of the relative positions of n,π^* and π,π^* triplets, it is not so easy to rationalize all the differences noted for ortho, meta, or para substitution. For example, the o-CF_3 group produces no change in $k_q\tau$. It might be argued that a small steric effect offsets the inductive effect, except that the o-pyridyl ketone triplet is only slightly more reactive than triplet valerophenone. The large inductive effect of o-aza substitution on the n,π^* triplet energy is not matched by a correspondingly large effect on triplet reactivity.

With the o-chloro ketone, all spectroscopic evidence indicates that the lowest triplet is n,π^*. The 3.5-fold increase in $k_q\tau$ probably indicates a steric effect of the o-chlorine on the rate of γ-hydrogen abstraction.

The behavior of the o- and m-methoxy ketones was unusual in that it was very difficult to obtain reproducible quenching results. The $k_q\tau$ values in Table I are really no better than preliminary. For both methyl and methoxy substituents, meta substitution is unusual in that it produces shorter triplet lifetimes[14,33] and lower quantum yields[14,57,62] than does para substitution. Together, these observations indicate an apparent k_i^{π} value for m-methoxy ketones some ten times larger than that for p-methoxy ketones.[14] We are studying this problem further. It is possible that quenching by ground-state ketone[65] increases apparent k_i^{π} values.

Three substituents prevent type II reaction altogether. The thiomethoxy group apparently stabilizes the π,π^* triplet so much that no n,π^* reactivity is observable. The hydroxy group has a substituent effect on excited states similar to that of the methoxy group. Therefore, the negligible reactivity of p-hydroxyvalerophenone presumably indicates that very rapid excited-state deprotonation[2] prevents the buildup of an appreciable concentration of n,π^* triplets. The fact that p-hydroxybenzophenone shows photoreactivity in hydrocarbon solvents[66] is not inconsistent with the absence of type II elimination from p-hydroxyphenyl alkyl ketones.[3] As pointed out earlier, the n,π^* triplet level of benzophenone is several kilocalories lower than that of phenyl alkyl ketones, while no great difference exists in the $^3\pi,\pi^*$ energies of the two systems, so that the relative energies of the two triplets in benzophenones substituted with very strong electron-donating groups (such as O^-) are much the same as in phenyl alkyl ketones substituted with a moderate electron donor such as methoxy.

It is known that bromo-substituted ketones undergo facile photolytic cleavage of C–Br bonds.[3,67] Since we now know that a π,π^* triplet is populated, regular internal conversion processes can deposit vibrational energy in the C–Br bond and no special energy transfer[3] from the carbonyl to bromine need be hypothesized. The lack of competing type II reaction in p-bromovalerophenone indicates a triplet rate of C–Br cleavage exceeding 10^{10} sec^{-1}, if it is assumed that intersystem crossing remains efficient.

Summary

(1) The phosphorescence behavior of ring-substituted phenyl alkyl ketones and the relative positions of their n,π^* and π,π^* triplets can be estimated fairly accurately by extrapolation of substituent and solvent effects on "pure" n,π^* and L_a π,π^* transitions.

(2) Those ketone triplets which are mostly π,π^*

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in character display greatly reduced reactivity, relative to n,π^* triplets, in hydrogen abstraction reactions.

(3) Analysis of the reactivity of various *p*-methoxyphenyl ketones strongly suggests that hydrogen abstraction takes place from low, equilibrium populations of the upper n,π^* triplet.

(4) Ketones with π,π^* lowest triplets may intrinsically possess a small amount of "n,π^*-like" reactivity because of conjugative effects. Given the probability of thermal equlibration of proximate excited states, there is no strong evidence either (a) that vibronic mixing imparts significant n,π^* reactivity to ketones with mostly π,π^* lowest triplets, or (b) that the extent of vibronic mixing (*i.e.*, the interaction matrix between ^{3}n,π^* and $^3\pi,\pi^*$ states) is very large.

Experimental Section

Chemicals. Benzene was purified as usual.[12] Reagent grade methanol was distilled from magnesium turnings. 2,5-Dimethyl-2,4-hexadiene from Chemical Samples Co. was used as received. Various heavy alkanes used as internal standards were distilled and passed through alumina.

The following valerophenones were commericial materials purified by a combination of distillation and recrystallization: *p*-chloro (Columbia Organic, mp 31°); *p*-fluoro (Pfaltz and Bauer, mp 26°); *p*-methyl (Pfaltz and Bauer, mp 19–20°); *p*-hydroxy (Eastman, mp 64–64°).

The following valerophenones were prepared by addition of *n*-butylmagnesium bromide to the appropriately substituted benzonitrile: *m*-methoxy (bp 134° (6 Torr)); *o*-chloro (bp 118° (6 Torr)); *m*-chloro (mp 38–39°); *o*-fluoro (bp 108° (10 Torr)); *m*-fluoro (bp 114° (10 Torr)); *m*-methyl (bp 129° (10 Torr)); *o*-trifluoromethyl (bp 122° (11 Torr)); *m*-trifluoromethyl (bp 117° (11 Torr)); *p*-trifluoromethyl (bp 116° (10 Torr)); mp 34–35°). *p*-Methoxyl-γ-methylvalerophenone (bp 138° (3 Torr)) was prepared by addition of the Grignard from 1-bromo-3-methylbutane to *p*-methoxybenzonitrile.

p-Thiomethoxyvalerophenone (mp 49–51°) and *o*-methoxyvalerophenone (bp 142° (7 Torr)) were prepared by the addition of the appropriately substituted phenyl Grignard to valeronitrile.

p-Methoxybutyrophenone (bp 115° (3 Torr)) and *p*-methoxyvalerophenone (bp 143° (6 Torr)) were prepared by Friedel–Crafts acylation of anisole, with an excess of aluminum chloride as catalyst. Each was purified by vacuum distillation followed by several recrystallizations from pentane–ethanol mixtures. The former was also vacuum sublimed. *p*-Phenyl-γ-methylvalerophenone (mp 71–72°) was prepared by Friedel–Crafts acylation of biphenyl with γ-methylvaleryl chloride in benzene. It was vacuum distilled, then recrystallized from absolute ethanol.

p-Methoxy-γ-carbomethoxybutyrophenone was prepared as Johnson describes the preparation of the ethyl ester.[68] It was purified by repeated recrystallization from methanol, mp 54–55°.

p-Methoxy-δ-carboethoxyvalerophenone (mp 54°) was prepared according to the general procedure of Diaper.[69] The Grignard from *p*-bromoanisole was added to cyclohexanone, and the resulting alcohol was dehydrated to 1-*p*-anisylcyclohexene (bp 155° (14 Torr), mp 35°). The olefin, in ethyl acetate solvent at −75°, was treated with ozone (from a Welsbach generator); the resulting ozonide was decomposed with zinc; the resulting keto-aldehyde was oxidized to γ-anisoylbutyric acid with hydrogen peroxide and formic acid. The crude acid was esterified by refluxing in ethanol–benzene containing a trace of acid. After work-up, the resulting oil was treated with decolorizing carbon and then recrystallized 12 times from pentane–benzene mixtures.

p-Methoxy-δ-cyanovalerophenone (mp 61°) was prepared by treating the δ-chloro ketone with sodium cyanide in dry DMSO at 90°. It was decolorized and recrystallized from ether–hexane mixtures. The δ-chloro ketone was prepared by adding *p*-methoxyphenylmagnesium bromide to δ-chlorovaleronitrile.

All ketones were identified by their mass spectra and were >99% pure to vpc analysis. Details of the preparation and purification of ketones in Table I are contained in ref 70; for those in Table II, see ref 71.

Procedures. Quantum yield measurements and quenching studies were performed as in our other studies.[12] In particular, the vpc response of each substituted acetophenone relative to the appropriate alkane internal standard was calibrated with commercially obtained samples.

Uv spectra of the ketones were recorded on a Cary 14. Concentrations of the ketones and therefore the reported extinction coefficients were accurate to only ±5%.

Phosphorescence spectra were determined on an apparatus already described.[72] All samples were contained in sealed 3-mm i.d. quartz tubes. Excitation from a 1-kW mercury–xenon arc was filtered through Pyrex. Under these conditions, the solvents neither cracked nor emitted. Lifetimes were determined at the 0-0 bands with the help of a Nuclear Data Model ND-2200 multichannel analyzer. Decay at both fast and slow phosphoroscope speeds was analyzed in order to separate both components. In several cases, neither lifetime nor spectra were affected by changes in ketone concentration from 10^{-5} to 10^{-3} M.

Epr spectra were recorded at 77°K with a Varian X-band Model 4502-15 spectrometer, with Mark II fieldial control. Magnetic field strength was calibrated with a Varian F-8 proton resonance fluxmeter and the frequency (9239 MHz) was monitored with a Hewlett-Packard Model 5245 frequency counter. Ethanol solutions $\sim 10^{-3}$ M in ketone were contained in 3-mm i.d. quartz tubes. $H_{\min}$ for the $\Delta M = 2$ transitions of valerophenone and its *m*-methyl, *p*-methyl, *o*-methoxy, *m*-methoxy *p*-methoxy, *p*-thiomethoxy, and *p*-phenyl derivatives occur at 1423, 1420, 1450, 1429, 1392, 1479, 1498, and 1531 G, respectively. For the latter ketone, $\Delta M = 1$ signals also appear at 2260, 4348, 2605, 3917, 2832, and 3666 G. These lead to $X = 0.0256$ cm^{-1}, $Y = 0.0404$ cm^{-1}, $Z = -0.0652$ cm^{-1}, from which $|D| = 0.0978$ cm^{-1} and $|E| = 0.0074$ cm^{-1}.

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