Modulation of Lifetimes and Diastereomeric Discrimination in Triplet-Excited Substituted Butane-1,4-diones through Intramolecular Charge-Transfer Quenching

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Abstract: Triplet lifetimes have been determined for the diastereomers of a broad set of butane-1,4-dione derivatives (**1**−**3**). A remarkable dependence of lifetimes on conformational preferences is revealed in that the lifetimes are shorter for the meso diastereomers of **1**−**3** than those for the racemic ones. The intramolecular β-phenyl quenching is promoted in the case of meso diastereomers by virtue of the gauche relationship between the excited carbonyl group and the β-aryl ring, while a distal arrangement in the lowest energy conformation (**H**-*anti*) in racemic diastereomers prevents such a deactivation. The involvement of charge transfer in the intramolecular β-phenyl quenching is suggested by the correlation of the triplet lifetimes of the meso diastereomers of compounds **2** with the nature of the substituent on the β-phenyl rings. In the case of racemic diastereomers, *p*-methoxy substitution on the β-phenyl ring (**2-OCH₃**, **3-OCH₃**) also led to a decrease of the triplet lifetimes when compared to those of the nonsubstituted compounds (**2-H**, **3-H**). This shortening is accounted for by the deactivation of a small proportion of the excited molecules through β-phenyl quenching. In addition to the above factors, the lifetimes in the case of meso diastereomers can further be controlled by increasing the energy spacing between the T_1 and T_2 states, since β-phenyl quenching occurs from the latter for compounds **2** and **3**. Through a rational conformational control, a surprisingly long triplet lifetime (300 ns) has been measured for the first time for a purely n,π* triplet-excited β-phenylpropiophenone dimer (**1**-*rac*).

Introduction

Carbonyl compounds have traditionally played a key role in the development of organic photochemistry as an independent, vital branch of chemistry as a whole.[1] The interest in ketone photochemistry continues unabated in the quest for comprehensive mechanistic details of even such seemingly simple reactions as photoreductions.[2] One aspect of ketone photochemistry that has attracted a great deal of attention is the conformational control of photochemical reactivity.[1,3−5] There are many reports in the literature to exemplify this aspect.[1,3−11] In noted contrast, little has been reported on the conformational

control of photophysical properties. Compounds for which photophysical properties can be conformationally controlled have the potential to probe how supramolecular structures affect the intramolecular mobility of an incorporated molecule. In this context, β-phenylpropiophenones are particularly interesting in that their triplet lifetimes are limited by the conformation, in which the triplet-excited carbonyl group and the β-phenyl ring are in close proximity.[12,13] Consequently, they have been employed as excellent probes of supramolecular systems.[14−21]

The involvement of charge transfer in the intermolecular quenching of triplet-excited ketones by arenes has been long recognized.[22−26] Detailed studies by Wagner and co-workers

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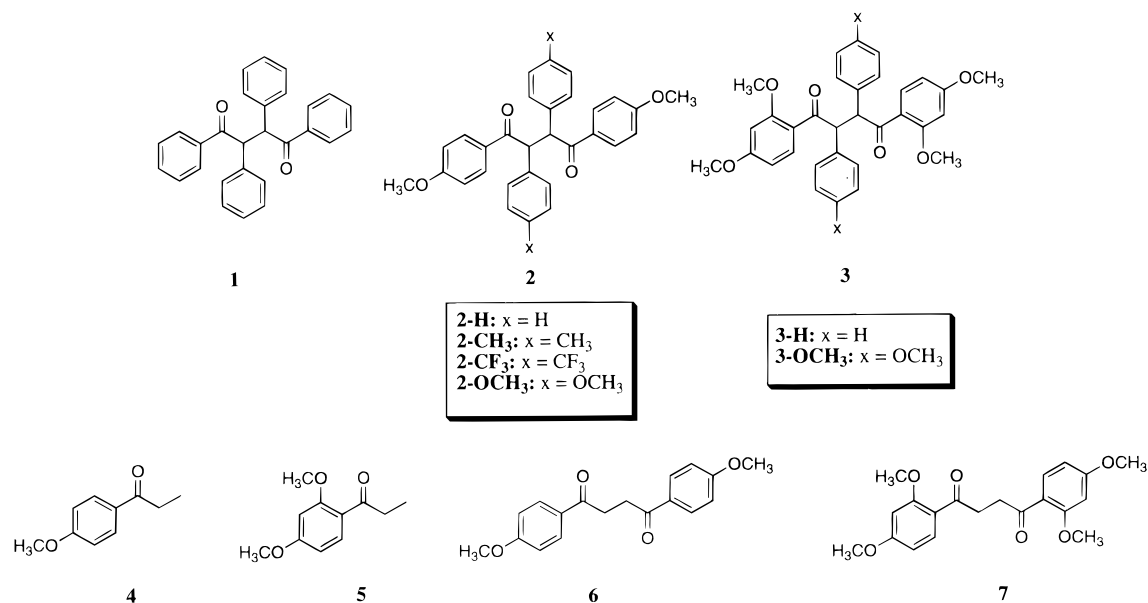(21) de Lucas, N. C.; Netto-Ferreira, J. C. *J. Photochem. Photobiol. A: Chem.* **1997**, *103*, 137.
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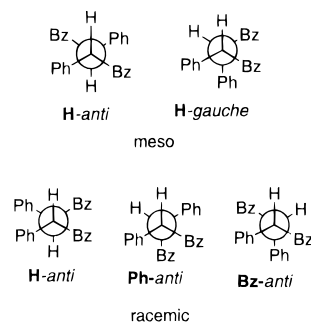
Chart 1

on the photoreduction of substituted acetophenones and benzophenones with alkylbenzenes showed that both n,π* and π,π* triplets react with alkylbenzenes predominantly by a rate-determining charge-transfer complexation.[25,26] However, the reactivity shifts to direct hydrogen transfer when the triplet ketone becomes harder to reduce.[26] β-Phenylpropiophenone constitutes an intramolecular case of quenching. Its lack of photoreactivity, which was recognized more than 50 years ago,[27] was explained as being due to efficient intramolecular charge-transfer quenching of the n,π* triplet-excited ketone by the phenyl ring at the β-position.[12,28-30] From time-resolved studies, a surprisingly short triplet lifetime of ca. 1 ns was revealed by Wismontski-Knittel and Kilp.[31] Subsequently, Scaiano and co-workers demonstrated that substitution in the β-phenyl ring by electron-donating groups has only a marginal effect on the triplet lifetimes of β-phenylpropiophenones.[13] This lack of dependence led them to suggest that bond rotations, which bring the excited carbonyl group and the β-phenyl ring into close proximity, determine the overall triplet decay. From Arrhenius parameters for the triplet decay, a tight transition state for quenching was suggested.[12,13] In contrast, for β-phenyl-*p*-methoxypropiophenones, the lifetime increases by 2 orders of magnitude ($^3\tau$ = 230 ns in methanol).[13,32,33] This increase is attributed to the need to thermally populate the high-energy n,π* state from the lowest triplet state with π,π* character.[13] In the case of β-aryl-*p*-methoxypropiophenone, the triplet lifetimes depend on the nature of the substituent on the β-phenyl ring.[33] The triplet decay rate constants correlate with the Hammett σ^+ constants, indicating that charge-transfer interactions between acceptor carbonyl and donor aryl groups are responsible for intramolecular quenching. For this reason, it was suggested that the rate-limiting

step for the triplet decay is the β-phenyl quenching process and not conformational motions to achieve the quenching geometry.[33] In addition to the substituent effects, conformational restrictions that lead to increased proximity between the carbonyl and the β-phenyl rings have been shown to influence the triplet lifetimes.[32,34]

We have recently demonstrated a diastereomeric discrimination in the triplet lifetimes of the racemic and meso diastereomers of a substituted 1,4-diketone (**2-H,** see Chart 1).[35] Conformational control was suggested to be responsible for the shorter triplet lifetime of **2-H**-*meso*, where the efficient intramolecular quenching was ascribed to the gauche relationship between the β-phenyl and carbonyl moieties in the excited-triplet conformer with lowest energy. In the case of **2-H**-*rac*, its triplet lifetime is mainly determined by the intrinsic decay of the triplet, with little contribution from intramolecular quenching. This initial study was expanded to compounds **1−3** (Chart 1) to establish how the triplet lifetimes of both diastereomers can be altered by substitution in the benzoyl and/or β-phenyl rings. Furthermore, we show that, through conformational control, it is possible to increase the lifetime to the nanosecond time domain for a purely n,π* triplet-excited β-phenylpropiophenone dimer (**1**-*rac*).
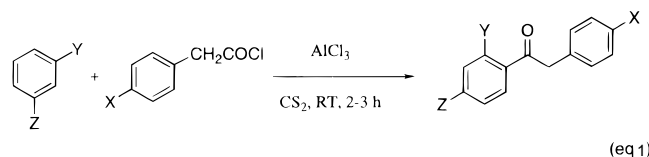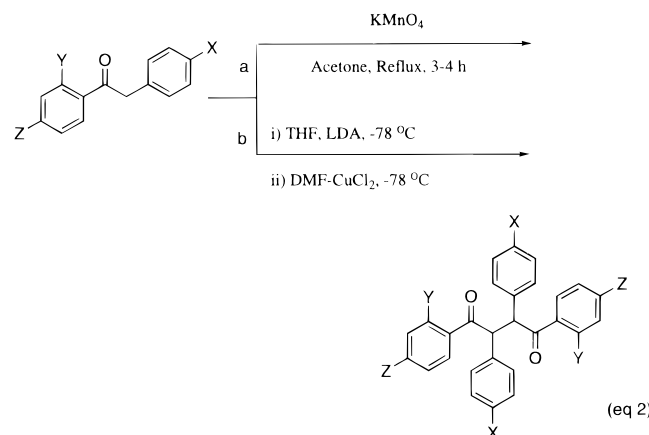
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Results

Synthesis of Ketones. The precursor benzyl phenyl ketones were synthesized from Friedel−Crafts reactions between α-aryl-

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acetyl chloride and anisole/1,3-dimethoxybenzene in the presence of AlCl$_3$ using carbon disulfide as solvent (eq 1).[36] The

$$\text{(eq 1)}$$

racemic and meso diastereomers of diketone **1** were prepared according to the reported procedure; benzyl phenyl ketone was subjected to oxidative dimerization by KMnO$_4$ in refluxing acetone (path a, eq 2).[37] Although this procedure afforded both

$$\text{(eq 2)}$$

diastereomers of the diketone **2-CF$_3$** in a rather low yield (9%), only the meso diastereomers were isolated in the cases of **2-H** and **2-OCH$_3$**. Therefore, the synthetic procedure was modified, and that involving CuCl$_2$-mediated oxidative dimerization of the respective lithium enolates (path b, eq 2) reported for the preparation of analogous diketones was adopted.[38] Thus, treatment of the lithium enolates at −78 °C with CuCl$_2$ afforded the racemic and meso diastereomers of diketones **2-H, 2-CH$_3$, 2-OCH$_3$** and **3-H, 3-OCH$_3$** in 10−30% yields. No attempt was made to optimize the reaction conditions to improve the yields. In general, the diketones were isolated in higher yields when the α-aryl ring was substituted with an electron-donating group at the para position; the reaction completely failed when the para substituent was trifluoromethyl.

The separation of racemic and meso diastereomers of ketones **2** and **3** was achieved by fractional crystallization in methanol and in diethyl ether−hexanes mixtures. Only in the case of **2-CF$_3$** was it not possible to isolate the pure diastereomers without contamination of each other; however, the extent of contamination (<5%) did not present a serious problem in the time-resolved work (see below). The stereochemical assignments for meso and racemic diastereomers of diketones **2** and **3** were made by comparison of the characteristic ^{1}H NMR chemical shifts of the benzylic protons with those of the diastereomers of diketones **1**. In the latter case, the stereochemical assignments were established on the basis of the influence of chiral chemical shift reagents on the benzylic resonances at δ ∼5.4 (racemic) and ∼5.7 (meso).[39]

2,4-Dimethoxypropiophenone (**5**) was synthesized from Friedel−Crafts acylation of 1,3-dimethoxybenzene with pro-

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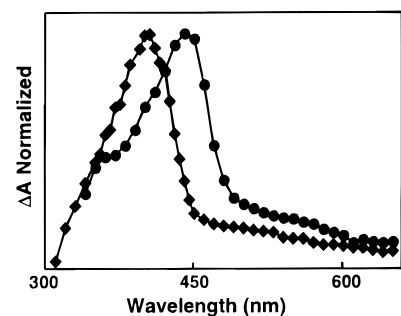

Figure 1. Triplet−triplet absorption spectra in methanol of **2-H**-*rac* (◆) and **3-H**-*rac* (●) measured respectively at delays of 1170 and 470 ns after the laser pulse.

Table 1. Triplet Lifetimes (μs) and T−T Absorption Maxima (nm) of Diketones **1**−**3**

diketone	acetonitrile		methanol	
	$^3\tau$	λ_{max}	$^3\tau$	λ_{max}
1-*rac*	0.25 (0.01)^a	340	0.31 (0.04)^a	340
1-*meso*	<0.01^c		<0.01^c	
2-H-*rac*	10 (1)^{b,d}	400	33 (8)^{b,d}	400
2-H-*meso*	0.23 (0.01)^a	400	0.63 (0.04)^a	410
2-CH$_3$-*rac*	>4.5^e	400	>6.6^e	410
2-CH$_3$-*meso*	0.06 (0.01)^a	410	0.17 (0.02)^b	410
2-CF$_3$-*rac*	>5.3^e	380	>6.1^e	400
2-CF$_3$-*meso*	>3.3^e	390	>5.3^e	400
2-OCH$_3$-*rac*	3.5 (0.1)^{b,d}	400	7.5 (0.2)^{b,d}	400
2-OCH$_3$-*meso*	<0.01^c		<0.01^c	
3-H-*rac*	4.1 (0.3)^a	430	10.2 (0.6)^{b,d}	440
3-H-*meso*	0.77 (0.05)^b	430	2.2 (0.1)^a	450
3-OCH$_3$-*rac*	1.2 (0.1)^a	430	2.3 (0.2)^a	430
3-OCH$_3$-*meso*	0.030 (0.002)^b	440	0.060 (0.003)^a	450

^{a} From three or more measurements; the errors in parentheses refer to standard deviations. ^{b} From two independent measurements; the error refers to an average deviation. ^{c} Limiting higher value; no signal was detected on the nanosecond time scale. ^{d} Lifetime as extrapolated to zero ketone concentration. ^{e} Minimum value since efficient bimolecular self-quenching occurs.

pionyl chloride. The diketone 1,4-bis(4-methoxyphenyl)butane-1,4-dione (**6**) was synthesized according to the reported procedure.[40] A similar procedure was employed for the preparation of 1,4-bis(2,4-dimethoxyphenyl)butane-1,4-dione (**7**). Thus, the Friedel−Crafts reaction between 1,3-dimethoxybenzene and succinyl chloride in the presence of AlCl$_3$ in refluxing carbon disulfide furnished the diketone **7**.

Triplet−Triplet Absorption Spectra and Triplet Lifetimes of the Ketones. Laser flash photolysis of all the ketones **2** and **3**, with the exception of **2-OCH$_3$**-*meso*, led to the detection of transient absorptions corresponding to their excited triplet states (Figure 1). The assignment of the transient with absorption maxima at 380−410 nm for compounds **2** and 430−450 nm for compounds **3** (Table 1) to the triplet state is based on the experiments described for **2-H**[35] and the similarity to the triplet−triplet (T−T) absorption spectra previously reported.[13,32] The spectra for the meso and racemic diastereomers of each compound were similar and were independent of the solvent used. The decay of compounds **2** and **3** showed a monoexponential behavior throughout the T−T absorption spectrum, and the same triplet lifetimes were measured at different wavelengths. A long-lived residual was observed after the decay of the triplet state. This residual at the T−T absorption maxima was smaller for the meso diastereomers (<5%) than for the racemic ones (<10%). In the cases of **2-OCH$_3$** and **3-OCH$_3$**, the residues were larger than those observed for **2-H** and **3-H**.

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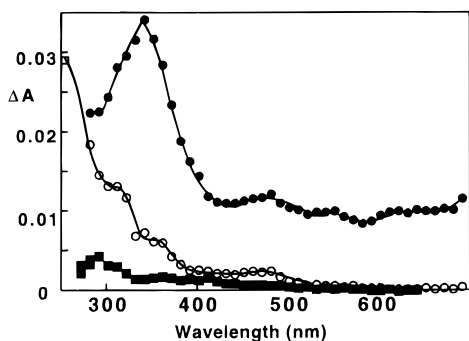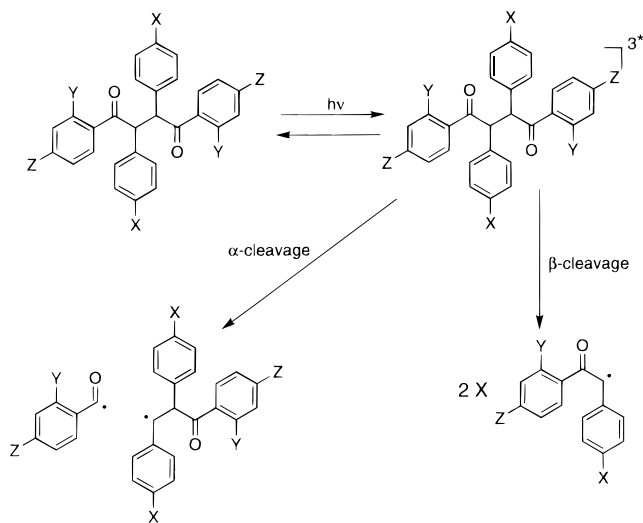
Figure 2. Transient absorption spectra in methanol of **1**-*rac* at delays of 85 ns (●) and 1.7 μs (○) after the laser pulse and for **1**-*meso* at a 220 ns delay (■).

Scheme 1

Residual absorptions after the decay of the triplet were previously reported for other β-phenylpropiophones,[32] and in the cases of the diketones **2** and **3** they are probably due to the formation of radical products from α- and β-cleavage reactions (Scheme 1).[41] The fact that no absorption corresponding to the triplet was observed for **2-OCH₃**-*meso* suggests that its lifetime is significantly shorter than the 10 ns time resolution of the laser flash photolysis system.

The transient phenomena for **1** were more complex since photodecomposition of this compound was significant. At short delays after the laser pulse, a transient with an absorption maximum at 340 nm was observed for **1**-*rac* in methanol but was absent for **1**-*meso* (Figure 2). The initial decay at 340 nm of the transient observed for **1**-*rac*, assigned to its triplet-excited state, was monoexponential, followed by a significant long-lived residual (15−20%) (Figure 3). The lack of the signal at 340 nm in the case of the **1**-*meso* suggests that its triplet lifetime is shorter than 10 ns. At long delays after the laser pulse, a featureless spectrum (Figure 2) was observed for both diaster-

(41) The photodecomposition of both diastereomers of **2-H** irradiated in a Rayonet reactor with 254 nm lamps was followed by HPLC. The photodecomposition of **2-H**-*rac* is faster than that observed for **2-H**-*meso*, as expected from the longer lifetime of the racemic diastereomer. The relative photodecomposition rate for **2-H**-*rac* is much smaller than that for **1**-*rac* and is similar to that observed for **1**-*meso*. Furthermore, the residuals observed in the laser flash photolysis experiment for the triplet decay of β-phenyl-*p*-methoxypropiophenone and **2-H** are similar, suggesting that photodecomposition of **2-H** is not a major component of its triplet deactivation, as shown previously for β-phenyl-*p*-methoxypropiophenone.[13] The mechanistic studies on the photocleavage reactions, which are not the subject of this work, will be described separately.
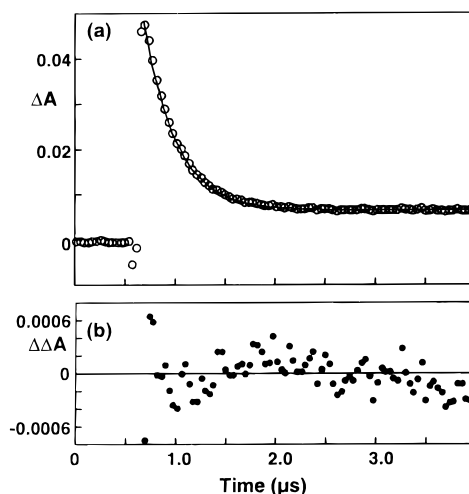

Figure 3. Decay of **1**-*rac* at 340 nm in methanol. The residuals ($\triangle\triangle A$) correspond to the difference between the experimental and calculated values for the fit of the decay to a monoexponential function with an offset of the baseline.

eomers of **1**, which probably corresponds to the radicals formed in the photodecomposition of this compound. Since the lowest triplet of **1** has an n,π* configuration, we expect the photocleavage to be competitive with other deactivation channels for the excited triplet state. Photodecomposition studies of **1** at 254 nm in a Rayonet reactor showed that both diastereomers are decomposed. However, the photodecomposition rate is at least 20 times faster for the racemic diastereomer than that for the meso compound.[42] The transient phenomena regarding the formation of the triplet of **1** in acetonitrile are similar to those observed in methanol. However, additional transients are formed in the 400−500 nm region.[43] In analogy to the results for **1** in methanol, we assign the fast decay at 340 nm to the triplet of **1**-*rac* (Table 1). No short-lived transient was observed for **1**-*meso* in acetonitrile.

The values for the triplet lifetimes of **1**-*rac* (Table 1) were independent of the ketone ground-state concentration. These lifetimes include the contribution from the photocleavage reaction, which is responsible for the residual absorption observed. Since the cleavage reaction is one of the decay pathways of the triplet, offsetting the baseline to the value corresponding to the residual absorption yields the correct triplet lifetimes.[44] The lifetimes for the meso diastereomers of **2-H** and **2-CH₃** in acetonitrile and methanol (Table 1) were found to be independent of the ketone concentrations, while a strong dependence was found in the case of the racemic diastereomers of all the diketones **2** and **2-CF₃**-*meso*. The shortening of the lifetimes with increasing diketone concentration is due to a bimolecular self-quenching process in which a ground-state diketone quenches the excited triplet state of another molecule. The bimolecular self-quenching rate constants for **2-H**-*rac* and **2-OCH₃**-*rac* (k_{sq}; $k_{obs} = k_0 + k_{sq}$[ketone]) were determined from the quenching plots at different diketone concentrations (Figure

(42) The photodecompositions of both diastereomers of **1** in methanol and acetonitrile were followed by monitoring the decrease of the concentration of **1** by HPLC. The estimated decomposition rates were 180 and 160 nM/s, respectively, for **1**-*rac* in methanol and acetonitrile and 5 and 7 nM/s, respectively, for **1**-*meso* in methanol and acetonitrile with matched absorbances at 254 nm.

(43) The UV−vis absorption spectra of the photodecomposition of **1** in acetonitrile are different from those observed in methanol.

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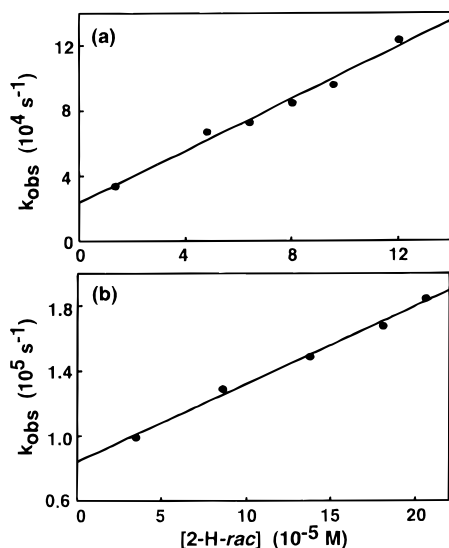
Triplet Lifetimes of Butane-1,4-dione Diastereomers

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Figure 4. Concentration dependence for the triplet decay of **2-H**-*rac* in (a) methanol and (b) acetonitrile.

Table 2. Triplet Lifetimes (μs)[a] and T−T Absorption Maxima (nm) of Ketones **4**−**7**

ketone	acetonitrile		methanol	
	$^3\tau$	λ_{max}	$^3\tau$	λ_{max}
4	5.6 (0.2)[b]	380	33 (4)	390
5	7 (0.4)	420	36 (6)	430
6	7 (1)	380	28 (1)	390
7	7 (2)	420	18 (2)	440

[a] Determined as extrapolated to zero ketone concentrations. The values in parentheses represent average deviations from two experiments. [b] No self-quenching was observed.
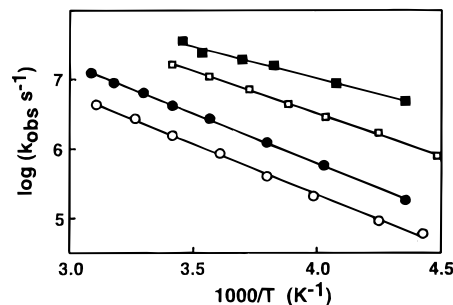

Figure 5. Arrhenius plots for triplet decay of **3-OCH₃**-*meso* in acetonitrile (■), **3-OCH₃**-*meso* in methanol (□), **2-H**-*meso* in acetonitrile (●), and **2-H**-*meso* in methanol (○).

4).[45] Thus, for diketones **2-H**-*rac* and **2-OCH₃**-*rac*, the triplet lifetimes were determined in methanol and acetonitrile as extrapolated to zero ketone concentrations. The concentration dependence was not examined for **2-CH₃**-*rac* and for both the diastereomers of diketones **2-CF₃**. Therefore, the values in Table 1 constitute the limiting lower values for their triplet lifetimes. The lifetimes for compounds **3** in methanol were found to be concentration-dependent for **3-H**-*rac*,[46] but no such dependence was revealed in acetonitrile. The diketones **3-H**-*meso*, **3-OCH₃**-*rac*, and **3-OCH₃**-*meso* displayed concentration-independent triplet lifetimes in both acetonitrile and methanol.

The results in Table 1 show that the triplet lifetimes for all the meso diastereomers of diketones **1**−**3** are remarkably shorter than those for the corresponding racemic ones.[47] A striking dependence of the lifetimes of meso diastereomers on the nature of the para substituent of the phenyl rings is observed. The lifetimes progressively increase in the order methoxy < methyl < hydrogen < trifluoromethyl (Table 1). A similar trend is observed in the case of diketones **3**. While a 4-fold difference is noted in the lifetimes for **3-H**-*rac* and **3-OCH₃**-*rac*, a 20−40-fold difference is evident in the lifetimes of the meso diastereomers.

Molecules **4** and **5** were studied to establish the triplet lifetimes of simple analogues of the racemic diastereomers of **2** and **3**. Ketones **6** and **7** were studied to establish the importance of intramolecular self-quenching, i.e., the quenching of one of the carbonyl chromophores by the other in the same molecule in compounds **2** and **3**. The T−T absorption spectra for *p*-methoxypropiophenone (**4**) and 1,4-bis(*p*-methoxyphenyl)-butane-1,4-dione (**6**) were found to be similar to those of diketones **2**, while the spectra for 2,4-dimethoxypropiophenone (**5**) and 1,4-bis(2,4-dimethoxyphenyl)butane-1,4-dione (**7**) resembled those for **3** (Table 2). The triplet lifetimes of all the ketones **4**−**7**, with exception of **4** in acetonitrile, exhibited strong dependences on the ketone concentrations. Therefore, the triplet lifetimes were determined at zero ketone concentrations as

described above (Table 2).[48] The lifetimes of **2-H**-*rac* (Table 1) are similar to those of **4** and **6**, whereas for **3-H**-*rac* one observes that its lifetime is shorter than those for **5** and **7**.

A strong solvent effect on the lifetimes of all the ketones is observed (Tables 1 and 2). A significant lengthening of triplet lifetimes is observed in a polar protic medium such as methanol; for example, the lifetime for **2-H**-*meso* varies from ca. 600 ns in methanol to 100 ns in apolar nonprotic solvent such as carbon tetrachloride,[35] while it is 220 ns in acetonitrile. A similar solvent dependence for the triplet lifetimes is observed for the model compounds **4**−**7**. Such an effect of medium on the lifetimes has long been recognized, and the effect of polar protic solvents has been interpreted in terms of hydrogen-bonding effects[13] and stabilization of π,π^* triplet-excited states.[49] Regardless of the mechanism involved, it is noteworthy that the lifetimes of both racemic and meso diastereomers of diketones **2**−**3** follow a similar trend in the different solvents.

Temperature Dependence of the Lifetimes. The dependence of lifetimes on the temperature was examined for **1**-*rac* and the meso diastereomers of **2-H**, **2-CH₃**, **3-H**, and **3-OCH₃** over a range of 223−323 K. The triplet decays were measured by monitoring the transient absorptions at 340, 400, and 440 nm for diketones **1**, **2**, and **3**, respectively. In all the cases, the decay traces followed first-order kinetics, and the values of k_{obs} were obtained from single-exponential fits. A linear behavior was observed for log k_{obs} vs $1/T$ (Figure 5). The activation energies and preexponential factors associated with triplet decays of the ketones examined are given in Table 3.

MM PI Calculations. The differences in the lifetimes for the meso and racemic diastereomers of each ketone are related to the relative population of the triplet-excited conformers and the rotational energy barriers for their interconversion. More detailed calculations than those previously reported[35] were

(45) The self-quenching rate constants (k_{sq}'s) for **2-H**-*rac* and **2-OCH₃**-*rac* in (a) methanol are $(6 \pm 2) \times 10^8$ and $(4 \pm 1) \times 10^8$ M⁻¹ s⁻¹ and in (b) acetonitrile are $(5 \pm 1) \times 10^8$ and $(3 \pm 1) \times 10^8$ M⁻¹ s⁻¹, respectively.

(46) $k_{sq} = (8 \pm 1) \times 10^8$ M⁻¹ s⁻¹.

(47) See also ref 35 for a figure showing the triplet decays for **2-H**.

(48) The k_{sq}'s for the ketones **4**−**7** in (a) methanol are $(4 \pm 1) \times 10^7$, $(6 \pm 1) \times 10^8$, $(2 \pm 1) \times 10^8$, and $(10 \pm 1) \times 10^8$ M⁻¹ s⁻¹, and in (b) acetonitrile are nonobservable, $(5 \pm 1) \times 10^8$, $(7 \pm 1) \times 10^7$, and $(14 \pm 5) \times 10^8$ M⁻¹ s⁻¹, respectively.

(49) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

Table 3. Activation Energies and Preexponential Factors for Triplet Decay of the Diketones **1**–**3**

	acetonitrile		methanol	
diketone	E_a (kcal/mol)	log A	E_a (kcal/mol)	log A
1-*rac*	6.4 (0.1)[a]	11.5 (0.1)[a]	5.9 (0.3)[a]	10.8 (0.3)[a]
2-H-*meso*	6.4 (0.1)[b]	11.4 (0.1)[b]	6.6 (0.1)[b]	11.1 (0.1)[b]
2-CH₃-*meso*	5.8 (0.1)[a]	11.6 (0.1)[a]	6.6 (0.2)[a]	11.7 (0.2)[a]
3-H-*meso*	6.0 (0.1)[b]	10.6 (0.1)[b]	7.0 (0.1)[b]	10.9 (0.1)[b]
3-OCH₃-*meso*	4.2 (0.2)[a]	10.7 (0.2)[a]	5.6 (0.1)[a]	11.4 (0.1)[a]

[a] From a single experiment; the error in parentheses represents statistical deviations of the data from a linear fit. [b] From two independent measurements; the error refers to an average deviation.

Table 4. Calculated Steric Energies and Relative Energies with Respect to the Lowest Energy Conformation for Both Diastereomers of **2-H** and **3-H** and Energy Barriers from the Lowest Energy Conformation for the Racemic Conformers of **2-H** and **3-H**
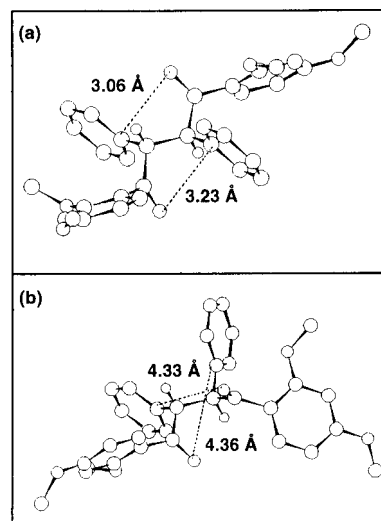
compound	conformation	min energy (kcal/mol)	rel energy (kcal/mol)	energy barrier (kcal/mol)
2-H-*meso*	**H**-*anti*	53.3	0	
	H-*gauche*	56.4	3.1	
2-H-*rac*	**H**-*anti*	51.1	0	
	Ph-*anti*	54.6	3.5	8.4
	Bz-*anti*	57.5	6.4	8.0
3-H-*meso*	**H**-*anti*	56.8	0	
	H-*gauche*	61.9	5.1	
3-H-*rac*	**H**-*anti*	55.3	0	
	Ph-*anti*	58.5	3.2	8.5
	Bz-*anti*	60.6	5.3	7.5

performed for both diastereomers of **2-H** and **3-H** to establish the difference in energies of their conformers. These calculations include the effect of π delocalization by explicitly identifying the phenyl groups, carbonyl moieties, and methoxy oxygen atoms. It was confirmed for both diastereomers that the conformers with lowest energy correspond to the **H**-*anti* conformers (Table 4). The relative energies for the other conformations are high enough to ensure that, under equilibrium conditions, most molecules will be populated in the **H**-*anti* ones. For the meso diastereomers, the **H**-*anti* conformation has the β-phenyl rings and the carbonyl moieties in close proximity, whereas in the **H**-*anti* conformation of the racemic compound, the shortest contact between these groups is larger than 4.3 Å, and the carbonyl oxygen is not directed toward the π cloud of the phenyl ring (Figure 6). All other conformations, i.e., **H**-*gauche* for the meso and **Ph**-*anti* and **Bz**-*anti* for the racemic diastereomers, have at least one contact between the carbonyl and β-phenyl moieties of 3 Å.[50] It is important to note that the interconversion barriers for the racemic diastereomers were calculated by varying the torsional angle about the central C–C bonds and reoptimizing the structure at each new angle. This procedure does not necessarily follow the lowest energy pathway. For this reason, the computed energy barriers (Table 4) represent upper limits.

Discussion

Apart from establishing the conformational dependence of triplet lifetimes, our rationale to study diketones **1**–**3** was twofold: first, to establish the extent of charge transfer for the intramolecular β-phenyl quenching for diketones **2**; second, to investigate the influence of the configuration of the lowest triplet-excited state on the lifetimes of diketones **1**, **2-H**-*meso*, and **3-H**-*meso*. It has long been known that substitution with electron-donating substituents in alkanophenones can invert the

(50) The calculated structures for the lowest energy conformers of **2-H** and **3-H** are given in the Supporting Information.

Figure 6. Structures for the calculated lowest energy **H**-*anti* conformations of **3-H**-*meso* (a) and **3-H**-*rac* (b). The shortest contacts between the carbonyl oxygen atoms and a carbon on the β-phenyl rings are shown.

ordering of proximate n,π* and π,π* levels and cause the lowest excited state to be π,π* in character.[51,52] Thus, the lowest excited triplet is purely n,π* in the case of **1**, while it is π,π* for diketones **2** and **3**.

The significant results from Table 1 are the remarkable diastereomeric discrimination and the variation in the triplet lifetimes, which range from <10 ns to 30 μs. While the former evidently pertains to conformational factors, the latter is traceable to substituent effects. Also, one observes shorter triplet lifetimes for **2-OCH₃**-*rac* versus **2-H**-*rac* and for **3-OCH₃**-*rac* versus **3-H**-*rac* caused by remote *p*-methoxy substitution in the β-phenyl ring. In the ensuing discussion, these observations are rationalized by addressing first the diastereomeric discrimination followed by substituent effects.

Diastereomeric Discrimination. A perusal of the results in Table 1 reveals that the triplet lifetimes for all the meso diastereomers, except for **2-CF₃**-*meso,* are significantly shorter than those for the corresponding racemic ones. We have established for diketones **2-H** that the difference in the lifetimes for the two isomers is, indeed, real and not due to the presence of an adventitious impurity, which efficiently quenches the triplet-excited state in one of the diastereomers.[35] To reconcile the different lifetimes for the racemic and meso diastereomers, the effect of intramolecular self-quenching and intramolecular triplet energy transfer on the lifetimes for the two diastereomers should be considered. The importance of these two factors has been examined in detail by Wagner and co-workers in analogous diketones.[53]

The intramolecular self-quenching which corresponds to the deactivation of one of the triplet-excited carbonyls by the other ground-state carbonyl in the same molecule can, in principle, occur. The rate constant for such a process in analogous n,π*-excited 1,2-dibenzoylethane has been shown to be 1.7×10^7 s^{-1}.[53] To investigate the importance of the intramolecular self-quenching, the triplet lifetimes of diketones **6** and **7** were measured. These lifetimes are comparable with those for the monoketones **4** and **5**, suggesting that intramolecular self-

(51) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978; p 628.

(52) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991; p 538.

(53) Wagner, P. J.; Freking, H. W., Jr. *Can. J. Chem.* **1995**, *73*, 2047.

quenching is not an important deactivation process.[54] Moreover, the lowest energy conformations of the racemic diastereomers of **2** (**H**-*anti*, Table 4) have the two benzoyl moieties in a gauche relationship, whereas for the **H**-*anti* conformation of the meso compound, the benzoyl groups are in an anti relationship. Consequently, the intramolecular self-quenching process should be faster for the racemic diastereomers. Therefore, the lifetimes for the racemic compounds would be expected to be shorter when compared to those for the meso isomers if intramolecular quenching was occurring. This is clearly not the case, since the lifetimes of the racemic diastereomers are longer than those measured for the respective meso compounds.

The intramolecular energy transfer between the two carbonyl moieties in diketones has been shown to occur with a rate constant of the order of 10^9 M^{-1} s^{-1}.[53,55] In the case of compounds **1**−**3**, this intramolecular energy-transfer process is isoenergetic, which would cause the excitation energy to reside on either of the carbonyl chromophores for half of the time. This intramolecular energy transfer cannot affect the triplet decays differently to account for the observed differences in the triplet lifetimes of the diastereomers.

As mentioned at the outset, the deactivation of triplet states by β-aryl rings occurs through an efficient intramolecular quenching mechanism.[13,28−33] The quenching process is believed to involve a conformation in which the triplet-excited ketone and the β-phenyl ring are sufficiently close (gauche geometry) to permit efficient overlap between the electron-deficient n-orbital on oxygen and the π-orbitals of the electron-rich β-phenyl ring. In this respect, the intramolecular β-phenyl quenching is expected to occur from the ketone excited states with n,π* configuration. The quenching of the π,π* triplet-excited ketone, which readily occurs for arenes as an inter-molecular process, is not involved in the case of β-phenylpro-piophenones. This is probably because the geometry with an effective overlap between the β-phenyl ring and the π-system does not occur in these ketones.[26,31,33] Therefore, we will consider throughout our discussion that β-phenyl quenching occurs only from excited states with n,π* configuration. The differences in the triplet lifetimes for the meso and racemic diastereomers of **1**−**3** are a consequence of how efficiently β-aryl quenching contributes to the triplet deactivation for each diastereomer. Since the diastereomers differ only in terms of spatial arrangement of atoms, their lowest energy conformations are of immediate interest. We assume, based on the calculations performed for **2-H** and **3-H**, that for all compounds the conformations with lowest energy for the meso as well as the racemic diastereomers are the **H**-*anti* conformers.

The lowest triplet-excited state (T$_1$) in the case of diketones **1** is n,π* in character, as is the case with β-phenylpropiophe-none. The intramolecular quenching in the latter occurs so efficiently that its triplet lifetime is short (<1 ns), and the α-cleavage reactions cannot compete with triplet deactivation.[13] For this reason, β-phenylpropiophenone is relatively photostable and has a very low photodecomposition quantum yield of ca. 10^{-3}.[13] In the case of **1**-*rac*, the photodecomposition yield increases when compared to that of β-phenylpropiophenone because the **1**-*rac* triplet lifetime is much longer, the carbon-centered radical formed is more stable, and β-cleavage could be an additional photodecomposition process. The large con-tribution from the photocleavage process is observed in the laser

flash photolysis studies, where a significant amount of residual absorption is apparent after the decay of the triplet state. In this respect, it is important to establish if photodecomposition is the factor responsible for the different triplet lifetimes observed for **1**-*meso* and **1**-*rac*, since the shorter lifetime for the former could be due to an enhancement of its photodecomposition rate constants. However, the photodecomposition yield for **1**-*meso* was much smaller than that for **1**-*rac*. This result shows that the shorter triplet lifetime for **1**-*meso* is not due to an enhanced photodecomposition rate constant. On the contrary, the larger photodecomposition observed for **1**-*rac* is due to the longer triplet lifetime of this diastereomer, which makes it possible for photocleavage to compete with triplet deactivation.

The lifetimes for β-phenylpropiophenones are shorter than 1 ns at 300 K, and they are not very dependent on the nature of the substituents on the β-phenyl ring.[13] These results were explained by suggesting that molecular motions to achieve the quenching conformation are rate limiting. In the case of compound **1**, the triplet lifetime is given by the sum of the intramolecular β-phenyl quenching process (k_β) and the pho-tocleavage rate constant ($k_{cleavage}$):[56]

$$k_d = k_\beta + k_{cleavage} \qquad (3)$$

In the case of **1**-*meso*, the lowest energy conformation (**H**-*anti*) has the β-phenyl rings gauche to the benzoyl moieties, and β-phenyl quenching after excitation occurs so readily as to preclude observation of the triplet in the nanosecond time domain. The small photodecomposition quantum yield when compared to that observed for **1**-*rac* also indicates that the β-phenyl quenching rate constant is much larger than the photocleavage rate constant. However, in the case of **1**-*rac*, the phenyl rings lie away from the benzoyl groups in the lowest energy **H**-*anti* conformation. For this reason, the β-phenyl quenching does not readily occur since it requires a rotation from the **H**-*anti* to either the **Bz**-*anti* or **Ph**-*anti* conformers. This rotation is slow, and photocleavage readily competes with intramolecular β-phenyl quenching. Based on the cleavage rate constant estimated for β-phenylpropiophenone of 10^6 s^{-1},[13] it is evident that $k_{cleavage}$ contributes considerably ($\geq$30%) to the triplet decay rate constant of **1**-*rac*. Therefore, the observed triplet decay rate constants constitute an upper limit for the β-phenyl quenching rate constant in **1**-*rac*. Since β-phenyl quenching for triplet **1**-*rac* requires bond rotation, the rate constants for these bond rotations are remarkably smaller ($\leq$2.8 $\times$ 10^6 and $\leq$ 2.3 $\times$ 10^6 s^{-1} in acetonitrile and methanol, respectively, assuming that ϕ_β is smaller than 70%) than the motion necessary for the intramolecular quenching in β-phe-nylpropiophenone (1×10^9 s^{-1}). This large difference suggests that rotation is much more hindered in the case of **1** than that for β-phenylpropiophenone. The activation energy for the β-phenyl quenching process in β-phenylpropiophenone has not been determined.[13] However, this value can be estimated from the activation energy for β-phenyl-*p*-methoxypropiophenone (4.3 kcal/mol),[13] taking into account that its activation energy incorporates an energy difference of ca. 2−3 kcal/mol between the T$_1$ state with π,π* configuration and the T$_2$ state with n,π* configuration.[13,49,57] Thus, the activation energy for β-phenyl quenching in β-phenylpropiophenone is ca. 1.3−2.3 kcal/mol. From the temperature dependence on the triplet decay kinetics of **1**-*rac*, we obtained activation energies for the triplet decay
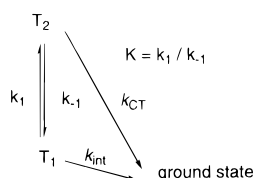
(54) Only in the case of **7** in methanol is a shortening of the lifetime observed, which may be due to an inefficient self-quenching process (3 $\times$ 10^4 s^{-1}).

(55) Bays, J. P.; Encinas, M. V.; Small, J., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 727.

(56) The photocleavage rate constant incorporates the rate constant for α-cleavage as well as any contribution from a β-cleavage process.

(57) Encinas, M. V.; Lissi, E. A.; Lemp, E.; Zanocco, A.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1856.

Scheme 2

of 5.9−6.4 kcal/mol (Table 3). These energies obviously include the activation barriers for photocleavage and β-phenyl quenching. Nevertheless, the activation energy for β-phenyl quenching in **1**-*rac* is 4−5 kcal/mol higher than that for β-phenylpropiophenone, which can readily account for the decrease of ca. 3 orders of magnitude for the β-phenyl quenching rate constant in **1**-*rac*. The marginal difference observed in the lifetimes for **1**-*rac* in the two different solvents, with moderate difference in their viscosities (η(methanol) = 0.55 and η(acetonitrile) = 0.36 cP),[58] is consistent with the rate-limiting step for the intramolecular quenching process being the bond rotation.

The introduction of *p*-methoxy substituents in aryl ketones, such as diketones **2** and **3**, leads to the stabilization of the triplet with π,π^* configuration relative to the n,π^* triplet and to a reduction of the photoreactivity of these compounds.[51,52] There are two models to explain this decrease in reactivity for ketones where the lowest triplet state has a π,π^* configuration. One model assumes that the reactivity occurs from the lowest triplet which has a mixed character, whereas the second model assumes that the upper n,π^* triplet state has to be thermally populated for reactions to occur.[49,59] The latter model was first proposed to explain the difference observed for the intramolecular hydrogen abstraction efficiency of phenyl ketones for which the lowest triplet states had a ^{3}n,π^* or $^3\pi,\pi^*$ configuration.[49] Steel and co-workers considered both models and showed that they can be differentiated by measuring the temperature dependence of the photoreaction rate constants.[59] In the case of the mixing model, the changes in reactivity would appear in the preexponential factors, whereas the equilibration model predicts higher activation energies as the energy gap between the lowest triplet with π,π^* character and the T$_2$ state with n,π^* character increases. The reactivity differences for the intramolecular hydrogen abstraction reactions involving triplet acetophenone derivatives were mainly due to changes in the activation energies, which is consistent with the equilibration model.[59] Additional support for the equilibration model is provided by the fact that *p*-methoxy substitution on aryl alkyl ketones led to the same increase in the activation energies for reactions that have different mechanisms, such as the hydrogens abstraction and α-cleavage processes.[57] Furthermore, the slower intramolecular deactivation of β-phenyl-*p*-methoxypropiophenone when compared to that of β-phenylpropiophenone has been explained using the thermal equilibration model.[13] For this reason, we adopt this model to explain the differences for the triplet lifetimes of the meso and racemic diastereomers of diketones **2** and **3**.

The intramolecular β-phenyl quenching and the photocleavage reactions occur only for the triplet state with n,π^* character (see above). For this reason, β-phenyl quenching for compounds **2** and **3** occurs from the upper triplet state (Scheme 2), and the triplet lifetimes of both diastereomers of these compounds are longer than that for **1**. The overall triplet decay (k_d) can be

described by the sum of the reactivities from the T$_1$ and T$_2$ states, taking into account the relative populations in each state. Provided that there exists a rapid equilibrium between the T$_1$ and T$_2$ states, i.e., $k_{-1} > k_{CT}$ and $k_1 > k_{int}$, the triplet decay can be described by eq 4, where K is the equilibrium constant between the two triplet states:

$$k_d = k_{int} + Kk_{CT} + Kk_{cleavage} \qquad (4)$$

Thus, the overall triplet decay rate constant is given by the sum of the intrinsic triplet decay, the product of the equilibrium constant and the rate constant for β-phenyl quenching, and the product of the equilibrium constant and the photocleavage rate constant. Since the amount of transients formed due to the photocleavage reaction for **2** and **3** is comparable to that observed for β-phenyl-*p*-methoxypropiophenone and much smaller than that for **1**-*rac*, we will consider that only the first two terms contribute significantly for the triplet decay of diketones **2** and **3**. The intrinsic decay rate constants in diketones **2** and **3** can be equated to those for the model compounds **6** and **7**, respectively. From the lifetime for **1**-*meso*, we have established that k_{CT} is $>10^8$ s^{-1}. The value of K is directly related to the energy spacing between T$_1$ and T$_2$. In this respect, the value of K should be smaller for **3** than that for diketones **2**, since the dimethoxy substitution in the benzoyl ring leads to additional stabilization of the π,π^* state. In addition, the methoxy substitution of the benzoyl rings will lower the electron affinity of the carbonyl group, which would lead to a decrease of k_{CT}. Both of these factors are expected to decrease the efficiency of the β-phenyl quenching reaction in **3** when compared to that in **2**.

The significant differences observed for the triplet lifetimes of the meso and racemic diastereomers of **2** and **3** can now be rationalized *on the basis of conformational preferences in the T$_1$ state and by considering the fact that the lifetime for T$_2$ is too short to permit bond rotations over torsional barriers*. The latter is easily established by comparing the T$_2$ lifetime (<1 ns) with that to overcome the rotational barrier in the case of **1**-*rac*, which is ≥250 ns. For this reason, the conformation in the T$_2$ state should be considered to be frozen in the geometry defined by the T$_1$ state from which thermal population occurs. As a result, population of the T$_2$ state in a conformation in which the phenyl ring and the carbonyl group are in an anti relationship does not lead to β-phenyl quenching, and the triplet decay will be determined by the intrinsic decay (k_{int}) from the T$_1$ state. On the other hand, when T$_2$ is populated in a conformation in which the β-phenyl is gauche to the excited carbonyl group, intramolecular quenching (Kk_{CT}) can occur efficiently, so that depopulation through this channel primarily dictates the triplet decay.

In the case of racemic diastereomers, the β-phenyl ring and the carbonyl are distal in the lowest energy conformations, and when the T$_2$ state is populated no deactivation by β-phenyl quenching occurs. Hence, the triplet decay is determined by k_{int}, and the lifetimes are long. Indeed, the lifetimes in the case of **2-H**-*rac* correspond to those measured for **6**, which lacks the phenyl rings in the β-positions. In the case of the meso diastereomers, both conformations have at least one carbonyl group in a gauche relationship with a β-phenyl ring. Consequently, irrespective of the conformation in which T$_2$ is populated, the triplet decay occurs primarily through intramolecular quenching (k_β), and hence the lifetimes are shorter than those for the racemic diastereomer. In addition, no slow decay component is expected for the **H**-*gauche* conformer of

(58) Scaiano, J. C. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 343.

(59) Berger, M.; McAlpine, E.; Steel, C. *J. Am. Chem. Soc.* **1978**, *100*, 5147.

the meso diastereomers, since intramolecular energy transfer between the benzoyl moieties is fast.

The above simple explanation which accounts for the discrimination in the triplet lifetimes of the meso and racemic diastereomers does not explain why the lifetime of **3-H**-*rac* is shorter than that observed for the model compound **7** and why *p*-methoxy substitution in the β-phenyl ring of the racemic diastereomers of **2-OCH$_3$** and **3-OCH$_3$** also leads to a reduction of the triplet lifetimes when compared to those of the model compounds **6** and **7**. There are two possibilities for the increase in the overall triplet deactivation rate constant: either a contribution from β-phenyl quenching (Kk_{CT}) or a contribution from the photocleavage reactions ($Kk_{cleavage}$) (eq 4).

The efficiency of the α- and β-cleavage reactions (Scheme 1) for compounds **3-H, 2-OCH$_3$,** and **3-OCH$_3$** is enhanced when compared to that for **2-H** because substitution of electron-donating groups on the benzoyl moiety will stabilize the benzoyl radicals formed in the α-cleavage reactions, whereas *p*-methoxy substitution on the β-phenyl ring stabilizes the radical formation in both cleavage processes. If the increase in k_d is solely due to an enhancement in the photodecomposition yield, the cleavage quantum yields can be equated to $(k_d - k_{int})/k_d$, where k_{int} corresponds to the lifetime of the model compounds **6** and **7**. This analysis leads to quantum yields in excess of 0.4. Furthermore, in the laser flash photolysis studies, the residuals observed after the triplet decay correspond to the radicals formed. Only a slight increase was observed for the residuals when **3-H**-*rac*, **2-OCH$_3$**-*rac*, and **3-OCH$_3$**-*rac* are compared to **2-H**-*rac*. In the latter case, the photocleavage reaction is not significant since the **2-H**-*rac* triplet lifetime is the same as that for the model compound **6**. The high quantum yields calculated above and the small increase in the residuals observed in the kinetic studies are clearly inconsistent with the decrease of the triplet lifetimes for **3-H**-*rac*, **2-OCH$_3$**-*rac*, and **3-OCH$_3$**-*rac* being solely due to an increase in the photocleavage process ($Kk_{cleavage}$).

The second possibility for the decrease in the triplet lifetimes of the racemic diastereomers of **3-H, 2-OCH$_3$,** and **3-OCH$_3$** is a contribution of β-phenyl quenching to the excited triplet deactivation. This intramolecular quenching process can occur from the **Ph**-*anti* and **Bz**-*anti* conformers. Population of these conformers can occur either directly upon excitation or by rotation from the most stable **H**-*anti* conformation during the triplet lifetime. There are two limiting scenarios for the relationship between the time necessary for bond rotation and the triplet lifetimes. If rotations are slow compared to the triplet lifetime, excitation into T$_1$ leads to the formation of three conformers, each of which would be considered to be frozen in their staggered conformation. Consequently, one would expect a decay which corresponds to the sum of two exponentials in which the fast component corresponds to the decay through β-phenyl quenching of the **Ph**-*anti* and **Bz**-*anti* conformations and the longer lifetime corresponds to the decay from the **H**-*anti* conformation. No double-exponential decays were observed, which suggests that the **Ph**-*anti* and **Bz**-*anti* conformations are not directly excited to a significant extent. In addition, the relative population of the triplet conformers in this scenario corresponds to their equilibrium population in the ground state. Based on the relative energies calculated for **2-H**-*rac* and **3-H**-*rac*, only a very small amount of triplets (<1%) would be excited in the **Ph**-*anti* and **Bz**-*anti* conformations. In this respect, the calculations are in agreement with the fact that only a monoexponential decay was observed. Likewise, for a scenario in which the rotation rate constants would be of the same order

of magnitude as the deactivation rate constants, one would predict a decay which corresponds to the sum of two exponentials (small and large), with each exponential factor representing a combination of all rate constants.

The second limiting scenario occurs when the T$_1$ lifetime is much longer than the time required for conformational equilibration to be achieved. A single-exponential decay is expected, which is given by the sum of the decays from each conformer with fractional equilibrium populations taken into account. In this respect, the decay from the **Ph**-*anti* and **Bz**-*anti* conformers formed by the rotation from the **H**-*anti* conformation corresponds to a leakage pathway because β-phenyl quenching from the former conformers is much faster than the intrinsic decay from the **H**-*anti* conformation. The shorter lifetime for the diketones with *p*-methoxy substitution on the β-phenyl ring can be understood on the basis of an enhancement of the β-phenyl quenching rate constant (Kk_{CT}, see below), which would lead to a more efficient leakage through the **Ph**-*anti* and **Bz**-*anti* conformations. In contrast, the increased triplet decay rate constant for **3-H**-*rac* when compared to that of **2-H**-*rac* is more difficult to interpret. One explanation would be that the rotational barriers between the conformers are lower for **3-H** than those for **2-H**. Unfortunately, the calculations performed do not lead to a conclusive answer to this question, since the calculated barriers may not represent the lowest energy path between the conformers. For this reason, subtle changes in the barriers which would lead to a change in rate constants by a factor of ca. 2 ($\sim$0.5 kcal/mol) are within the errors of these calculations.

Substituent Effect. In the case of the meso diastereomers of **2** and **3**, where β-phenyl quenching is the rate-limiting factor for the triplet decay, the triplet lifetime depends on the nature of the para substituent on the β-phenyl ring (Table 1). While the lifetime for **2-CF$_3$**-*meso* approaches that for **2-CF$_3$**-*rac*, the lifetime for **2-OCH$_3$**-*meso* is so short as to be undetectable on the nanosecond time scale. This dependence can be explained by the electronic effect of the substituents on k_{CT}, where electron-donating groups enhance this rate constant, whereas electron-withdrawing groups decrease the charge-transfer efficiency. Assuming a lifetime of 10 and 3 ns for **2-OCH$_3$**-*meso* in methanol and acetonitrile, respectively,[60] a linear correlation is obtained for the triplet decay of meso diastereomers of diketones **2** with Hammett σ^+ constants of the substituents (ρ^+ = -1.9 ± 0.2 and -2.1 ± 0.1 in methanol and acetonitrile, respectively), which falls in excellent agreement with that reported for a broad set of β-phenyl-*p*-methoxypropiophenone derivatives (ρ^+ = -1.8 ± 0.2 in methanol).[33] This clearly attests to the fact that Kk_{CT} is the process that controls the decay in the meso diastereomers of the diketones **2** and **3**. In contrast, only a weak correlation with σ^+ was observed for n,π*-excited β-phenylpropiophenones,[13] where rotational barriers probably constitutes the rate-limiting step.

The activation energies measured for the triplet decay of the meso diastereomers incorporate the energy difference between the T$_2$ and T$_1$ states and the activation energy for the β-phenyl quenching:

$$E_a = E(T_2 - T_1) + E_a(\beta) \qquad (5)$$

The preexponential factors in acetonitrile (Table 3) do not depend on the nature of the substituent on the β-phenyl ring.

(60) A lifetime of 10 ns for **2-OCH$_3$**-*meso* in methanol was assumed since the signal corresponding to the triplet was not detected within the time resolution of the nanosecond laser flash photolysis setup. This value was considered reasonable by comparison to an estimated lifetime of 8 ns for β-(4-anisyl)-*p*-methoxypropiophenone.[33] Since the lifetimes in acetonitrile are approximately 3-fold shorter when compared those in methanol, a lifetime of 3 ns was derived for **2-OCH$_3$**-*meso* in acetonitrile.

For this reason, the data in acetonitrile will be employed to analyze the effect of substituents on the activation energies. In methanol, a more complex behavior is observed, probably due to the effect of hydrogen bonding of the solvent to the diketone. Indeed, the effect of hydrogen bonding on the rate of β-phenyl quenching has been proposed before for the intramolecular triplet quenching of β-phenylpropiophenone[13] and α-guaiacoxy-acetoveratrone.[61]

The value for the spacing between the T_1 and T_2 states may, in principle, be determined from the phosphorescence spectra. Unfortunately, the structureless broad spectral features did not permit unequivocal identification of the maxima for n,π* and π,π* transitions. Assuming that substitution on the α-phenyl ring in the diketones does not affect the spacing between these levels, one calculates that the difference in the activation energies between **2-H**-*meso* and **2-CH₃**-*meso* and between **3-H**-*meso* and **3-OCH₃**-*meso* is 0.6 and 1.8 kcal/mol, respectively. The lower activation energies when a *p*-methyl or *p*-methoxy substituent is introduced in the β-phenyl ring are in agreement with the explanation that electron-donating substituents increase the charge-transfer rate constant for β-phenyl quenching.

The lifetimes for the meso diastereomers of compound **3** are much longer than those for compounds **2**. For example, the dimethoxy substitution causes a 3-fold increase in triplet lifetime for **3-H**-*meso* when compared to that for **2-H**-*meso*. Also, the triplet, which is not observable in the case of **2-OCH₃**-*meso*, becomes sufficiently long-lived in **3-OCH₃**-*meso* to be monitored in a nanosecond time scale. As expected, the dimethoxy substitution increases the energy spacing between T_2 and T_1 by 0.4 kcal/mol. However, changes in the preexponential factor also contribute to the increase in the lifetimes, suggesting that the steric crowding created by the substituent at the ortho position is important.

Tunability of the Triplet Lifetimes. The present investigation has shown that conformational preferences and electronic factors can be exploited to modulate the triplet lifetimes over a range which spans 4 orders of magnitude. This property can be explored to probe organized environments. The tunability of lifetimes is related to the configuration of the lowest excited state and the conformational preferences, which determine the competition between intrinsic decay and intramolecular β-phenyl quenching. In the case of the meso diastereomers of **1**–**3**, the lifetimes are always determined by β-phenyl quenching because both staggered conformations have at least one carbonyl moiety and the β-phenyl group in a gauche relationship. The lifetimes can be tuned by changing the configuration of the lowest triplet state and, in the case of π,π* triplets, by changing the T_1–T_2 energy spacing. Further control can be achieved by changing the charge-transfer efficiency with appropriate substituents on the β-phenyl ring. In addition, the lifetimes of the meso diastereomers are influenced by the nature of the solvent, and this property can be explored to probe the local environments of supramolecular structures.

The longer triplet lifetimes for the racemic diastereomers are due to the anti relationship of the carbonyl and β-phenyl moieties for the conformer with lowest energy, which precludes the intramolecular β-phenyl quenching process. However, some variability of the triplet lifetimes has been observed, probably due to leakage through the **Ph**-*anti* and **Bz**-*anti* conformers from which β-phenyl quenching is possible. Inclusion of the racemic diketones in appropriate supramolecular structures could lead

to a larger population of the **Ph**-*anti* and **Bz**-*anti,* which should lead to shorter lifetimes or the observation of double-exponential decays. In this respect, the complexation of the enantiomers of the racemic diketones to supramolecular structures with chiral environments could lead to the observation of different triplet lifetimes for each enantiomer.

In conclusion, a remarkable diastereomeric discrimination is demonstrated in the triplet lifetimes of racemic and meso diastereomers of a broad set of 1,4-diketones. The differences in the lifetimes for meso and racemic diastereomers are reconciled from preferential operation of intramolecular β-phenyl quenching in the former. It is shown that, by making an appropriate choice of the substitution in the β-phenyl ring and by controlling the spacing between the n,π* and π,π* triplet states through substitution in the benzoyl group, the triplet lifetimes can be modulated. The detailed study on a broad set of substrates has permitted an appreciably longer lifetime (230 ns) to be measured for a pure n,π* triplet-excited β-phenylpro-piophenone derivative for the first time.

Experimental Section

General Aspects and Synthesis. The detailed description of the general instrumentation, synthesis of various compounds, and their characterization is provided in the Supporting Information.

Laser Flash Photolysis. Nanosecond laser flash photolysis experiments were carried out using the pulses from a Lumonics Excimer laser (308 nm) or a Spectra Physics Nd:YAG laser (266 nm). The full details of signal detection, monitoring, and data processing have been described elsewhere.[62]

The transient absorption spectra were recorded using a flow system to avoid interference of the photoproducts resulting from several laser shots. For this purpose, a freshly prepared solution was pumped, under nitrogen atmosphere, through a custom-designed Suprasil-cell (7 × 7 mm) at a rate of 1.5–2.0 mL/min. As a result, a fresh solution was irradiated by each laser shot. For kinetic measurements, the samples were contained in cuvettes made of Suprasil quartz cells (7 × 7 mm), sealed with rubber septa, and deoxygenated with nitrogen for >15–20 min. The absorptions of the solutions at the excitation wavelengths were in the range 0.07–0.7. Approximate concentrations for an absorbance of 0.3 in the Suprasil cells are as follow: **1**, (2–3) × 10⁻⁵ M at 266 nm; **2**, (0.5–1) × 10⁻⁴ M at 308 nm; and **3**, (1–2) × 10⁻⁵ M at 308 nm.

For temperature-dependent studies, a Brucker B-VT-100 temperature control system was employed to control the sample temperature. The sample holder was surrounded by an in-house quartz jacket, which was equipped with four windows for excitation and monitoring beams. The liquid nitrogen, which was boiled off from the Dewar reservoir and allowed to pass through a heating element, was let into the quartz jacket. The degree of heating was set by the Bruker control unit. Prior to each measurement, the sample was allowed to equilibrate at the defined temperature for 15–20 min. The temperature of the sample holder was registered by a thermocouple (Omega, model DP 2000), and the information was transferred to a computer.

Photodecomposition Studies. The relative photodecomposition rates for both diastereomers of diketones **1** and **2-H** in acetonitrile and methanol were followed by HPLC (Hewlett-Packard series 1100). The samples were filtered through Millipore filters into quartz cells. After N₂ was bubbled for at least 25 min, the absorbances at 254 nm were matched by addition of deoxygenated solvent. These solutions were irradiated in a Rayonet reactor with four 254-nm lamps, and samples were drawn at appropriate irradiation times. These samples were analyzed by UV–vis absorption and HPLC (3:1 acetonitrile/water, 0.5 mL flow, 30 °C, Supelco Supelcosil LC-PAH column, 10 cm × 4.6 mm, 3 μm particle size, detection at 250 nm for **1** and 280 nm for **2**). Several photodecomposition products were observed by HPLC. The purity of the peak for the diketone was checked by the HP series 1100 data analysis software by comparison of the absorbance spectra taken

(61) Schmidt, J. A.; Goldsmidt, E.; Heitner, C.; Scaiano, J. C.; Berinstain, A. B.; Johnston, L. J. In *Photochemistry of Lignocellulosic Materials*; Heitner, C., Scaiano, J. C., Eds.; American Chemical Society: Washington, DC, 1993; Vol. 531, p 122.

(62) Liao, Y.; Bohne, C. *J. Phys. Chem.* **1996**, *100*, 734.

at regular intervals across the width of the peak. Repeated injections of equal volumes of the same sample led to a reproducibility of 1% of the absorption values measured. The rate of decomposition was determined from the amount of decomposed diketone measured from the decrease in the absorption of the HPLC peak corresponding to the diketone. The photodecompositions of **1**-*meso*, **2-H**-*rac*, and **2-H**-*meso* were kept below 10%, whereas the decomposition for **1**-*rac* was kept below 30%.

Calculations. Molecular mechanics calculations on **2-H** and **3-H** were carried out using the MMX force field in the PCMODEL program (Serena Software, Bloomington, IN). The effect of conjugation was explicitly included by treating the carbonyl group, phenyl rings, and methoxy substituents as π atoms. Minima corresponding to **H**-*anti* and **H**-*gauche* conformers were optimized in the meso compounds, while H-*anti*, Ph-*anti*, and Bz-*anti* were considered for the racemic structures. Since the molecules are sterically crowded and considerable conformational flexibility is possible, several initial geometries (typically 10) were used to obtain the lowest energy conformations. Barriers for interconversion between the different minima were calculated by varying the torsional angle about the central C−C bonds in 2-deg

intervals and reoptimizing the structure at each stage. This procedure need not necessarily follow the lowest energy pathway. Hence, the computed values represent upper limits for the barriers.

Supporting Information Available: Details of the general instrumentation, syntheses of various compounds, and figures showing the calculated structures of the staggered conformations of **2-H** and **3-H** with the lowest calculated energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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