

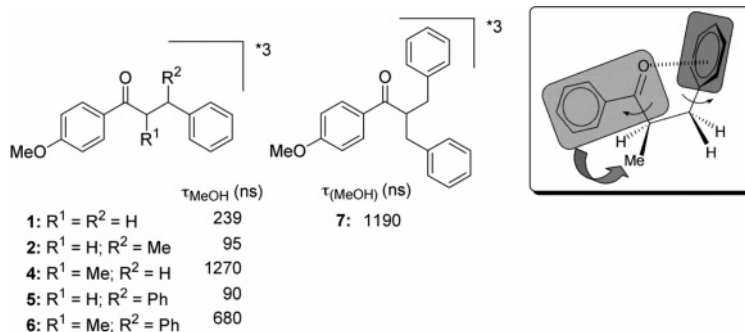
β -Phenyl Quenching of Triplet Excited Ketones: How Critical Is the Geometry for Deactivation?

Subhas Samanta,[†] Brijesh Kumar Mishra,[†] Tamara C. S. Pace,[‡]
Narayanasami Sathyamurthy,[†] Cornelia Bohne,^{*,‡} and Jarugu Narasimha Moorthy^{*,†}

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India, and Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC, Canada V8W 3V6

moorthy@iitk.ac.in; bohne@uvic.ca

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The phenomenon of β -phenyl quenching has been examined by laser-flash photolysis in a series of α - and/or β -substituted ketones **4–8** with similar excited-state characteristics. It is found that α -substitution markedly increases the triplet lifetimes in contrast to β -substitution. The force field calculations for the various staggered conformers of ketones **4–6** and **8-syn** show that the lowest-energy conformation in all these ketones has the carbonyl group and the β -phenyl ring gauche to each other. Despite this geometrical requirement, the longer lifetimes observed are interpreted as being due to the influence of the α -substituent on the rotational freedom of the planar benzoyl moiety as a whole. The experimental results are suggestive of the attainment of what appears to be a *critical geometry* for quenching. This scenario may be likened to Norrish type II reactions, where the α -substituent has long been known to suppress the elimination pathway and promote Yang cyclization. In addition, we have shown that the diastereomers of α,β -disubstituted ketones exhibit distinct lifetimes.

Introduction

The rapid deactivation of the lowest and thermally populated n,π^* triplet excited states in aryl alkyl ketones containing an aryl ring at the β -position, e.g., β -phenylpropiophenone, has been known for well over three decades.^{1,2} Although the exact mechanism of deactivation has not been fully understood, it is firmly believed that charge transfer from the β -aryl ring to the

electron-deficient triplet excited carbonyl oxygen is responsible for the deactivation.^{2,3} In support of this mechanism, the triplet lifetimes of various ketones have been found to decrease with a variation of increasingly electron-rich β -aryl rings.³ Indeed, the involvement of charge transfer in intermolecular quenching of triplet excited-state ketones by arenes is well established.⁴ In the case of intramolecular β -phenyl quenching in solution, the conformation in which the β -aryl ring is gauche to the carbonyl group has been presumed to be crucial for charge-

[†] Indian Institute of Technology.

[‡] University of Victoria.

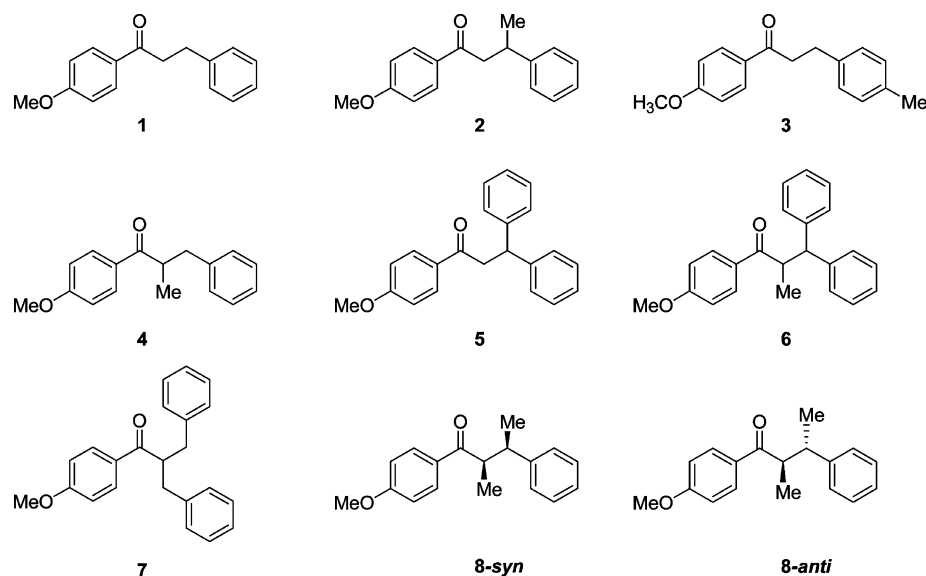
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CHART 1



transfer-mediated deactivation.^{3,5,6} Proximity effect has also been shown to be important for β -phenyl quenching deactivation in the solid state.⁷ Accordingly, the remarkably shorter lifetime observed for β -phenylpropiofenone containing a methyl substituent at the β -position, i.e., β -methyl- β -phenyl-*p*-methoxypropiofenone (vide infra), has been rationalized on the basis of conformational restrictions,⁵ which promote the existence of a major population of molecules in the gauche conformation from which the charge-transfer deactivation may ensue readily. It is precisely this requirement of the gauche relationship between the carbonyl group and the β -aryl ring that we exploited a few years ago in rationally designing and demonstrating the diastereomeric discrimination in a photophysical property, viz., triplet lifetimes, for the first time.⁶

In our recent work, we have shown that the substituents at the α and β positions and their relative stereochemistry determine the photochemical outcome of α,β -disubstituted β -arylpropiofenones,⁸ whereas the diastereomers with anti stereochemistry were found to undergo Yang cyclization predominantly, the syn isomers were found to undergo Norrish type II elimination. Furthermore, for the diastereomers with a preferred gauche geometry in their lowest-energy conformations, intriguingly longer lifetimes were observed as compared to the lifetime for the prototypical *p*-methoxy- β -phenylpropiofenone. This prompted us to investigate if the charge-transfer deactivation is critically dependent on the achievement of a particular geometry for effective deactivation. Although the importance of achievement of a specific geometry for deactivation has been previously suggested,^{2c} no systematic study on this mechanistic aspect has been reported. In the present study, the lifetimes of ketones **1–3**, documented already in the literature,⁵ are com-

pared with the lifetimes determined by laser-flash photolysis for ketones **4–8**, which were rationally designed to investigate the effect of α - and β -substituents on the intramolecular quenching mechanism (Chart 1).

Our choice of the *p*-methoxy derivatives was guided by the fact that in unsubstituted ketones such as β -phenylpropiofenone with a pure n,π^* lowest excited triplet state the deactivation is so rapid (τ ca. 1 ns) that the decay kinetics cannot be followed with nanosecond laser-flash photolysis.² The methoxy substitution in the benzoyl ring leads to the so-called state switching, which causes the lowest excited state to be π,π^* in character.⁹ Thus, the charge-transfer quenching can occur only from the thermally populated proximate n,π^* excited state leading to longer triplet lifetimes measurable by nanosecond transient absorption spectroscopy (cf. Discussion).^{2c,3,5} A further consequence of state switching is that the *p*-methoxy derivatives are fairly unreactive in their triplet states. Herein, we present our results of laser-flash photolysis (triplet lifetimes) of a set of ketones with similar excited-state characteristics, which strongly point to a dramatic influence of the substituent at the α -position and achievement of a *critical geometry* for the long-known β -phenyl quenching phenomenon in triplet excited states.

Results

Synthesis and Characterization of Ketones. The ketones **4** and **8** were synthesized by quenching the lithium enolate of *p*-methoxypropiofenone with benzyl bromide and α -phenylethyl bromide. A similar procedure was employed for the preparation of ketone **7**, but by employing β -phenyl-*p*-methoxypropiofenone in place of *p*-methoxypropiofenone. Ketones **5** and **6** were synthesized via 1,4-addition of phenylmagnesium bromide (PhMgBr) to the precursor chalcones (Scheme 1). The stereochemistry of the diastereomers of ketone **8** was assigned by comparing the diagnostic ¹H and ¹³C NMR signals of the α -methyl protons with those of the closely related systems reported in the literature.^{8b} Accordingly, the ¹H NMR signal of

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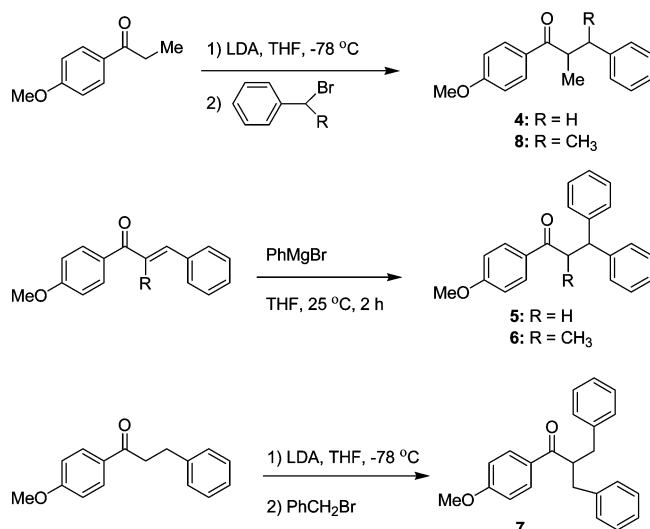
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SCHEME 1. Synthesis of Ketones 4–8



α -methyl protons of the anti diastereomer is found to appear at ca. 0.2 ppm downfield relative to that of the syn diastereomer. A similar trend has been noted in the ^{13}C NMR signals as well, where the signal due to an α -methyl carbon of the anti isomer has been found to appear at ca. δ 17.0, and that of the syn occurs at ca. δ 13.0.

Laser-Flash Photolysis and Triplet Lifetimes. Laser-flash photolysis (Excimer Laser, 308 nm)¹⁰ of ketones 4–8 led to the detection of strong transient absorptions with their maxima centered around 390 nm. The transients responsible for the absorptions were attributed to triplet states of ketones by comparison of their spectral features to those already documented in the literature for ketones 1–3.^{2,5} The typical T–T (triplet–triplet) absorption spectrum recorded for ketone 4 is shown in Figure 1. Decay profiles observed for the syn and anti diastereomers of ketone 8 are shown in Figure 2. All decays followed a monoexponential function. The lifetimes determined in two solvents, viz., CH_3OH and CH_3CN , are given in Table 1. The triplet lifetimes are uniformly found to be longer for all ketones in methanol as the solvent than for those in acetonitrile. This solvent effect has been previously observed for ketones 1–3.⁵ The enhancement of lifetimes for phenyl ketones in a polar protic solvent has previously been attributed to solvation of the carbonyl group via hydrogen bonding, which presumably hinders the deactivation by intramolecular quenching^{2c} and stabilization of π,π^* triplet excited states.¹¹

The triplet lifetimes for ketones 1–3 have been reported already in the literature.⁵ Although the parent triplet excited β -phenyl-*p*-methoxypropiofenone has a lifetime of ca. 240 ns, the substitution of a methyl group in the β -position and in the *p*-position of the β -phenyl ring as in 2 and 3 has been previously shown to lower the lifetime to ca. 30–90 ns (entries 2 and 3, Table 1). Indeed, a similar lifetime is observed for β,β -diphenyl-*p*-methoxypropiofenone 5 (entry 5). In marked contrast, methyl substitution at the α -position as in 4 and 6 increases the triplet lifetime to 1270 and 680 ns, respectively (entries 4 and 6). The triplet in the case of α -benzyl- β -phenyl-*p*-methoxypropiofenone 7 is remarkably long-lived, despite the fact that two β -phenyl groups are present, and from a statistical point of view,

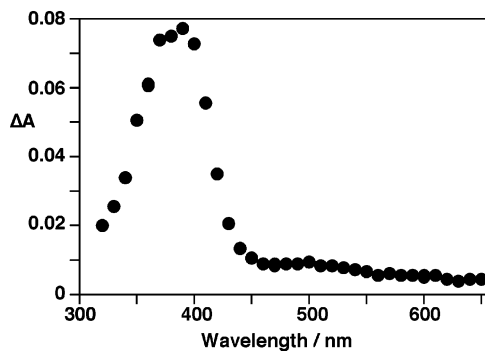


FIGURE 1. Transient absorption spectrum for ketone 4 in acetonitrile collected after a delay of 48 ns.

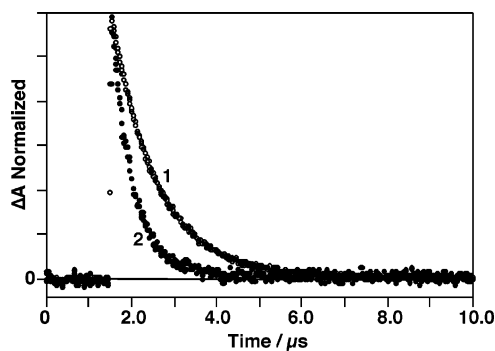


FIGURE 2. Decay of the triplet excited state of 8-anti (1) and 8-syn (2) in methanol monitored at 400 nm.

TABLE 1. Triplet Lifetimes (ns) of Ketones 1–8 at Room Temperature

entry	ketone	methanol	acetonitrile
1	1 ^a	239	50
2	2 ^a	95	19
3	3 ^a	31	9
4	4	1270 \pm 60	310 \pm 10
5	5	90 \pm 10	<20
6	6	680 \pm 30	280 \pm 20
7	7	1190 \pm 90	340 \pm 20
8	8-syn	510 \pm 40	140 \pm 20
9	8-anti	1060 \pm 80	230 \pm 10

^a From ref 5.

the quenching efficiency could be expected to double (entry 7). The diastereomers of ketone 8 exhibit a difference in their triplet lifetimes; whereas the triplet lifetime for the anti diastereomer is ca. 1060 ns, that for the syn diastereomer is found to be significantly shorter, 510 ns in methanol.

Relative Energies of Staggered Conformations of Ketones 1, 2, 4–6, and 8. United force field calculations (UFF) were carried out for ketones 1, 2, 4–6, and 8 with the Gaussian 03 suite of programs.¹² To compute the energies of the different staggered conformations, the following strategy was adopted. Initially, for ketones 2 and 4, the dihedral angle about the $\text{C}\alpha\text{--}\text{C}\beta$ bond was kept constant at a certain angle and the rest of the geometry was optimized. Subsequently, the dihedral angle was varied incrementally by 10° and the energy was computed for each such geometry. From the resultant dihedral angle energy profiles for 2 and 4, the staggered conformations were identified. In the case of ketones 1, 5, 6, and 8, the low-energy staggered conformations were optimized fully. Figure 3 shows the consolidated energies of all staggered conformations for ketones

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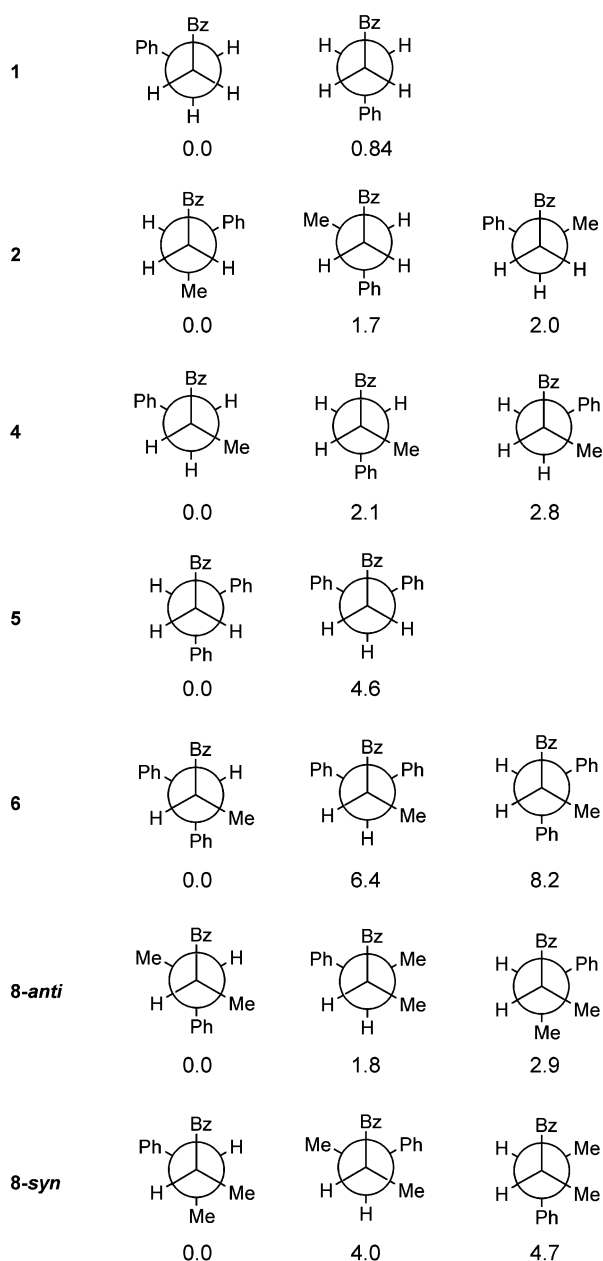


FIGURE 3. UFF-calculated relative energies (kcal/mol) for all staggered conformers of **1**, **2**, **4–6**, and **8**.

1, **2**, **4–6**, and **8**. The objective of these calculations was to obtain relative energies for the different staggered conformations. The relative stability of different conformers for the different ketones, in principle, can be computed ab initio. However, this was not done in present examples because of the structural complexity of the ketones and the number of ketones involved. In addition, past experience shows that force field calculations do give relative stabilities, albeit qualitatively.^{5,6b} The full-energy dihedral angle profiles for ketones **2** and **4** show that the relative order of the energies of the eclipsed conformations follows that of the energies of the staggered conformations. For example for compound **2**, the conformer with a gauche interaction between the methyl and benzoyl groups has a higher energy than the conformer with a gauche interaction between the phenyl and benzoyl groups. The same effect is observed for the eclipsed conformations such that the conformation for

which the methyl and benzoyl groups overlap corresponds to the highest energy.

Discussion

It is well established that substitution of an electron-donating group in the benzene ring of an aryl alkyl ketone at an ortho or para position results in the so-called state switching.⁹ For example, the character of the lowest-energy triplet excited state of unsubstituted β -phenylpropiophenone changes from n,π^* to π,π^* upon methoxy substitution as in β -phenyl-*p*-methoxypropiophenone. Thus, the lowest excited triplet state for all the ketones **1–8** is π,π^* (T_1) with the n,π^* state (T_2) being proximately placed; the latter is populated via thermal equilibration with the former state. Norrish type I cleavage and β -phenyl quenching are reactions that occur from triplet states with n,π^* character, which in the case of ketones **1–8** is the T_2 state. Assuming, as in the previous studies, that the thermal equilibration between the T_1 and T_2 states^{2c,6,11,13} is faster compared to the deactivation processes, the triplet decay rate constant (k_T), which is the inverse of the triplet lifetime, is given by:

$$k_T = k_{\text{int}} + K(k_\beta + k_{\text{cleavage}}) \quad (1)$$

where k_{int} is the intrinsic decay rate constant for the π,π^* triplet, K is the equilibrium constant between T_1 and T_2 , k_β is the rate constant for β -phenyl quenching, and k_{cleavage} is the rate constant for the Norrish type I reaction. The value of K may be assumed to be the same for ketones **1–8** because the chromophore, i.e., *p*-methoxypropiophenone, is the same for all these compounds.

The model compound that may serve for k_{int} is *p*-methoxypropiophenone,^{6b} which has a lifetime of 5.6 μs in acetonitrile and 33 μs in methanol. These lifetimes are more than an order of magnitude larger than the lifetimes for **1–8**, and for this reason, the intrinsic decay of **1–8** from the T_1 state needs not be taken into account when analyzing the differences in the lifetimes observed. The low photoreaction quantum yield observed for **1** and β -phenylpropiophenone indicates that the Norrish type I reactivity cannot compete with β -phenyl quenching. In **4–8**, the only transient observed by laser-flash photolysis is the triplet state, which shows further that the Norrish type I cleavage does not occur for these ketones. Therefore, the differences in the lifetimes for ketones **1–8** must be related to differences in the efficiencies for β -phenyl quenching.

The β -phenyl quenching involves charge transfer, and the quenching efficiency can be modulated by changing the donor ability of the β -phenyl ring^{3,5} (cf. lifetimes of **1** and **3** in Table

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1). Substitution at the β -position has been shown to influence the lifetime leading to a shorter lifetime;⁵ in this case, the conformation with the lowest energy has been shown to contain the β -phenyl ring in a gauche relationship to the carbonyl group (**1** vs **2**). Given that the lifetime of a ketone in the upper triplet state, i.e., T_2 , is short, bond rotations will not occur in the upper excited state. However, the ketone is unreactive in the T_1 state, and equilibration between the different conformers may occur in this state. Thus, the thermal population of the T_2 state will reflect the equilibrium population in the T_1 state. If the conformation with the lowest energy has the β -phenyl ring gauche to the carbonyl group, quenching will occur. This rationale has previously been used to explain the differences between the lifetimes of **1** and **2** and the diastereomeric discrimination between 1,4-diones and α,β -disubstituted β -aryl-propiophenones.^{5,6,8b} In the present investigation, ketones **4–8** were studied to determine if the mere attainment of a gauche conformation is sufficient for β -phenyl quenching to occur or if a *critical geometry* is necessary. With the assumption that the energy differences calculated for various staggered conformations in the ground state will apply in the excited state as well, we shall consider the relative energies of the staggered conformations in Figure 3 to analyze the differences in triplet lifetimes (Table 1). We do not have information on the changes in the geometry for the excited states as compared to their ground states. However, the chromophore for all ketones studied is the same, and any changes in geometries for the excited states will occur for all ketones. As mentioned earlier, the results of force field calculations can only be used in a qualitative manner to correlate the energy differences with the observed differences in the lifetimes for ketones **1–8** because small differences in energy, which are within the errors of the calculations, lead to large differences in lifetimes. For example, a change in the lifetime by a factor of 2 corresponds to a change in the energy of only 0.5 kcal/mol. As a first approximation, we assume that most of the T_2 states are thermally populated from the lowest-energy conformer (vide infra). The computed results in Figure 3 show that for all ketones, **1**, **2**, **4–6** and **8-syn**, the lowest-energy conformation is the one in which the carbonyl group and the β -phenyl ring are gauche. The triplet lifetimes for these compounds vary by more than 1 order of magnitude (Table 1). Evidently, the mere gauche relationship between the carbonyl group and the β -phenyl ring in the lowest-energy conformation does not suffice to reconcile the observed lifetimes. The lifetimes of **2** and **5** in methanol are the same. If the unreactive conformer with higher energy was significantly populated for **2**, a longer lifetime would be expected for **2** as compared to **5** because for the latter compound there is always a β -phenyl group gauche to the carbonyl moiety. Compound **2** is the one, when compared to ketones **4–8**, that has the smallest energy difference between the two conformers with lowest energy (each one having one gauche interaction). This analysis suggests that for ketones **4–8** the population of the highest-energy conformers does not have to be considered to explain the differences in lifetimes, as assumed above. Intriguingly, the lifetimes observed for ketones **4** and **6** are significantly longer, despite the similarity of the lowest-energy conformations to those of **5**. Indeed, the lifetime observed for ketone **7** with double the statistical probability for β -phenyl quenching as compared to that for **1** is also inexplicable based on proximity considerations, as is the lifetime for **8-syn** with the preferred gauche conformation between the carbonyl group and the β -phenyl ring in the lowest-energy conformation.

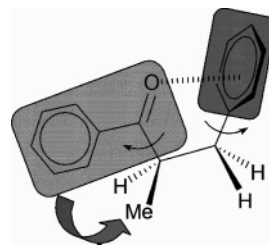
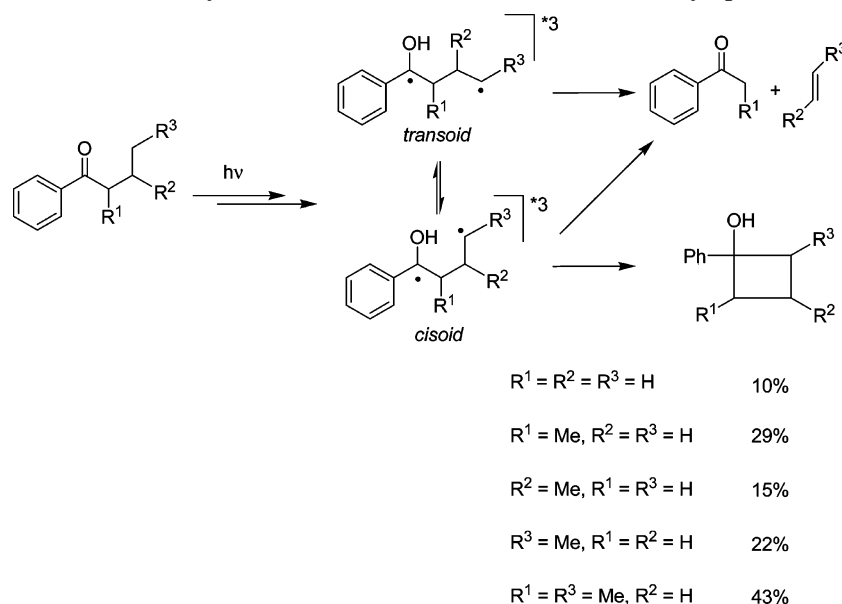


FIGURE 4. Influence of the α -methyl group on the quenching conformation.

What then is the origin of the longer triplet lifetimes observed for **4**, **6**, **7**, and **8-syn**? A structural attribute that is common to all of them is the “ α -substitution”. The striking influence of the α -substituent becomes evident when the lifetimes for ketones **4** and **6** are compared with those for **2** and **5**, respectively. Analysis of ball-and-stick models of the ketones containing α -substituents reveals that the free rotation of the benzoyl moiety as a whole becomes restricted because of the presence of an α -substituent. Presumably, this hinders the attainment of the “*right geometry*” in which the carbonyl group is accessible to the β -phenyl ring for quenching leading thereby to a slower deactivation of the triplets and hence longer lifetimes (Figure 4). Implicit in this rationalization is the fact that quenching requires attainment of a *critical geometry* between the benzoyl group and the phenyl ring, which is achieved from the initial gauche relationship. On the basis of the proposal that β -phenyl quenching involves charge transfer^{3,5} between the electron-deficient carbonyl oxygen and the electron-rich β -aryl ring, one may envisage the *critical geometry* involving the orientation of the *planar* benzoyl moiety such that one of the n-orbitals of oxygen points toward the center of the β -phenyl ring (Figure 4). Indeed, in the early investigations based on temperature-dependent triplet decay analysis by laser-flash photolysis, Scaiano and co-workers showed that the β -phenyl quenching occurs via a tight transition-state structure.^{2c} It is rather surprising that the influence of an α -substituent on the β -phenyl quenching, i.e., restriction of the rotational freedom of the benzoyl ring on the β -phenyl quenching, has not been investigated earlier. Interestingly, a similar influence in a closely related process has been known for a few decades.¹⁴ The cyclization/elimination ratio in the photochemical outcome of Norrish type II reactions has long been shown to depend on the substituents at the α and β positions (Scheme 2). In this reaction, the α -substituent presumably hinders the attainment of the transoid geometry for the intermediary triplet 1,4-biradical, thereby facilitating the cyclization via the cisoid conformation.

The diastereomeric discrimination in the observed lifetimes for **8-syn** and **8-anti** can be readily reconciled on the basis of the difference in the lowest-energy conformers. In the former, the lowest-energy conformer is destined to undergo β -phenyl quenching due to the proximity, which contributes predominantly to the overall decay. In **8-anti**, such a possibility does not arise because of the anti relationship between the benzoyl group and the β -phenyl ring in the lowest-energy conformer. In other words, the predominant triplet decay of **8-anti** occurs via the contribution of higher-energy equilibrium conformers, which may undergo β -phenyl quenching due to the gauche relationship. Thus, the operation or otherwise of the β -phenyl

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SCHEME 2. Dependence of the Yield of Cyclobutanol on the Substitution Pattern of Butyrophenone^a

^a Data from ref 14.

quenching in the lowest-energy conformers of the two diastereomers accounts for the observed difference in their triplet lifetimes. This result parallels previous observations where diastereomeric discrimination in the lifetimes of triplet excited states has been shown to be due to conformational preferences.^{6,7a,15}

Conclusions

We have investigated the phenomenon of β -phenyl quenching in a series of α - and/or β -substituted ketones **4–8** with similar excited-state characteristics by laser-flash photolysis and found that the α -substitution markedly increases the triplet lifetimes in contrast to β -substitution; incidentally, the dependence of β -phenyl quenching on α -substitution has not been heretofore investigated. The force field calculations for the various staggered conformers of ketones **4–6** and **8-syn** show that the lowest-energy conformation in all these ketones has the carbonyl group and the β -phenyl ring gauche to each other. Despite this geometrical requirement, the triplet lifetimes for these ketones are found to be different. The longer lifetimes observed for α -substituted ketones are interpreted as being due to the influence of the α -substituent on the rotational freedom of the benzoyl moiety as a whole. Ball-and-stick models show that the α -substituent hinders the attainment of what appears to be a *critical geometry* for quenching. This scenario may be likened to a Norrish type II reaction, where the α -substituent has long been known to suppress the elimination pathway and promote Yang cyclization. In addition, we have shown that the diastereomers of α,β -disubstituted ketones exhibit distinct lifetimes.

Experimental Section

Synthesis. The ketone **1** was synthesized by Friedel–Crafts acylation of anisole with β -phenylpropionyl chloride. For the preparation of ketones **4** and **8**, the lithium enolate of *p*-methoxy-

propiophenone was reacted with benzylbromide and 1-phenylethyl bromide, respectively. The ketones **5** and **6** were prepared via 1,4-addition of PhMgBr to the precursor chalcones. The reaction of *p*-methoxyacetophenone with excess benzyl bromide in the presence of solid KOH in DMSO afforded ketone **7** in rather low yield.

β,β' -Diphenyl-*p*-methoxypropiophenone 5. Colorless needles, 37%; mp 110–112 °C (lit. 113 °C);¹⁶ IR (Nujol) cm^{-1} 1715, 1580, 1480, 1400, 1305, 1290, 1230, 1160; ¹H NMR (CDCl_3 , 400 MHz) δ 3.68 (d, $J = 7.0$ Hz, 2H), 3.84 (s, 3H), 4.83 (t, $J = 7.0$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 2H), 7.20–7.40 (m, 2H), 7.25–7.35 (m, 8H), 7.93 (d, $J = 8.0$ Hz, 2H); ¹³C NMR (CDCl_3 , 100 MHz) δ 44.3, 46.0, 55.5, 113.7, 126.3, 127.9, 128.5, 130.2, 130.4, 144.3, 163.5, 196.5; HRMS m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}_2$ 316.1458, found 316.1460.

Procedure for the Preparation of Ketones 4 and 8. To a magnetically stirred solution of freshly distilled diisopropylamine (11 mmol, 1.53 mL) in 20 mL of THF was added, under nitrogen atmosphere, 2.5 mol % *n*-butyllithium in hexanes (11 mmol, 4.4 mL) at -78 °C. To the resulting solution was added, after 15–20 min, the ketone (10 mmol) all at once. After stirring for 30 min, the appropriate benzyl bromide (11 mmol) was introduced slowly into the reaction mixture. After 1 h, it was gradually allowed to attain the room temperature and was treated with diluted HCl. The organic material was extracted with dichloromethane (2×100 mL), and the combined extracts were washed with water and dried over MgSO_4 . The solvent was removed in vacuo, and the crude reaction mixture was subjected to silica gel column chromatography.

α,β -Dimethyl- β -phenyl-*p*-methoxybutyrophenone 8. Column chromatography of the reaction mixture with 20% ethyl acetate in hexanes yielded 1.48 g of the ketone (57%) as a 65:35 mixture of two diastereomers as revealed from ¹H NMR analysis. The mixture was subjected to repetitive column chromatography to isolate pure major and minor diastereomers, which were characterized as anti and syn diastereomers from their ¹H and ¹³C NMR data.

8-anti: Colorless viscous oil; IR (neat) cm^{-1} 2940, 1705, 1585, 1495, 1405, 1300, 1250; ¹H NMR (CDCl_3 , 300 MHz) δ 0.92 (d, $J = 7.0$ Hz, 3H), 1.18 (d, $J = 7.0$ Hz, 3H), 3.05–3.20 (m, 1H), 3.55–3.70 (m, 1H), 3.90 (s, 3H), 6.96 (d, $J = 9.0$ Hz, 2H), 7.15–7.35 (m, 5H), 8.10 (d, $J = 9.0$ Hz, 2H); ¹³C NMR (CDCl_3 , 100 MHz) δ 17.5, 21.0, 43.3, 46.8, 55.5, 113.8, 126.3, 127.7, 128.4, 130.4,

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130.6, 145.2, 163.5, 203.2; HRMS m/z calcd for $C_{18}H_{20}O_2$ 268.1458, found 268.1456.

8-syn: Colorless viscous oil; IR (neat) cm^{-1} 2940, 1705, 1585, 1490, 1400, 1300, 1250; 1H NMR ($CDCl_3$, 300 MHz) δ 1.12 (d, $J = 7.0$ Hz, 3H), 1.21 (d, $J = 7.0$ Hz, 3H), 3.10–3.25 (m, 1H), 3.55–3.70 (m, 1H), 3.76 (s, 3H), 6.79 (d, $J = 9.0$ Hz, 2H), 7.15–7.25 (m, 5H), 7.75 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 17.3, 41.6, 46.8, 55.4, 113.6, 126.1, 127.3, 128.2, 129.8, 130.4, 145.8, 163.1, 202.4; HRMS m/z calcd for $C_{18}H_{20}O_2$ 268.1458, found 268.1456.

α -Benzyl- β -phenyl-*p*-methoxypropiophenone 7: Viscous colorless oil, 0.49 g (15%); IR (neat) cm^{-1} 3000, 2900, 1705, 1590, 1485, 1405, 1300, 1250, 1230; 1H NMR ($CDCl_3$, 300 MHz) δ 2.67–2.75 (m, 2H), 3.00–3.08 (m, 2H), 3.70 (s, 3H), 3.90 (m, 1H), 6.72 (d, $J = 9.0$ Hz, 2H), 7.02–7.18 (m, 10H), 7.65 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) 38.3, 50.0, 55.4, 113.6, 126.2, 128.4, 129.0, 130.4, 130.5, 139.7, 163.3, 201.7; HRMS m/z calcd for $C_{23}H_{22}O_2$ 330.1614, found 330.1619.

α -Methyl- β -phenyl-*p*-methoxypropiophenone 4: Colorless oil, 1.45 g (57%); IR (neat) cm^{-1} 2940, 2900, 1705, 1595, 1490, 1400, 1300, 1250, 1230, 1160; 1H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, $J = 7.0$ Hz, 3H), 2.63–2.69 (m, 1H), 3.10–3.16 (m, 1H), 3.65–3.71 (m, 1H), 6.90 (d, $J = 9.0$ Hz, 2H), 7.15–7.30 (m, 5H), 7.90 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.5, 39.4, 42.3, 55.4, 113.7, 126.1, 128.3, 129.1, 129.3, 130.6, 140.1, 163.3, 202.3; HRMS m/z calcd for $C_{17}H_{18}O_2$ 254.1302, found 254.1307.

Preparation of α -Methyl- β,β' -diphenyl-*p*-methoxypropiophenone 6. To a round-bottom flask containing 4.0 mL of anhydrous DMSO and 0.33 g (2 mmol) of *p*-methoxypropiophenone was added 0.44 g of powdered KOH followed by 0.99 g (4 mmol) of benzhydryl bromide. The mixture was stirred under a nitrogen gas atmosphere for 7 days to yield a dark brown liquid. The reaction mixture was subsequently treated with diluted HCl, and the organic material was extracted with dichloromethane (2 \times 40 mL). The combined extract was washed with water, dried over $MgSO_4$, and filtered. The solvent was removed in vacuo, and the crude product mixture was submitted to silica gel column chromatography (20% ethyl acetate in hexanes) to isolate 0.14 g (21%) of colorless crystals, mp 128–130 $^{\circ}C$.

IR (Nujol) cm^{-1} 1690, 1580, 1295, 1250, 1230, 1190, 1160; 1H NMR ($CDCl_3$, 300 MHz) δ 1.09 (d, $J = 7.0$ Hz, 3H), 3.85 (s, 3H),

4.25–4.45 (m, 2H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.95–7.35 (m, 10H), 7.92 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) 18.2, 44.4, 54.4, 55.6, 113.9, 126.2, 126.6, 127.8, 128.5, 128.7, 129.9, 130.6, 143.4, 143.8, 163.5, 201.9; HRMS m/z calcd for $C_{23}H_{22}O_2$ 330.1614, found 330.1618.

Laser-Flash Photolysis. Nanosecond laser-flash photolysis was carried out using the pulses from an excimer laser (308 nm). The full details of signal detection, monitoring, and data processing have been described elsewhere.¹⁰

The transient absorption spectra were recorded using a flow system to avoid possible interference of photoproducts resulting from several laser shots. For this purpose, a freshly prepared solution was pumped, under a nitrogen gas atmosphere, through a custom-designed Suprasil-cell (7 \times 7 mm) at a rate of 1.5–2.0 mL/min. As a result, the solution that was subjected to a few laser shots was constantly displaced with the fresh one. For kinetic measurements, the samples were contained in suprasil quartz cells (7 \times 7 mm), sealed with precleaned rubber septa, and deoxygenated with nitrogen for >15–20 min. It was made sure that the samples did not receive more than 7–10 laser shots. The concentrations of the solutions at the excitation wavelength were typically in the range $1.0\text{--}5.0 \times 10^{-4}$ M ($0.1 < A < 0.6$).

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Supporting Information Available: General aspects of the Experimental Section as well as 1H NMR and ^{13}C NMR spectra for compounds 4–8. Output files of theoretical calculations with energies and coordinates of the refined structures are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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