Deactivation of Triplet Phenyl Alkyl Ketones by Conjugatively Electron-Withdrawing Substituents†

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Abstract: Para-cyano, -carbomethoxy, and -acyl substituents decrease the triplet reactivity of valerophenone (γ-hydrogen abstraction), whereas comparable meta substituents increase reactivity. Spectroscopic results are presented which indicate that para-(−R) substituents lower π,π^* triplet energies so much more than n,π^* energies that the lowest triplets become largely π,π^* in nature. Meta-(−R) substituents do not stabilize π,π^* triplets enough to invert triplet levels. Both substitution patterns support a largely 1,4-biradical structure for the lowest π,π^* triplet of acylbenzenes. Ortho substituents show the usual steric anomalies: ortho cyano enhances valerophenone triplet reactivity by stabilizing the n,π^* triplet; ortho carbomethoxy deactivates valerophenone by stabilizing the π,π^* triplet but not the $n,\pi.^*$

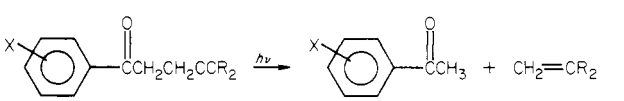
Effects of ring substituents on the spectroscopy and photoreactivity of phenyl ketones have been of widespread interest right from the beginning of modern photochemical research.[1,2] The following general picture has emerged. Unsubstituted phenyl ketones have n,π^* lowest triplets with a π,π^* triplet a few kilocalories per mole higher in energy.[3] In terms of substituent effects on chemical reactivity, changes in the energies of the two triplets and thus in the nature of the lowest triplet have proven to be of much greater importance than changes in the electronic nature of individual triplets. The n,π^* triplet is similar electronically to an alkoxy radical and displays similar reactivity.[4] The π,π^* triplet shows little radical-like reactivity, presumably because of charge-transfer components and a lack of strong spin localization.[2]

In terms of individual substituents, it was noticed very early that electron-donating (+R) substituents at any ring position decrease quantum efficiencies[2,5a] and rate constants[6] for triplet-state hydrogen atom abstraction. Such substituents lower π,π^* [2,5] and raise n,π^* [7,8] transition energies; in phenyl alkyl ketones they cause an inversion of triplets such that the unreactive π,π^* state is lowest in energy.[5,6,9] Careful analysis in our laboratories[9] prompted the now widely accepted[10] conclusion that in such cases hydrogen abstraction occurs from low equilibrium levels of the upper n,π^* triplet; the observed reduced reactivities reflect the fractional population of that state.[9] The two triplets also mix to a small extent,[3d] but this mixing does not affect reactivity significantly.[9,10]

Inductively electron-withdrawing (−I) substituents such as CF_3 and the nitrogen of pyridyl ketones slightly increase rates of triplet-state hydrogen abstraction.[6,9,11] Such substituents lower n,π^* transition energies relative to π,π^* energies and also make the lowest n,π^* triplet more electron deficient.

These substituent effects on n,π^* triplet energies correlate very well with substituent σ values,[7,8] probably because the two orbitals involved are orthogonal. However, the π,π^* states of substituted benzenes are complicated mixtures of configurations[12] such that no simple or coincidental correlation with a ground-state parameter is possible. For example, electron-donating substituents are somewhat more stabilizing when meta than when para,[13] in accord with the better known behavior of excited singlets.[14] Likewise para Cl stabilizes both triplets, the n,π^* inductively and the π,π^* conjugatively, such that the π,π^* state is lowest.[9,15] This effect was compared to the positive σ^+ value of para F with the added proviso that excited states are more demanding of electron density from +R substituents than are ground states.[9]

Despite the large amount of work summarized above, the effects of conjugatively electron-withdrawing (−R) substituents on the photochemistry of phenyl ketones have not been studied *at all*. It is known that para CN stabilizes ketone n,π^* triplets.[7] However, para-(−R) sbustituents also strongly stabilize π,π^* triplets of benzoate esters.[16] Since esters of *p*-acylbenzoic acid have provided unique information about intramolecular bifunctional photoreactions,[17] we decided to complete our otherwise systematic study of substituent effects on phenyl alkyl ketone photochemistry by looking at the effects of cyano, carboxy, and acyl substituents. This paper reports the results, the most important of which is that para-(−R) substituents produce π,π^* lowest triplets in such ketones. We followed our earlier[9] approach of monitoring type II photoelimination of substituted valerophenones in order to measure triplet rate constants.



† Dedicated to George S. Hammond on the occasion of his 60th birthday.

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Table I. Photokinetic Parameters for Ring-Substituted Valerophenones[a]

substituent	solvent	Φ_{II}[b]	Φ_{max}[c]	$k_q\tau$,[d] M^{-1}	$1/\tau$,[e] $10^7\ s^{-1}$
H	benzene	0.33[f]	0.85[f]	47	11
H	acetonitrile	0.85		63	16
o-CN	benzene	0.15		22	23
o-CN	acetonitrile	0.54		33	30
m-CN	benzene	0.20	0.65	19	26
m-CN	acetonitrile	0.68		20	50
p-CN	benzene	0.19	0.43	74	6.8
p-CN	acetonitrile	0.74		87	11
o-CO_2CH_3	benzene	0.04	0.15	138	3.6
o-CO_2CH_3	acetonitrile	0.15		338	3.0
m-CO_2CH_3	benzene	0.25	0.54	18	28
m-CO_2CH_3	acetonitrile	0.90		21	48
p-CO_2CH_3	benzene	0.19	0.31	42	12
p-CO_2CH_3	acetonitrile	0.60		58	17
m-$CO(CH_2)_3CH_3$	benzene	0.22	0.54	37	14
m-$CO(CH_2)_3CH_3$	acetonitrile	0.70		46	22
p-$CO(CH_2)_3CH_3$	benzene	0.12	0.17	183	2.7
p-$COCH_3$	benzene	0.09		350 ± 50	1.4
o-CF_3	benzene	0.15	0.90	38[f]	13
m-CF_3	benzene	0.19	0.73	16[f]	32
p-CF_3	benzene	0.23	0.94	18[f]	28

[a] 0.04 M ketone irradiated at 313 nm to ≤5% conversion. [b] Quantum yield for acetophenone formation. [c] Quantum yield maximized with 0.5–1.0 M pyridine. [d] Averages of duplicate runs with average precision of ±7%. [e] $k_q = 5 \times 10^9\ M^{-1}\ s^{-1}$ in benzene and $1 \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile. [f] Reference 9.

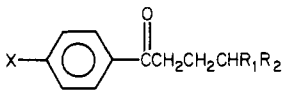
Results

Synthesis of Substituted Ketones. All para-substituted ketones were prepared by treatment of the para-fluoro ketone with sodium cyanide. Meta- and ortho-substituted ketones were prepared by addition of alkyl Grignard reagents to the appropriate cyanobenzaldehyde and oxidation of the resulting alcohol. Hydrolysis of the cyano ketones yielded the acids from which esters were prepared. Addition of alkyl Grignard reagents to ketals of the cyano ketones or to dinitriles and then hydrolysis afforded the diketones.

Photokinetics. Sealed, degassed samples containing 0.04 M ketone in benzene or wet acetonitrile were irradiated at 313 nm to 5–10% conversion. Yields of substituted acetophenone formation and of ketone disappearance relative to known concentrations of alkane internal standard were determined by gas chromatographic (GC) analysis. These yields were converted to quantum yields by analysis of valerophenone actinometric solutions[18] which had been irradiated in parallel with samples. Acetophenones and cyclobutanols accounted, within experimental error, for all reacted ketone. Ketone solutions containing added pyridine, dioxane, or *tert*-butyl alcohol were also irradiated and analyzed for "maximum" type II quantum yields.[18] All measured values are listed in Table I. Samples containing various concentrations of conjugated dienes as triplet quenchers were also irradiated in parallel. The resulting linear Stern–Volmer plots yielded the $k_q\tau$ values listed in Table I from which triplet decay rates were calculated. For comparison's sake, comparable data for the CF_3-substituted valerophenones are listed in Table I.

Variation in γ C–H Bond Strength. Unlike most other substituted valerophenones,[9] including the CF_3-substituted ones, these (–R)-substituted ketones do not display type II quantum yields near unity in the presence of added Lewis bases, although they come closer in wet acetonitrile. Consequently the behavior of *p*-cyano-γ-methylvalerophenone was also studied. Table II compares the photokinetics of the two cyano ketones to the two unsubstituted ones. In both cases, the ketone with the tertiary γ C–H bond is four times as reactive as the one with secondary C–H bonds, both cyano ketones being a little more than half as reactive and reacting in half the quantum yield as their corresponding unsubstituted models.

Table II. Photokinetic Parameters for Phenyl Alkyl Ketones as a Function of γ-Substitution[a]



X	R_1	R_2	Φ_{II}	Φ_{max}	$k_q\tau$,[b] M^{-1}	$1/\tau$, $10^7\ s^{-1}$
H	H	CH_3	0.33[c]	0.85	47	11
H	CH_3	CH_3	0.25[c]	0.90	10[c]	50
CN	H	CH_3	0.19	0.46	74	6.7
CN	CH_3	CH_3	0.13	0.46	18	28

[a] 0.4 M ketone in benzene irradiated at 313 nm to ≤ 10% conversion. [b] Averages of duplicate runs. [c] Reference 9.

Table III. Spectroscopic Data for Ring-Substituted Valerophenones

substituent	E_T[a]- (isopentane)[b]	E_T[a]- (ETOH)	$^1L_a\ \lambda_{max}$, nm (ε)	E_{red},[c] eV
none	71.6 (74.2)	73.8	238 (14 000)[d]	−2.07
o-CN	67.2	69.8	236 (9000)	−1.64
m-CN	70.7 (73.1)	73.3	226 (16 000)	−1.78
p-CN	(69.2)	69.5	255 (13 000)	−1.58
o-CO_2CH_3	69.6	69.1[e]	228 (9000)	−1.93
m-CO_2CH_3	71.2	74.0	230 (11 000)	−1.90
p-CO_2CH_3	68.5 (70.2)	70.2	254 (13 000)	−1.63
m-COC_4H_9	69.1	71.9	238 (14 000)	−1.86
p-COC_4H_9		67.8	260 (18 000)	−1.55
p-$COCH_3$		67.7	260 (17 000)	−1.55
o-CF_3	71.1[f]	71.1[f]	218[d] (4000)	−1.90
m-CF_3	71.5[f]	71.5[f]	234[d] (10 000)	−1.86
p-CF_3	70.8[f]	70.8[f]	234[d] (13 000)	−1.76

[a] From phosphorescence 0,0 band at 77 K. [b] Values in parentheses in methylcyclohexane–isopentane (5:1). [c] In acetonitrile relative to SCE. [d] Reference 9. [e] In EPA. [f] In reference 16b.

Intersystem Crossing Yields. *p*-Cyano- and *p*-(carbomethoxy)acetophenone were found to have the same efficiency at sensitizing the cis-to-trans isomerization of 1,3-pentadiene as does acetophenone.[20] Therefore the –R substituents do not lower the efficiency of intersystem crossing from 100%.

Spectroscopy and Electrochemistry. Phosphorescence spectra were measured for 10^{-4} M solutions of the various ketones in several glasses at 77 K. All of the meta- and para-substituted ketones showed nicely structured emission. Table III lists triplet energies calculated from the 0,0 bands. Figure 1 compares the spectra of *m*- and *p*-cyanovalerophenone to that of valerophenone itself. In all cases, para-(–R) substituents lower triplet energies by several kcal/mol and introduce many low frequency vibrational modes, whereas meta substituents have only minor effects. Ortho cyano also is strongly stabilizing; ortho-carbomethoxy substitution broadens the spectra substantially.

UV spectra of the ketones were measured in heptane; λ_{max} values and extinction coefficients for the $S_0 \rightarrow {}^1L_a$ transitions are listed in Table III. The spectra also show n,π* absorption between 300–370 nm and ^1L_b bands below 300 nm.

Half-wave reduction potentials of all the ketones were measured from cyclic voltammograms of 10^{-4} M acetonitrile solutions. These values are also listed in Table III.

Several substituted benzophenones were synthesized. Their phosphorescence spectra were recorded, and their triplet energies are listed in Table IV.

Discussion

Substituent Effects on Triplet Energies. Table IV lists the effects of electron-withdrawing substituents on measured triplet energies of several benzophenones, benzonitriles, and methyl benzoates.

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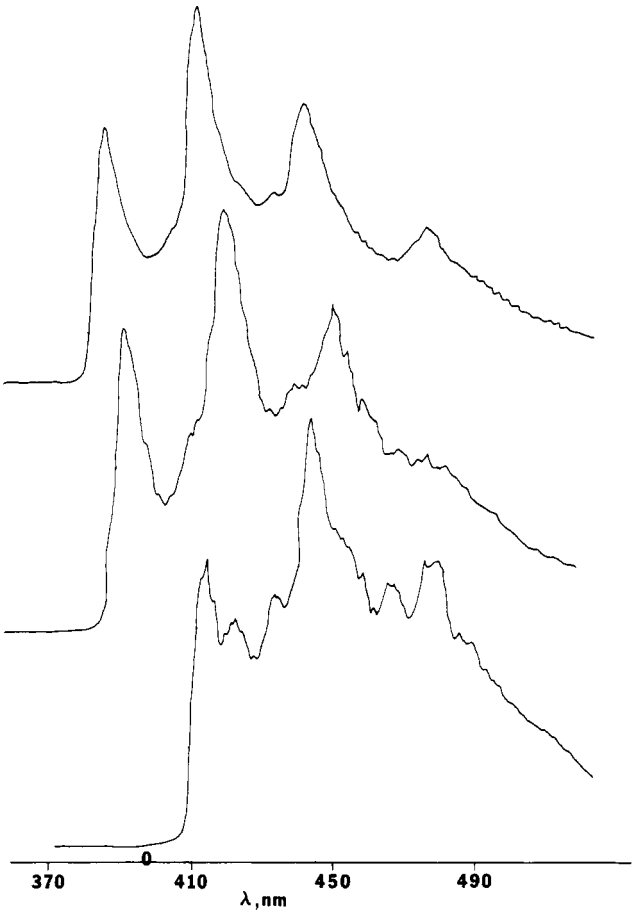


Figure 1. Phosphorescence spectra of 10^{-4} M valerophenones in 5:1 methylcyclohexane–isopentane at 77 K. Top, valerophenone itself; middle, *m*-cyanovalerophenone; bottom, *p*-cyanovalerophenone.

The latter two series have only π,π^* triplets while the substituted benzophenones all display n,π^* emission. This comparison allows estimates of how substituents affect both n,π^* and π,π^* triplet energy levels in phenyl alkyl ketones. These estimates are listed in the right-hand columns, with the starting point being the individual triplet energies deduced from a variety of chemical and spectroscopic observations for the unsubstituted case in benzene solution at room temperature.[13] It is worth repeating the two main reasons for differences between n,π^* energies in solution and 0,0 phosphorescence energies in frozen glasses: (1) there is a large Stokes shift between the 0,0 bands of $S \rightarrow T$ absorption and phosphorescence;[5b] (2) n,π^* triplets undergo a conformational relaxation in nonviscous solvents[21] (see isopentane values in Table III).

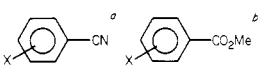
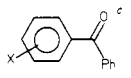
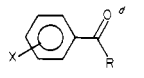
All meta electron-withdrawing substituents have only minor effects on n,π^* energies but the –R substituents lower π,π^* energies approximately 2 kcal/mol. The net effect is to bring the two triplet levels of phenyl alkyl ketones closer together, but the n,π^* is predicted to remain slightly lower. Para-(–R) substituents greatly lower π,π^* energies by some 6 kcal/mol. They also lower n,π^* energies but only by some 2 kcal/mol. Therefore, it is predicted that in para-(–R)-substituted ketones the π,π^* triplet is lower in energy than the n,π^* triplet.

The actually measured phosphorescence spectra support the accuracy of these estimates in two ways. First, the 0,0 bands of the para-substituted ketones occur exactly where the π,π^* levels are predicted to be. Second, the para-substituted ketones, but not the meta, display the additional vibrational structure characteristic of π,π^* emission.[3d]

As usual, ortho substituents show a mixture of steric and electronic effects, a mixture known to strongly affect π,π^* triplets.[22] Both CN and the "larger" CO_2CH_3 lower π,π^* triplet energies, the former being slightly more stabilizing. We did not have *o*-cyanobenzophenone available to directly test n,π^* phosphorescence. However, the reduction potential of *o*-cyanovalerophenone is almost as low as that of the para isomer. Since there is a very good correlation between n,π^* triplet energies and reduction potentials,[8] as obvious from the data in Tables III and IV, we conclude that the sterically undemanding ortho-cyano produces the expected significant inductive stabilization of the n,π^* triplet. In contrast, both the phosphorescence and the reduction potential of the ortho-carbomethoxy ketones suggest no lowering of n,π^* triplet energies, presumably because of steric interference with coplanarity of the benzoyl group. The interesting outcome is that *o*-(carbomethoxy)valerophenone is predicted to definitely have a π,π^* lowest triplet, whereas in *o*-cyanovalerophenone the two triplet levels are predicted to be very similar.

These spectroscopic results clearly indicate an inversion of triplet levels caused by para-(–R) substituents and suggest nearly isoenergetic triplets in some other cases; but they are not exact enough to provide actual energy differences in a given ketone. Fortunately the necessary evidence is provided by the photochemistry of these substituted ketones.

Table IV. Measured Substituent Effects on Triplet Energies and Predicted n,π^*-π,π^* Separations in Phenyl Alkyl Ketones

X	 π,π^*	π,π^*	 n,π^*	 π,π^*	n,π^*
H	77.3	77.9	68.6	75.5[e]	73.4[e]
o-CN	72.9	73.4	~66.8[f]	71.0	~71.6
m-CN	75.5	76.2	68.5	73.8	73.3
p-CN	70.9	72.0	66.4[g]	69.3[h]	71.2
o-CO_2Me	73.4		69.0	71.5	73.4
m-CO_2Me	76.2[b]	76.9	68.8	74.5	73.6
p-CO_2Me	72.0[b]	72.9	66.7	70.3	71.5
m-COnBu				~73[h]	73
p-COnBu	69.5[i]	70.2[i]		67.7[h]	71
o-CF_3	74.7		68.8[g]	73.0	~73[f]
m-CF_3	76.5		68.4	74.7	72.8
p-CF_3	76.1		67.6[g]	74.3	72.4

[a] In ethanol at 77 K.[16b] [b] In 4:1 ethanol/methanol at 77 K.[16a] [c] In MCIP at 77 K, this work. [d] Predicted values in benzene at 25 °C. [e] Reference 13. [f] Estimated from E_{red}. [g] Reference 7. [h] Same values as measured in reference 7. [i] This work.

Substituent Effects on Photoreactivity. It has been shown previously that eq 1 describes the observed rate constant for γ-hydrogen abstraction in substituted valerophenones which have a π,π^* lowest triplet, where k_n is the actual rate constant for the

$$k_{obsd} = \chi_N \cdot k_n \quad (1)$$

$$\chi_N = (1 + e^{\Delta E/RT})^{-1} \quad (2)$$

reacting n,π^* state, χ_N is the equilibrium fractional population of the n,π^* state, and ΔE is the energy difference between the n,π^* and π,π^* triplets.[9] To calculate ΔE from the triplet decay rates in Table I one needs to determine only two other things: whether any other reactions besides γ-hydrogen abstraction contribute to triplet decay and what the value of k_n is.

The latter problem is solved by assuming that CN, CO_2R, and COR, which all have σ values similar to that of CF_3,[23] all enhance k_n by the same *small* amount that CF_3 does. Therefore we assume that k_n for all of the ketones equals the measured k_n values for the CF_3 substituted ketones. Since the actual rate enhancement is so small, any variations in k_n among the various ketones must be minor and would not introduce any errors of consequence in the calculation of ΔE.

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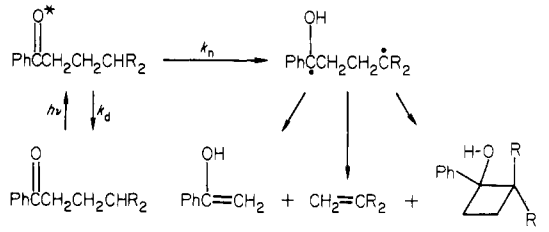
Scheme I



Scheme I shows the well-established mechanism for type II photoelimination. The key feature is that Lewis bases usually solvate the biradical intermediate so as to completely prevent its normal reversion back to ground-state reactant. In such cases, total type II quantum yields approach unity.

Some substituents such as methoxy slow γ-hydrogen abstraction to such an extent that other triplet decay processes become competitive.[9] The net result is that maximum quantum yields in the presence of Lewis bases do not approach unity. For all valerophenones previously studied in which substituents lower k_n no more than a factor of 1/20, maximum quantum yields remain close to unity such that $1/\tau$ equals k_n. These -R substituents do not greatly decrease $1/\tau$ values but do lower maximum quantum yields appreciably below unity. Therefore we had to determine whether some other triplet reaction lowers type II quantum yields or whether the intermediate biradicals for some reason cannot be pushed completely to product by Lewis bases. Three separate experiments indicate the latter answer.

If some process with rate k_d were competitive with k_n, its rate would not be changed by changes in C–H bond strength which change k_n. Therefore quantum yields would become proportional to k_n while $1/\tau$ would no longer vary exactly as k_n values are known to. Table II shows that increasing the rate of γ-hydrogen abstraction does not increase the type II quantum yield but does increase $1/\tau$ by exactly the amount expected if $1/\tau = k_n$. Therefore we can conclude that there is no competitive triplet decay in the para-cyano ketones and that $k_d < 10^6\ s^{-1}$. Exactly the same experimental test has already been applied to show that methoxy-substituted ketones do undergo competitive triplet decay[9] while pyridyl ketones do not.[11]

In independent studies of the photoreduction of substituted phenyl ketones[24] we have shown that k_d for *p*-cyanoacetophenone is indeed only $10^5\ s^{-1}$ in acetonitrile. The high measured intersystem crossing yields for these -R-substituted ketones leave no other culprit for the significant quantum inefficiency except unsuppressed reversion of the biradicals to ketone.

Since we can now equate k_{obsd} values with $1/\tau$, we see that in benzene para COC_4H_9, CN, and CO_2CH_3 lower triplet reactivity to 10%, 25%, and 40%, respectively, of that in the para-CF_3 model. From these χ_N values we deduce ΔE values of 1.3, 0.67, and 0.3 kcal/mol, respectively, in benzene. These values cannot be much different in acetonitrile since all the ketones studied show an average 50% increase in $1/\tau$ in acetonitrile relative to benzene.

The meta-cyano and -carbomethoxy ketones show exactly the same reactivity, within experimental error, as does the model meta-CF_3 ketone. As expected, the n,π* triplet remains lowest in these compounds. *m*-Divalerylbenzene, however, shows only half the triplet reactivity of the model. This situation would arise if the two lowest triplets were effectively isoenergetic and therefore equally populated.

It is interesting that the observed reactivity of *p*-acetylvalerophenone is only half that of *p*-divalerylbenzene. In the former, half the n,π* excitation must reside on the acetyl group which cannot undergo type II elimination; in the latter, each acyl group is equally reactive.

o-Cyanovalerophenone is twice as reactive as the ortho-CF_3 ketone, while ortho carbomethoxy is only $^1/_4$ as reactive. Apparently the ortho-cyano ketone barely maintains an n,π* lowest triplet, as predicted from the spectroscopy. Since ortho-CO_2CH_3 is predicted to have a π,π* triplet, the lower k_{obsd} may indeed bear out the prediction. Unfortunately, the model itself reacts more slowly than expected, probably because of some small steric effect imposed by CF_3 which is not imposed by the linear CN substituent. It is impossible to quantitatively separate any steric effect on k_n from the apparent triplet level inversion caused by CO_2CH_3.

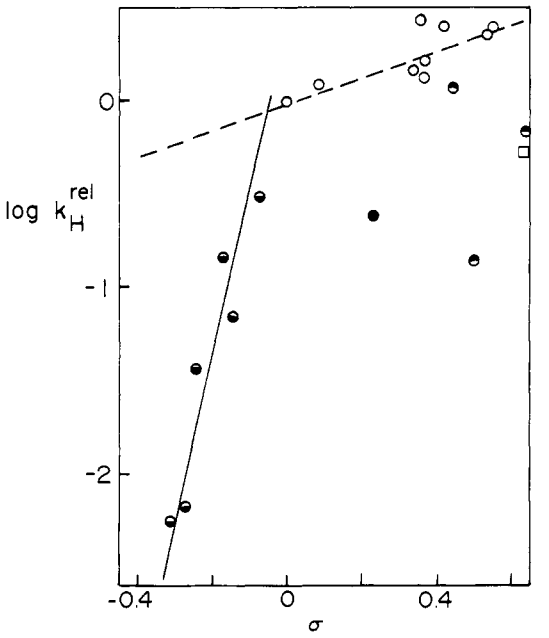


Figure 2. Linear free energy plot of relative k_{obsd} values as function of ground-state substituents parameters. (○) -I substituents; (◒) electron-donating substituents; (◓) para-(-R) substituents; (●) para Cl; (□) para SCF_3.

Overview of Substituent Effects on Phenyl Alkyl Ketone Photoreactivity. Figure 2 adds these -R-substituted valerophenones to the Hammett plot already published[13] for -I and +R substituents. Previously, para Cl was the only substituent which did not lie on a monotonically increasing plot. Ignoring ortho substituents, we now see four more para substituents (CN, CO_2CH_3, COR, and SCF_3[25]) and probably meta COR which produce reactivities measurably lower than would be predicted by a simple linear Hammett relation. In all cases, these substituents stabilize π,π* triplets conjugatively much more than they stabilize n,π* triplets inductively.

As we pointed out earlier, the inappropriateness of any attempted Hammett plot has two causes. First, k_{obsd} values are dominated by Boltzman factors once the π,π* triplet becomes lowest, with only very small substituent effects on the actual k_n values. Second, ΔE values do not correlate with Hammett constants because Hammett constants do not adequately describe substituent effects on energies of π,π* transitions. These results reveal a new example of excited-state/ground-state differences. The conjugative effects on π,π* states clearly lie in the order of COR > CN > CO_2R, whereas ground-state σ values decrease in the order of CN > COR > CO_2R. The greater conjugating ability of acyl groups in the excited state relative to the ground state probably reflects the coplanarity of excited benzoyl groups compared to the twist of the ground states.[26]

Nature of the π,π* Triplets of Phenyl Ketones. Theoretical[12b,27] and EPR[27,28] results indicate that the lowest triplet of benzonitrile and presumably of other -R-substituted benzenes is strongly 1,4-diradical in nature. Such substitution stabilizes the antisymmetric (in C_{2v}) π* orbital and destabilizes the corresponding π orbital such that the S → L_a transition is predominantly $\pi_A \rightarrow$

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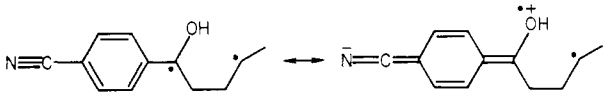
π_A* with little contribution from $\pi_S \rightarrow \pi_S$*.

The basis of the destabilization of π_A in ketones is the mixing of π_A with the lower energy carbonyl π orbital.[26,29] This conjugative mixing overcomes the expected slight inductive stabilization of π_A provided by a strong electron-accepting substituent. The π_A* orbital is stabilized inductively as well as by strong mixing with the carbonyl π* orbital.

A second –R substituent para to the first reinforces this orbital splitting and can further delocalize the spin density. In fact two such substituents lower the triplet energy of benzene exactly twice as much as does one. A second –R substituent meta to the first lowers the triplet energy by another $^1/_4$ the amount afforded by the first. Since the simple MO picture of the π_A orbitals indicates $^1/_4$ as much spin density at meta position as at the para, the meta effects are in embarrassingly good agreement with the quite simple model expressed in Schemes II and III if one assumes that the extent of conjugative stabilization is proportional to the spin density at the site of substitution.

The orbital model in Scheme III, with the highest π orbital localized primarily on the benzene ring and the lowest π* orbital located more on the carbonyl, has been used to indicate the partial CT nature of the L_a transitions in phenyl ketones.[29] Ketones with electron-donating substituents show a greater $^3n,\pi^* - {}^3\pi,\pi^*$ gap in polar solvents than in benzene,[9] the increase coming from a slight raising of the n,π^* energy and lowering of the π,π^* energy. These ketones with two –R substituents are symmetrically substituted and would not be expected to incur much charge separation during electronic excitation. The experimental results support this picture since ΔE values in wet acetonitrile do not appear to differ at all from those in benzene.

Quantum Efficiencies. These ketones represent the first simply substituted valerophenones which do not undergo type II elimination in 100% efficiency in the presence of sufficient Lewis base. Long alkyl chains[30] and α substitution[18,31] are two structural features known to diminish the efficiency of product formation from the intermediate biradicals. So too do electron-withdrawing ring substituents, although the –I variety still allow quantum yields near unity.[32] We are not able to explain why –R-substituted biradicals do not also go on completely to products. Certainly they must be solvated as fully as other biradicals since the substituent enhances the acidity of the hydroxy proton. Perhaps the resulting charge separation shortens the biradical lifetime. Perhaps the polar nature of the Lewis bases enhances charge separation so much as to make disproportionation competitive even in the solvated biradical.



Experimental Section

Chemicals. Benzene[18] and acetonitrile[33] solvents were purified as previously described. Valerophenone and alkane internal standards were available from earlier studies, as were CF_3-substituted valerophenones.[9] Chemical Samples Co. 1,3-pentadiene and 2,5-dimethyl-2,4-hexadiene were used as received.

***p*-Fluorovalerophenone.** This was prepared by Friedel–Crafts acylation of Aldrich fluorobenzene with valeryl chloride. It was purified by vacuum distillation, bp 95 °C (0.16 torr), mp 26 °C. IR (neat) 1691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H), 1.1–2.1 (m, 4 H), 2.89 (t, 2 H), 6.8–7.2 (m, 2 H), 7.7–8.0 (m, 2 H); MS, *m/e* 180, 138, 123.

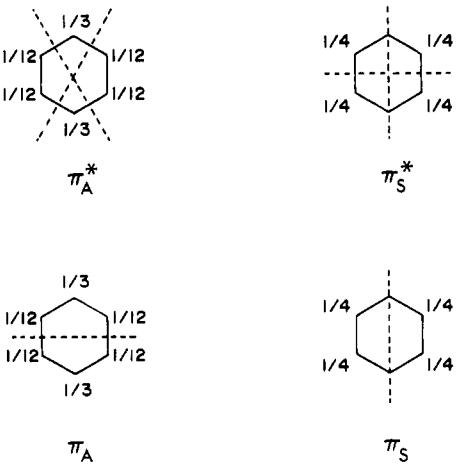
***p*-Cyanovalerophenone.** Sodium cyanide (20 g, 0.41 mol) was partially dissolved by heating in 300 mL of Me_2SO; *p*-fluorovalerophenone (65 g, 0.36 mol) was added slowly to the mixture. The solution was heated to 110–130 °C for 5 h, the reaction being followed by NMR monitering of the aromatic region. The viscous brown mixture was poured into 600 mL of water and extracted several times with ether. The combined ether extracts were washed first with water, then with saturated sodium bicarbonate solution, and were dried over sodium sulfate. The solvent was removed under vacuum, and a brown oil (58 g, 0.31 mole) was isolated in 87% yield. NMR Analysis of crude product showed ~75% conversion. Vacuum distillation provided 50 g (0.27 mol) of *p*-cyanovalerophenone as an oil, bp 114 °C (0.1 torr). Recrystallization from hexane gave white crystals, mp 34–36 °C (lit. 32–33 °C).[34] IR (KBr) 1696, 2225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.1–2 (m, 4 H), 2.85 (t, 2 H), 7.78 (q, 4 H); MS, m/e 187, 145, 130.

***p*-Fluoro-γ-methylvalerophenone.** This was synthesized by Freidel–Crafts acylation of Aldrich fluorobenzene with γ-methylvaleryl chloride. IR (neat) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–1.1 (d, 6 H), 1.2–2.0 (m, 4 H), 2.8 (t, 2 H), 6.7–7.2 (m, 2 H), 7.6–8.0 (m, 2 H); MS, *m/e* 194, 138, 123.

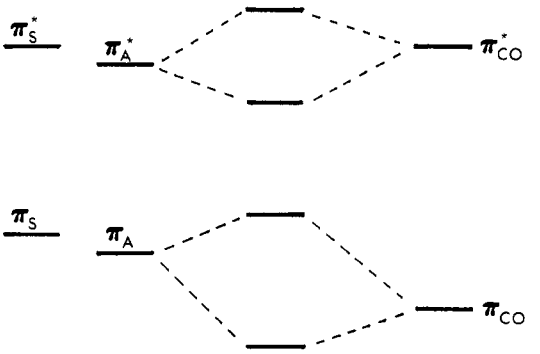
***p*-Cyano-γ-methylvalerophenone.** This was prepared, as described for *p*-cyanovalerophenone, as a colorless liquid, bp 108 °C (0.8 torr). IR (neat) 1690, 2225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, 6 H), 1.4–1.8 (m, 3 H), 2.90 (t, 2 H), 7.80 (q, 4 H); MS, *m/e* 201, 145, 130.

***m*-Cyanovalerophenone.** *n*-Butylmagnesium bromide was prepared by adding 1-bromobutane (28 g, 0.2 mol) in 200 mL of ether to Mg turnings (4.9 g, 0.2 mol) covered with ether. Aldrich *m*-cyanobenzaldehyde (26 g, 0.2 mol) was partially dissolved in 200 mL of benzene, and the Grignard reagent was added dropwise with stirring. After being refluxed for 2 h and then cooled, the solution was poured over dilute H_2SO_4/ice mixture. Normal work up gave 1-(3-cyanophenyl)-1-pentanol as a light yellow oil (32 g, 0.17 mol). A solution of the crude alcohol (30 g, 0.16 mol) in 85 mL of benzene was added slowly to a cooled mixture of 20 g (0.07 mol) of sodium dichromate, 10 mL of glacial acetic acid, 30 mL of concentrated sulfuric acid, and 85 mL of water.[35] After the solution was stirred at room temperature for 3 h, the layers were separated and the aqueous layer was extracted with benzene. The combined organic layers were washed first with 5% KOH solution and then with water and then were dried over sodium sulfate. The oily solid (22 g, 0.12 mol) resulting from solvent removal was recrystallized several times from

Scheme II



Scheme III



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hexane to give white crystals, mp 52–53 °C. IR (KBr) 1682, 2230, cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.1–2.0 (m, 4 H), 2.94 (t, 2 H), 7.2–8.3 (m, 4 H); MS, *m/e* 187, 158, 145, 130.

***p*-Valerylbenzoic Acid.** A solution of *p*-cyanovalerophenone (20 g, 0.11 mol), 30% KOH (100 mL), and ethanol (20 mL) was refluxed overnight. Careful acidification of the warm solution with dilute HCl resulted in precipitation of *p*-valerylbenzoic acid. Suction filtration of the solid followed by drying in a dessicator gave a white solid (16 g, 0.085 mol), mp 155–157 °C. IR (KBr) 1679, 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.1–2.0 (m, 4 H), 2.94 (t, 2 H), 8.00 (d of d, 4 H), 9.7 (br s, 1 H); MS, *m/e* 206, 189, 164, 149.

***m*-Valerylbenzoic Acid.** Hydrolysis of *m*-cyanovalerophenone (15 g, 0.980 mol) with 100 mL of 30% KOH/ethanol solution according to the above procedure resulted in precipitation of an oily solid. The solution was extracted with ether, and the combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of solvent followed by recrystallization of the crude product from ethanol/water gave white crystals (11 g, 0.053 mol), mp 115–118 °C. IR (KBr) 1688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.1–2.0 (m, 4 H), 2.94 (t, 2 H), 8.00 (q, 4 H), 10.7 (br s, 1 H); MS, *m/e* 206, 189, 164, 149.

***p*-(Carbomethoxy)valerophenone.** *p*-Carboxyvalerophenone (10.3 g, 0.050 mol), sodium bicarbonate (17 g, 0.15 mol), and methyl iodide (22 g, 0.15 mol) in 100 mL of dry DMF were stirred at room temperature in the dark for 18 h.[36] The mixture was poured into 400 mL of saturated NaCl solution, and the solution was extracted with ether. The combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of solvent and recrystallization of the crude product from hexane (charcoal) gave white crystals (9.4 g, 0.043 mol), mp 81–82 °C (lit. 81 °C).[34] IR (KBr) 1676, 1724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (m, 3 H), 1.1–2.0 (m, 4 H), 2.91 (t, 2 H), 3.88 (s, 3 H) 7.91 (d of d, 4 H); MS, *m/e* 220, 189, 178, 163.

***m*-(Carbomethoxy)valerophenone.** *m*-Carboxyvalerophenone (21 g, 0.10 mol), sodium bicarbonate (34 g, 0.4 mol), and methyl iodide (44 g, 0.3 mol) in 100 mL of dry DMF were treated in a similar manner to the para compound. After workup, evaporation of the solvent gave an oil (18 g, 0.8 mol) which was purified by vacuum distillation [bp 182 °C (10 torr)] followed by low-temperature recrystallization from hexane. IR (neat) 1690, 1729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.1–2.0 (m, 4 H), 2.94 (t, 2 H), 3.89 (s, 3 H), 7.2–8.5 (m, 4 H); MS, *m/e* 220, 189, 178, 163.

***p*-Divalerylbenzene.** This was prepared by reaction of Aldrich terephthalonitrile with 4 equiv of *n*-butylmagnesium bromide. Mg turnings (9.7 g) were covered with anhydrous ether and 1-bromobutane (73 mL, 0.47 mol) in 200 mL of ether was added dropwise with stirring. A slurry of terephthalonitrile (12,8 g, 0.10 mol) in benzene was added slowly. After being refluxed overnight (solution turned orange), the mixture was poured into dilute HCl/ice solution and extracted with ether. A small amount of *p*-divalerylbenzene precipitated out of the aqueous layer and was collected. The combined organic extracts were washed with water and dried over sodium sulfate. Removal of the solvent gave a yellow, oily solid (12.6 g, 0.05 mol). The crude product was chromatographed on an alumina column by using various petroleum ether/ether mixtures, and the resulting eluted solid was recrystallized from hexane to give white crystals in 30% overall yield, mp 96–97 °C. IR (KBr) 1676 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.2 (m, 6 H), 1.2–2.0 (m, 8 H), 2.95 (t, 4 H), 7.90 (s, 4 H); MS, *m/e* 246, 204, 189, 162, 147.

***m*-Divalerylbenzene.** Similar synthetic and pruification methods were used as described above for the para compound. Aldrich isophthalonitrile (12.8 g, 0.10 mol) in benzene was added slowly to *n*-butylmagnesium bromide (0.4 mol). After workup, 11 g of a yellow oil was obtained (45% yield). After elution through an alumina column and repeated recrystallizations from petroleum ether, white crystals were obtained, mp 25 °C. IR (KBr) 1682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (m, 6 H) 1.1–2.1 (m, 8 H), 2.98 (t, 4 H), 7.2–8.5 (m, 4 H); MS, *m/e* 246, 204, 189, 162, 147.

***p*-Acetylvalerophenone.** A solution of Aldrich *p*-acetylbenzonitrile (8.0 g, 0.055 mol), ethylene glycol (10 mL), and *p*-toluenesulfonic acid (0.1 g) in 50 mL of benzene was refluxed in a Dean–Stark trap until no more water azeotroped off. The cooled solution was washed first with water and then with saturated sodium bicarbonate and was dried over sodium sulfate. Evaporation of solvent gave the ketal as a white solid (9.8 g, 0.052 mol), mp 68–70 °C; ^1H NMR ($CDCl_3$) δ 1.60 (s, 3 H), 3.4–3.8 (m, 2 H), 3.8–4.2 (m, 2 H), 7.48 (s, 4 H).

Magnesium turnings (1.25 g, 0.052 mol) were covered with dry ether; 1-bromobutane (7.1 g. 0.052 mol) in 200 mL of ether was added dropwise to maintain reflux. A slurry of the ketal (9.0 g, 0.047 mol) in 200 mL of benzene was added slowly with stirring. After being refluxed for 6 h, the solution was poured into HCl/ice mixture and extracted with ether. Evaporation of the ether gave only starting material (2.2 g, 0.012 mol). The desired product (white solid) precipitated out of the aqueous solution (3.2 g, 0.016 mol) and, after recrystallization from hexane, gave white crystals, mp 77–78 °C. IR (KBr) 1676 cm^{-1}; NMR ($CDCl_3$) δ 0.7–1.1 (m, 3 H), 1.1-2.0 (m, 4 H), 2.94 (t, 2 H), 7.90 (s, 4 H); MS, *m/e* 204, 189, 162, 147.

***o*-Bromovalerophenone.** *n*-Butylmagnesium bromide was made by the addition of 1-bromobutane (16 g, 0.12 mol) in 200 mL of ether to magnesium turnings (2.8 g. 0.115 mol) in ether. A slurry of Aldrich *o*-bromobenzaldehyde (18.5 g, 0.10 mol) in benzene was added slowly with stirring. After being refluxed for 2 h and cooled, the solution was hydrolyzed with dilute HCl/ice water. Normal workup gave a yellow oil (20.5 g, 0.085 mol) in 85% yield; IR (neat) 3300 cm^{-1}. The crude 1-(2-bromophenyl)-pentan-1-ol (9.7 g, 0.004 mol) was oxidized by using sodium dichromate (24 g, 0.008 mol), glacial acetic acid (17 mL), and concentrated sulfuric acid (30 mL) in 100 mL of water following the procedure of Bruce.[35] The solution was stirred for 5 h at room temperature and then extracted with ether. The ether extracts were washed with 5% KOH solution and water and then dried over sodium sulfate. Removal of solvent gave a yellow oil (5.1 g, 0.02 mol); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (t, 3 H) 1.1–2.0 (m, 4 H) 2.82 (t, 2 H), 6.9–7.5 (m, 4 H).

***o*-Cyanovalerophenone.** A solution of *o*-bromovalerophenone (20 g, 0.08 mole) and CuCN (10.0 g, 0.16 mol) in 25 mL of pyridine was refluxed for 2 h. The mixture was added to 75 mL of water and extracted with ether. The combined ether layers were washed with water and dried over sodium sulfate. Evaporation of solvent gave a brown oil (13 g, 0.07 mol). Vacuum distillation gave a colorless oil, bp 117 °C (8 torr). From low-temperature recrystallization in hexane, a white solid was obtained, mp ~ 25 °C. IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–1.1 (t, 3 H), 1.1–2.0 (m, 4 H), 2.82 (t, 2 H), 7.4–7.9 (m, 4 H); MS, *m/e* 187, 145, 130.

***o*-(Carbomethoxy)valerophenone.** *o*-Valerylbenzoic acid was synthesized following a procedure for keto acids developed by De Benneville.[37] *n*-Butylmagnesium bromide (0.5 mol) in ether was cooled in an ice bath, and oven-dried $CdCl_2$ (46 g, 0.25 mol) was added slowly to the mixture. The mixture was allowed to warm and was refluxed for 1.5 h. Solid phthalic anhydride (37 g, 0.25 mol) was added slowly with stirring to the cooled (0 °C) solution. After being refluxed for 2.5 h, the solution was cooled and dilute H_2SO_4/ice water was added. The organic layer was separated and combined with ether extracts of the aqueous layer. The product was extracted from the ether layer with 10% K_2CO_3 solution, which was then filtered and acidified with dilute H_2SO_4. The ketoacid was then extracted into ether; solvent evaporation left a clear oil (36.5 g, 0.17 mol). The oil eventually solidified in the refrigerator and was washed with cold hexane to give a white solid, mp 40–42 °C. The free acid exists mainly as its γ-hydroxy lactone isomer; IR (KBr) 1750, 3360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.6–1.0 (m, 3 H), 1.1–1.6 (m, 4 H), 2.2 (br t, 2 H), 6.0 (br s, 1 H), 7.2–7.9 (m, 4 H); MS, *m/e* 206, 189, 164, 149 (base).

The crude *o*-valerylbenzoic acid (20 g, 0.097 mol) was esterified according to the procedure previously described involving stirring overnight with methyl iodide (30 mL, 0.48 mol) and sodium bicarbonate (15 g, 0.17 mol) in DMF (100 mL) in the dark. After ether workup, evaporation of the solvent gave an orange oil (17 g, 0.078 mol) in 80% yield. Three consecutive vacuum distillations of the crude product gave a colorless oil, bp 116 °C (0.4 torr). IR (neat) 1713, 1735, cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.1 (t, 3 H), 1.1–2.0 (m, 4 H), 2.74 (t, 2 H), 3.8 (s, 3 H), 7.2–7.9 (m, 4 H); MS, *m/e* 220, 189, 178, 163, 146.

3-Benzoylbenzonitrile. Phenylmagnesium bromide (0.08 mol) in ether was added dropwise with stirring to Aldrich *m*-cyanobenzaldehyde (9.0 g, 0.075 mol) in 250 mL of benzene. The solution was refluxed for 1 h, cooled, and then added to dilute HCl/ice water. After hydrolysis was complete, the layers were separated and the aqueous layer extracted with ether. Normal workups gave a light yellow oil (12 g, 0.057 mol) in 76% yield; IR (neat) 2210, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (br s, 1 H), 5.7 (d, 1 H), 7.0–8.0 (m, ~9 H). The crude alcohol was oxidized to 3-benzoylbenzonitrile without further purification by the method described previously for 1-(3-cyanophenyl)-1-pentanol. After benzene workup, an oily solid was obtained which, after recrystallization from hexane, gave 3.0 g (0.14 mol) of white crystals, mp 88–90 °C (lit. 91–92 °C).[7b] IR (KBr) 1710, 2200 cm^{-1}; ^1H NMR ($CDCl_3$) 7.1–8.1 (m); MS, *m/e* 207, 130, 105 (base).

Methyl 2-Benzoylbenzoate. Aldrich 2-benzoylbenzoic acid (9.1 g, 0.040 mol) was esterified as previously described by using CH_3I (10 mL, 0.16 mol) and $NaHCO_3$ (5 g, 0.06 mol) in 100 mL of DMF. Upon

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normal workup, a yellow oil was isolated which was recrystallized twice from hexane to give a white solid (6.2 g, 0.026 mol), mp 48–49.5 °C (lit. 52 °C).[38] IR (KBr) 1670, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.52 (s, 3 H), 7.1–8.0 (m, 9 H); MS, *m/e* 240, 209, 163, 105.

Methyl 4-Benzoylbenzoate. Aldrich 4-benzoylbenzoic acid (4.0 g, 0.018 mol) was esterified by refluxing overnight in methanol (50 mL) containing sulfuric acid (0.5 mL). Most of the solvent was removed under aspirator pressure and water was added. The solution was made basic with K_2CO_3 and extracted with benzene. The combined benzene extract was washed with water and dried over sodium sulfate. Removal of solvent gave a white solid, which was recrystallized from hexane (3 g, 0.13 mol), mp 108–109 °C. IR (KBr) 1640, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (s, H), 7.0–8.1 (m, 9 H); MS, *m/e* 240, 209, 163, 105.

Methyl 3-Benzoylbenzoate. 3-Benzoylbenzonitrile (1.4 g, 0.0068 mol) was hydrolyzed in 50 mL of 30% alcoholic KOH according to the procedure described previously. After workup, 1 g (0.004 mol) of 3-benzoylbenzoic acid (tan solid) was obtained, which was recrystallized from MEK/hexane to give a solid, mp 161–163 °C (lit. 161–162 °C).[39] IR (KBr) 1650, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) 7.3–8.5 (m, 9 H), 9.9 (br s, 1 H).

The ester was synthesized from 3-benzoylbenzoic acid (0.5 g, 0.003 mol) by refluxing overnight in 50 mL of methanol containing a trace of sulfuric acid, the procedure previously described for the para analogue. After similar workup and recrystallization from hexane, white crystals were obtained (~0.2 g), mp 43–45 °C. IR (KBr) 1650, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.82 (s, 3 H), 7.1–8.4 (m, 9 H); MS, *m/e* 240, 209, 163, 105.

3-(Trifluoromethyl)benzophenone. Aldrich *m*-(trifluoromethyl)-benzonitrile (4.3 g, 0.025 mol) in benzene was added dropwise to an ether solution containing 0.03 mol of phenylmagnesium bromide; the mixture was refluxed for 2 h. Dilute HCl/ice water was added and the layers were separated. The organic layer contained mostly unreacted bromobenzene. The aqueous layer was heated on the steam bath for 2 h followed by cooling and extraction with ether. The combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent gave the crude product; recrystallization from hexane gave white crystals (1.4 g, 0.006 mol), mp 49–51 °C. IR (KBr) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–8.0 (m); MS, *m/e* 250, 173, 145, 105 (base), 77.

Irradiation and Analysis Procedures. These were conducted as in earlier studies.[9] Most substituted acetophenones for calibrating GC responses were avaliable commerically. Ones which were not were assumed to respond the same as their isomers to FI detectors. Type II products were identified by their GC retention times on column containing either 4% QF-1 and 1% Carbowax 20 M on Chromosorb G or 5% FFAP on AW-Chromosorb P. Hexadecane was used to measure acetophenone concentration, and eicosane, docosane, or tetracosane were used for the substituted ketones. Pentadiene isomerization was monitored on a 25-ft column containing 25% 1,2,3-tris(2-cyanoethoxy)propane. Infotronics digital intergrators were used to measure product/standard peak area ratios.

Samples were irradiated in degassed and sealed 13 × 100-mm Pyrex tubes in a "merry-go-round" apparatus.[40] The 313-nm band of an Hanovia 450-W mercury arc was isolated with an alkaline $KCrO_4$ filter solution.

UV spectra were recorded on a Cary 219 spectrophotometer. Phosphorescence spectra were recorded on 10^{-4} M solutions on a Perkin-Elmer MPF-44A spectrofluorimeter with a phosphoroscope. Reduction potential were measured relative to SCE at a hanging mercury drop electrode by cyclic voltammetry with a PAR 174A analyzer. With 10^{-4} M acetonitrile solutions, half-wave potentials were independent of sweep rate between 100–500 mV/s.

Acknowledgment. This work was supported by NSF Grants CHE76-11892 and CHE79-10831. It is a great pleasure for the senior author (P.J.W.) to wish George Hammond a happy birthday, for it was in George's laboratory that we began these kinds of photochemical experiments.[41]

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Communications to the Editor

Regioelectronic Control of Intramolecular Charge-Transfer Quenching in Excited Triplet *p*-Acylbenzoate Esters

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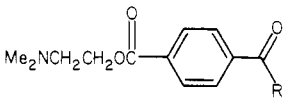
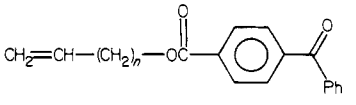
It is now widely recognized that charge-transfer (CT) interactions are the most common cause of excited-state quenching.[1] The kinetics of CT quenching and exciplex formation are usually correlated with the thermodynamics for full electron transfer.[2,3] With the close orbital overlap required for exciplex formation, steric effects often make such correlations rough.[3,4] Another important factor in CT interactions should be the accessibility of the donor orbital to the appropriate acceptor orbital. Small rate variations in several systems have already been interpreted as proof of this factor's importance.[5,6] We now report that electronic configuration is also a major factor.

The best test of the importance of orbital accessibility is provided by bifunctional molecules in which overlap between donor and acceptor orbitals is limited by the connecting skeleton's flexibility. We find a huge difference in intramolecular quenching rates depending on whether the excited acceptor has an n,π* or π,π* configuration, the first report of any significant configurational effect on CT quenching. The molecules of interest are the β-(dimethylamino)ethyl esters of *p*-benzoyl- and *p*-valerylbenzoic acid.



1-B, R = Ph
1-V, R = $CH_2CH_2CH_2CH_3$
1-A, R = CH_3



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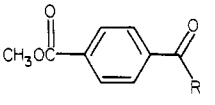

3, R = Ph
4, R = $CH_2CH_2CH_2CH_3$

† Dedicated to George S. Hammond on the occasion of his 60th birthday.
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