# Effects of Methyl Substitution on the Photoreactivity of Phenyl Ketones. The Inapplicability of Hammett σ Values in Correlations of Excitation Energies

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Abstract: The photoreactivity of various ring-methylated butyrophenones and valerophenones is correlated with the effects of methyl substitution on the triplet energy of benzoic acid. *meta*-Methyl substitution stabilizes the π,π^* triplets of the benzoyl chromophore somewhat more than does para substitution. *para*-Methyl substitution destabilizes n,π triplets whereas *meta*-methyls have at most a slight effect. As the energy difference ΔE_T between n,π^* and π,π^* triplets of the methylated ketones increases, the observed rate constant for triplet-state hydrogen atom abstraction decreases and is proportional to $\exp(-\Delta E_T/RT)$. No evidence for vibronic mixing induced reactivity in π,π^* ketone triplets is apparent; all reactivity seems to arise from equilibrium levels of the upper n,π^* states. The results illustrate the inapplicability of Hammett σ values in correlations of excited-state reactivity.

It is now well established that ketones with π,π^* lowest triplets are appreciably less reactive than those with n,π^* triplets in hydrogen-abstraction reactions, both intermolecular[1-3] and intramolecular.[4,5] In cases where the two triplets are close enough in energy to equilibrate thermally before decaying, hydrogen abstraction can occur from low concentrations of n,π^* triplets even when the π,π^* triplets are lower.[5,6] It has also been suggested[3] that vibronic mixing[7,8] of the two triplets might induce n,π^*-like reactivity in the lowest triplet. Despite the lack of any theoretical or experimental evidence on the quantitative extent of state mixing induced by vibronic coupling, it is certain that coupling is maximal when the energy gap separating the two triplets is minimal. Methyl groups are the most weakly electron-donating substituents in terms of their effects on the π,π^* excitation energies of benzene.[5,9] Consequently we have systematically varied the number and positions of methyl groups on butyrophenone and valerophenone. Normal analysis of triplet lifetimes and type II quantum yields[5,10] has allowed us to measure reactivity as a function of $^3n,\pi^* - {^3}\pi,\pi^*$ energy gaps.
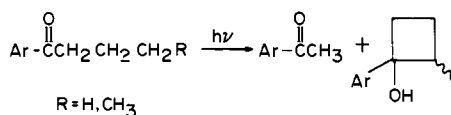
Results

Quantum Yield and Quenching Measurements. Degassed benzene solutions 0.1 M in one of the ketones listed in Table I were irradiated at 313 nm to conversions of 5–10%. Quantum yields of substituted acetophenone and cyclobutanol formation were determined relative to a valerophenone actinometer.[10] Quantum yields were lower when low concentrations of 2,5-dimethyl-2,4-hexadiene were present. Stern–Volmer plots of ϕ^0/ϕ vs. diene concentration were linear; their slopes yield $k_q\tau$ values. With k_q equal to 5×10^9 M^{-1} s^{-1},[11] triplet decay rates $(1/\tau)$ listed in the table were calculated. Quantum yields were also determined as a function of added pyridine concentration;[12] the maximum values (observed at 0.5–1.0 M pyridine) are listed in the table. Low concentrations (<0.5 M) of added alcohols also increased quantum yields, but higher concentrations often decreased them, as observed earlier.[5] In most of the ketones, acetophenone and cyclobutanol products accounted for all of the reacted ketone. Only in the case of 3,5-dimethylbutyrophenone was the quantum yield for ketone disappearance significantly higher (by 13%) than that of type II product formation. No other products could be detected.

The quantum yields of 4-methyl- and 3,5-dimethylbutyrophenone and of 3,4-dimethylvalerophenone decreased slightly with increasing ketone concentration over the range 0.05–0.2 M. The quantum yields for the other ketones were invariant over that concentration range.

Spectroscopic Studies. Uv spectra of each ketone in heptane were measured; λ_{max} energies are listed in Table II. All ketones phosphoresce strongly at 77 K, but our apparatus could not resolve the band structure in the more heavily substituted ketones. Phosphorescence spectra for the various methylated benzoic acids were recorded in ethanol. These all showed vibrational spacings of 1020 and 1540 cm^{-1}. The 0–0 band energies are recorded in Table II. The phosphorescence of ethyl benzoate at 77 K was identical in a rigid MCIP glass and in an isopentane slush.

Discussion

Triplet-state rate constants were determined as usual[10] from eq 1. It is assumed that pyridine prevents disproportionation

$$k_H = \Phi_{max}/\tau \qquad (1)$$

$$1/\tau = k_H + k_d \qquad (2)$$

of the diradical[12] intermediate such that any residual quantum inefficiency results from another triplet decay process (rate $= k_d$) competing with γ-hydrogen abstraction (rate $= k_H$). Values of the two competing rate constants are listed in Table I.
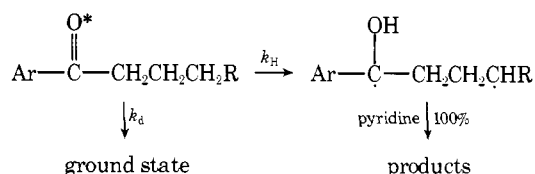
It is difficult to interpret the k_d values, since they include impurity quenching, self-quenching,[13] and solvent quenching.[11b,14] The former two are definitely important for the three ketones which showed concentration-dependent quantum yields. In the case of the 3-methyl- and 3,5-dimethylvalerophenones, however, the large k_d values are puzzling, since quantum yields for these ketones were concentration independent. We surmise that a small fraction of the diradicals may cyclize to products which can revert thermally to reactant ketone.[4] Whatever the cause for the anomaly, the k_H values for these two ketones can be no more than 15% higher than those listed.

**Table I.** Photokinetic Parameters for Methyl-Substituted Butyro- and Valerophenones[a]

Ring substitution	Φ_{II}[b]	Φ_{CB}[b]	Φ_{max}[c]	$k_q\tau$, M^{-1}[d]	$10^{-6}/\tau$, s^{-1}[e]	k_d, 10^6 s^{-1}	k_H, 10^6 s^{-1}
			Butyrophenones				
H[f]	0.35	0.03	1.0	660	7.6		7.6
3-Methyl	0.14	0.012	0.60	1140 ± 100	4.4	1.8	2.6
4-Methyl	0.27	0.019	0.69	3600 ± 400	1.4	0.4	1.0
3,5-Dimethyl	0.13	0.008	0.32	3100 ± 260	1.6	0.5	1.1
3,4-Dimethyl	0.13	0.010	0.40	6050 ± 300	0.83	0.3	0.50
3,4,5-Trimethyl	0.015	0.004	0.030	2650	1.9	1.8	0.06
			Valerophenones				
H[f]	0.33	0.07	1.0	40	125.		125.
3-Methyl[f]	0.35	0.05	0.84	128	39.	7.0	32.
4-Methyl	0.39	0.08	1.0	270 ± 6	18.5		18.
3,5-Dimethyl	0.30	0.04	0.65	366 ± 10	13.8	4.7	9.0
3,4-Dimethyl	0.37	0.05	0.80	1170 ± 50	4.3	0.9	3.4
3,4,5-Trimethyl	0.09	0.02	0.17	2530	2.0	1.7	0.34

[a] Benzene solutions 0.10 M in ketone irradiated at 313 nm. [b] All quantum yields were reproducible to ±6% and were extrapolated to zero ketone concentration. [c] Sum of maximum acetophenone and cyclobutanol yields at 0.1 M ketone and 0.5–1.0 M pyridine. [d] Slopes of Stern–Volmer plots; average of duplicate runs. [e] $k_q = 5 \times 10^9$ M^{-1}. [f] From ref 10.

Table II. Substituent Effects on π,π^* Triplet Energies (in kcal/mol) of Benzoyl Derivatives[a]

Substitution	PhCN[b]	PhCO$_2$CH$_3$[c]	PhCOOH[d]	PhCOR T → S[e]	PhCOR S → T[e]	^1L_a[f]
None	77.3	77.9	77.9			120
3-Methyl	75.4	75.9	75.6	72.5		118
4-Methyl	75.8	76.4	76.5	72.8	74.1	116
3,4-Dimethyl			75.2	71.5	73.0	115
3,5-Dimethyl			74.4	71.3	73.4	116
3,4,5-Trimethyl				70.8		114
4-Methoxy	75.4	75.4	75.3	71.5	73.1	108

[a] All measurements except for ketones represent phosphorescence 0–0 bands at 77 K. [b] In ethanol; M. J. May and P. J. Wagner, unpublished work. [c] In ethanol;methanol; D. R. Arnold, unpublished work. [d] In ethanol; this work. [e] In EPA; ref 3. [f] λ_{max} in heptane.
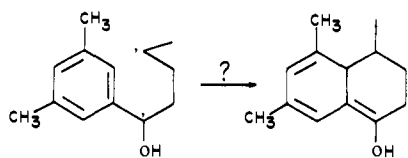
Correlations of k_H Values. Table III lists the average relative effects of methyl substitution on rate constants for hydrogen abstraction and includes, for comparison, the effect of the well-studied[5,6] p-methoxy group. Figure 1 is a Hammett plot of the relative rates of triplet-state γ-hydrogen abstraction. The σ values used for the polymethyl ketones were obtained by adding the single substituent values ($\sigma_m = -0.07$, $\sigma_p = -0.17$;[15] σ^+ substituent parameters gave a very scattered plot). Also included are some values for valerophenones with electron-withdrawing groups (F, Cl, CF$_3$).[5] No ortho substituents are included.

As discussed earlier,[5] the ketones with electron-withdrawing substituents (except for p-chloro) maintain n,π^* lowest triplets and show slightly enhanced reactivity. The dashed line ($\rho = 0.6$) should predict the reactivity of the n,π^* triplets of the ketones with electron-donating groups and, in fact, is almost identical with the plot actually observed[16] for substituted benzophenones which all have n,π^* lowest triplets.

The much steeper slope ($\rho = 8.5$) for the electron-donating substituents indicates a discontinuity in mechanism which is now readily ascribable to the fact that these ketones all possess π,π^* lowest triplets.[3-5] As discussed in more detail below, the fact that photoreactivity correlates at all with ground-state substituent parameters can be attributed to our choice of

methyl as a weakly interacting substituent. (For example, as the plot shows, the ground-state σ value of chlorine does not adequately describe its electron-donor properties in excited benzene.)

Equation 3 describes the reactivity of these ketone triplets in terms of equilibrium populations of an upper, mostly n,π^* triplet and possible vibronically induced reactivity in the lowest, mostly π,π^* triplet. The rate constant k_H^n is that for a "pure" n,π^* triplet. The χ's (sum = 1) represent the equilibrium fractions of the two triplets; a and b are the coefficients for vibronic mixing. We have previously shown[5,6] that, for p-methoxy ketones, the first term in eq 3 is dominant. The rate constant for hydrogen abstraction by the π,π^* triplet, k_H^τ, is presumably proportional to b^2 if vibronic coupling can induce reactivity. Any activity of the lowest triplet would manifest itself as a larger k_H^{obsd} value than predicted by a Boltzman distribution of triplets.

$$k_H^{obsd} = \chi_{n,\pi}k_H^n + \chi_{\pi,\pi}k_H^\pi \tag{3}$$

$$\Psi(T_1) = a\psi_{\pi,\pi} + b\psi_{n,\pi} \tag{4}$$

$$\Psi(T_2) = a\psi_{n,\pi} - b\psi_{\pi,\pi} \tag{5}$$

$$\frac{\chi_{n,\pi}}{\chi_{\pi,\pi}} = e^{-(\Delta E_T/RT)} \tag{6}$$

Since the extent of vibronic mixing (i.e., the value of b) is inversely proportional to ΔE_T, we need to examine how k_H varies with ΔE_T. Unfortunately, it is impossible to measure the precise energy levels of both triplets under reaction conditions. However, enough is now known about substituent and medium effects on S–T transition energies that reasonable

Table III. Effects of Electron-Donating Groups on Relative Rates of Triplet State Hydrogen Abstraction

Substitution	Rel k_H [a]	ΔE_T^{equil} [b]	$E_{n,\pi}$ [c]	$E_{\pi,\pi}$ [c]	ΔE_T
None	1.0		73.4	75.5	−2.1
3-Methyl	0.30	0.4	73.5	73.2	0.3
4-Methyl	0.14 (0.09)[d]	1.0	74.1	73.4	0.7
3,5-Dimethyl	0.070	1.5	73.6	72.3	1.3
3,4-Dimethyl	0.036 (0.02)[d]	1.8	74.2	72.2	2.0
3,4,5-Trimethyl	0.0055	2.9	74.3	71.5	2.8
4-Methoxy	0.0065	2.8	74.8	72.0	2.8

[a] Average relative values for butyrophenones and valerophenones. [b] From eq 6 and 7, k_H corrected as predicted by Figure 1. [c] In benzene at RT, average of S → T and T → S 0–0 bands. See text for derivation of these estimated values. [d] Reference 3b, acetophenones in 2 M 2-propanol.

estimates of ΔE_T values can be made. We have proceeded on the basis of the following spectroscopic observations.

The 0–0 bands for n,π* S → T and T → S transitions differ by 1.5[17] to 2.8[3b] kcal/mol for acetophenones in rigid glasses at 77 K; the corresponding Stokes shift for $^3\pi,\pi*$ transitions ranges from 1.1 to 2.0 kcal/mol.[3b,17] We find no effects of solvent viscosity on the 0–0 phosphorescence band energies of several benzonitriles[18] and of ethyl benzoate. In contrast, the ^{3}n,π* emission of several phenyl ketones is some 2 kcal/mol lower in energy in nonrigid media (including room-temperature solutions) than in rigid glasses.[19,20] We conclude that solution E_T values generally are lower by 2 kcal than the average of the rigid medium S → T and T → S 0–0 bands, but only for n,π* transitions. (Apparently n,π* triplets differ in geometry from ground states more significantly than do π,π* triplets.)

All of the substituted ketones which we have studied have long-lived (>0.1 s) phosphorescence and therefore π,π* lowest triplets, just as Yang found for the identically substituted acetophenones.[3a] No n,π* emission is observable; but S → T absorption has been reported.[3] Substituents raise n,π* S → T transition energies as follows: m-CH$_3$, ≤0.1 kcal; p-CH$_3$, 0.8 kcal; p-OCH$_3$, 2.6 kcal. The effect of disubstitution on benzophenone phosphorescence (all n,π*) is smaller: 3,3'-Me$_2$, no change; 4,4'-Me$_2$, +0.2,[21] 0.3[13c] kcal; 4,4'-(OCH$_3$)$_2$, +0.5,[21] 0.8[13c] kcal. Finally, it has been observed that n,π* triplet energies correlate with ketone reduction potentials,[22] from which the following substituent effects can be estimated: m-CH$_3$, ≤0.1 kcal;[23] p-CH$_3$, +0.7 kcal; p-OCH$_3$, +1.8 kcal.

The triplet energies of the various substituted acetophenones have been measured[3a] and are listed in Table II. Assuming equal values for the butyro- and valerophenones, we note that these correspond to the lowest π,π* triplets and that the actual values must reflect any vibronic coupling with the nearby n,π* triplets. We include in Table II substituent effects on the triplet energies of benzonitrile, ethyl benzoate, and benzoic acid, all of which have no low-lying n,π states to perturb the π,π* triplet. In these latter compounds, meta substitution is considerably more stabilizing than para substitution. The difference persists in the ketones, although it is not so great.

Table III includes ΔE_T values calculated from relative k_H values, corrected for inductive effects (Figure 1), on the basis of eq 6 and 7 (i.e., on the assumption that all reactivity comes from upper n,π* triplets). Also included are n,π* and π,π* energies estimated as follows:

$$k_H^{obsd} \simeq \chi_{n,\pi} k_H^n \qquad (7)$$

We know that the 0–0 n,π* phosphorescence band of the unsubstituted phenyl alkyl ketones lies at 72 kcal in hydrocarbon solutions.[20] To this value we add 1.4 kcal to correct for the Stokes shift observed in rigid media.[3b] We also know that the n,π* and π,π* triplets of the p-methoxy ketones lie, respectively, 1.4 kcal above and 1.4 kcal below this value.[6] (Our
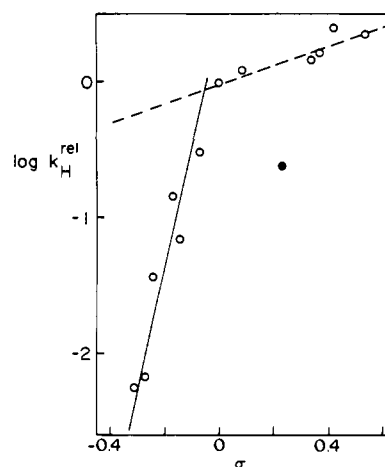
Figure 1. Hammett plot of relative rates of γ-hydrogen abstraction of ring-substituted phenyl ketones.

measured 1.4 kcal difference between n,π* levels agrees with the effects of p-methoxy substitution indicated by benzophenone phosphorescence and by reduction potentials. The higher difference suggested by phosphorescence excitation[3,17] is probably incorrect since the S → T absorption of p-methoxyacetophenone occurs on the tail of the S → S absorption,[17] and thus the apparent band maximum is probably shifted to too high energy.) The other n,π* values were estimated by adding, to 73.4 kcal, 0.1 kcal per meta-methyl and 0.7 kcal per para-methyl. The values so derived are 3.5 kcal lower than the observed 0–0 bands of the n,π* S → T absorptions in a polar glass,[3] the difference reflecting both the Stokes shift and the viscosity effect.

The "actual" π,π* values for the methylated ketones were estimated by averaging the reported S → T and T → S 0–0 bands or by adding 0.7 kcal to the T → S 0–0 band. It is reassuring that the resulting π,π* E_T value for the p-methoxy ketones (72.3 kcal) is so close to that based on measured photoreactivities,[6] especially when one considers the ±0.2 kcal error in each phosphorescence measurement. The π,π* E_T value for the unsubstituted phenyl ketone was obtained by adding 2.3 kcal to the value for the meta-methyl ketone, the difference observed for benzoic acid. The ΔE_T value so derived for the phenyl ketone is comparable with earlier estimates.[24] The resultant 3.2 kcal difference between phenyl and p-anisyl π,π* E_T values (in comparison to the 1.9 kcal difference in nitriles and the 2.5 kcal difference in benzoates) is reasonable since the importance of para-CT conjugation increases in the same order.[25] Although ^3L_a states mix with CT states much less than do ^1L_a states,[26] somewhat greater mixing in the ketone triplets than in the benzoate triplets probably explains the relatively greater stabilizing effects of para substitution in the ketones.

We see that the observed reactivities are pretty much what might be expected from equilibrium populations of the n,π^* triplets, inasmuch as these latter can be reasonably estimated. There is no evidence for any significant additional reactivity which might be ascribed to vibronic mixing. The generality of this conclusion rests on the whole pattern of substituent effects. The combined errors in estimated triplet energies for any one substituent may be half as great as the ΔE value; but much of the combined error cancels out in comparisons of relative ΔE values.

Not even in the two monomethyl ketones, where ΔE_T is the smallest and vibronic mixing should be greatest, is the observed reactivity greater than the predicted reactivity. In fact, *what vibronic coupling occurs would push the two triplets farther apart than predicted and reduce* k_H^{obsd} *accordingly!* Both $\chi_{n,\pi}$ and b^2 must be smaller than 0.5. The greater the mixing of states, the greater they repulse each other, so that any increase in b^2 is accompanied by a decrease in $\chi_{n,\pi}$.

Finally, we note that relative k_H values of the ring-substituted ketones are even lower in polar solvents.[3b,5] It is well known that n,π^* phosphorescence occurs at higher energies in polar solvents than in nonpolar solvents,[21] so that $\chi_{n,\pi}$ is lower in polar solvents. This solvent effect lowers type II quantum yields at high alcohol concentrations.[5]

Pattern of Substituent Effects. An important sidelight of this work is the realization that the pattern of substituent effects on triplet energies differs for n,π^* and π,π^* triplets. A *meta*-methyl produces a negligible effect on $^3n,\pi^*$ energies but an even larger effect than *para*-methyl on $^3\pi,\pi^*$ energies. Ground-state substituent constants are inappropriate for excited state properties, so Hammett plots such as Figure 1 must be interpreted very cautiously. In the present case, we included the plot merely to demonstrate a change in mechanism.

To a first approximation both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations populate much the same π^* orbital. It is widely accepted that, in phenyl ketones, the lowest π^* orbital is located primarily on the carbonyl and is mixed with the benzene π^*_s orbital.[27] To a good approximation, an $n \rightarrow \pi^*$ excitation can be viewed as a one-electron reduction of the π system. There is very little electron density at the meta position of the π^*_s orbital,[28] so meta substituents have negligible effects on energies. The reactivity of the n,π^* state is dominated by the hole in the oxygen n orbital. Since the n orbital is orthogonal to the π system, ring substituents can produce normal inductive effects on reactivity.
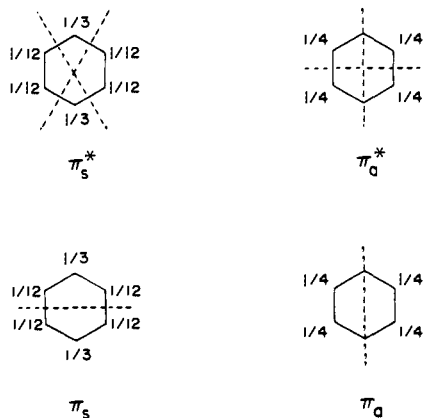
We pointed out earlier than the lowest π,π^* triplets of these phenyl ketones correspond to the L_a singlets, with λ_{max} at 238 nm for acetophenone, and suggested that triplet reactivity may correlate with the energies of these singlet π,π^* transitions.[5,29] Unfortunately, substituent effects on the ^1L_a and ^3L_a states differ. The L_a states of benzenes are combinations of $\pi_a \rightarrow \pi_a^*$ and $\pi_s \rightarrow \pi_s^*$ transitions. The presence of a conjugated elec-

tron-withdrawing substituent maximizes the $\pi_s \rightarrow \pi_s^*$ contribution to the lowest triplet,[30,31] so that the following VB forms predominate. In the absence of strong substituent-to-

^3L_a
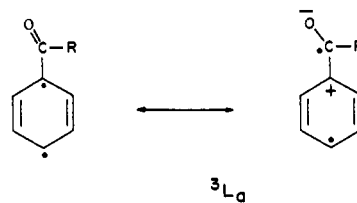
substituent charge transfer, meta orientation of a donor-acceptor pair of substituents is more effective than para orientation at stabilizing L_a π,π^* states.[9] In the singlets, mixing with CT states is quite important, so that 1,4 donor-acceptor conjugation is strong, and what looks like a "normal" ground state order of substituent effects is observed for ^1L_a band energies (Table II). In the lower energy triplets, however, mixing with the high-energy CT states is much weaker, so that the normal meta > para substitution pattern takes over. This large meta substituent effect on transition energies does not involve any direct conjugation of substituents but rather the vector addition of substituent effects on transition dipoles.[9] For example, with two electron-*accepting* substituents, the para compound's triplet energy is considerably lower than the meta compound's.[32]

Experimental Section

erophenone, bp 110 °C (1 Torr); MS m/e 190, 148, 133, 105; NMR δ 0.98 (t, 3 H), 1.65 (m, 4 H), 2.35 (s, 6 H), 2.95 (t, 2 H), 7.20–7.85 (m, 3 H); 3,5-dimethylvalerophenone: bp 106 °C (1.2 Torr); MS m/e 190, 148, 133, 105; NMR δ 0.94 (t, 3 H), 1.60 (m, 4 H), 2.35 (s, 6 H), 2.93 (t, 2 H), 7.20 (s, 2 H), 7.65 (s, 1 H).

Method 3.[33] 1,2,3-Trimethylbenzene (18.3 g, 0.15 mol) (Chemical Samples Company) and 10.6 g (0.08 mol) of $AlCl_3$ were stirred in 100 ml of 1,2-dichloroethane at 0 °C. Butyryl or valeryl chloride (0.30 mol) was added dropwise over 2 h. The reaction mixture was stirred for an hour until further generation of HCl was minimal; it was then poured into chopped ice containing enough added HCl to dissolve all $Al(OH)_3$. The mixture was extracted with chloroform; the organic layer was dried and distilled. GC analysis indicated an 80:20 mixture of 3,4,5- and 2,3,4-trimethyl isomers. The latter isomers distilled over first, followed by the desired isomers (120–130 °C, 1–2 Torr), which were then recrystallized several times: 3,4,5-trimethylbutyrophenone, mp 60 °C; MS m/e 190, 162, 147, 119; NMR δ 1.00 (t, 3 H), 1.67 (m, 2 H), 2.24 (s, 3 H, para CH_3), 2.35 (s, 6 H, 3,5-CH_3), 2.83 (t, 2 H), 7.52 (s, 2 H, ortho H); 3,4,5-trimethylvalerophenone, mp 37–38 °C; MS m/e 204, 162, 147, 119; NMR δ 0.98 (t, 3 H), 1.65 (m, 4 H), 2.25 (s, 3H), 2.35 (s, 6H), 2.85 (t, 2H), 7.53 (s, 2H).

Solvents and quencher were purified as usual.[10] All of the benzoic acids whose phosphorescence was measured were Aldrich products.

Irradiation and analysis procedures were also conducted as usual.[10] The methyl- and dimethylacetophenones for calibrating the GC response were available commercially. That for the trimethylacetophenone was extrapolated from those of the reactant ketones. The cyclobutanols were assumed to have the same response as the parent ketones; they were not isolated; their identity was assumed from their characteristic GC retention times. Pentadecane, hexadecane, and heptadecane were used as internal standards for GC analysis of the acetophenone products (on 4% QF-1, 1% Carbowax 20 M columns).

Phosphorescence spectra were measured on an Aminco-Bowman spectrofluorimeter with a phosphoroscope attachment. Samples were contained in 2 mm i.d. quartz tubes. Benzoic acid derivatives were irradiated at 270 nm; 3,3′-dimethylbenzophenone at 362 nm.

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