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Addition of the Carbonyl Oxygen to the *ipso*- or *ortho*-Carbon Atoms of the *β*-Phenyl Ring Followed by Intersystem Crossing and Rapid Relaxation to the Ground-State Ketones: A Mechanism for *β*-Phenyl Quenching of the First Triplet Excited States of Derivatives of *β*-Phenylpropiophenone

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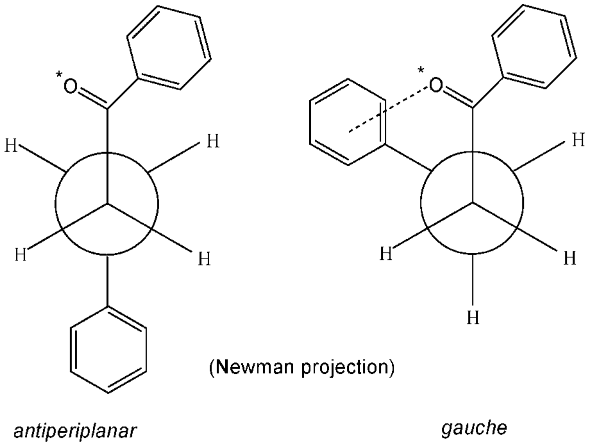
The first triplet excited states of β-phenylpropiophenone **1a** and derivatives are known to have unusually short triplet lifetimes. On the basis of pronounced substituent and solvent effects observed in the case of 4-methoxy-β-phenylpropiophenone **1b**, a mechanism involving substantial electron transfer has been assumed to be operative. This contribution outlines an alternative mechanism involving addition of the excited carbonyl moiety at the ipso (preferred) or ortho positions of the β-phenyl ring. The triplet biradicals thus formed may undergo rapid intersystem crossing to the singlet manifold. On the singlet hypersurface, the biradicals are not predicted to be minima, relaxing to the singlet ground-state ketones. Overall, this addition, intersystem crossing, elimination sequence provides a plausible reaction pathway for β-phenyl quenching. Calculated activation enthalpies and substituent effects are in agreement with experimental data published in the literature.

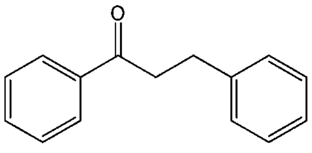
Introduction

n,π* triplet excited states of aryl ketones bearing a phenyl ring in β-position, such as β-phenylpropiophenone **1a**, are quenched very efficiently by an intramolecular reaction called β-phenyl quenching (BPQ).[1–8] While the exact mechanism of BPQ has not yet been elucidated, experimental evidence collected so far, including the observation of substantial substituent and solvent effects, indicates that the reaction involves a relatively tight transition state and a substantial amount of charge transfer.[3,5] Generally, electron-withdrawing substituents in the β-phenyl ring significantly slow down the reaction, whereas π-electron donors such as a methoxy group in the para position of the β-phenyl ring increase the rate of BPQ.[5] In contrast to **1a**, which has a lowest *n*,π* triplet excited state, 4-methoxy-β-phenylpropiophenone **1j** has been reported to have a lowest triplet excited-state of π,π* character, but its slightly (ca. 2 kcal mol^{-1}) higher lying *n*,π* triplet excited-state is populated thermally.[9,3]

BPQ has been assumed to occur via an interaction of the carbonyl moiety of the *n*,π* triplet excited state with the π system of the β-phenyl ring, yielding an intramolecular exciplex that subsequently relaxes to the ketone singlet ground state.[3] This π interaction requires the acyl and phenyl substituents in the RCO−CH$_2$−CH$_2$−Ph moiety to be gauche ($\theta \approx 60°$), while the preferred antiperiplanar arrangement ($\theta \approx 180°$) does not allow for such an interaction.

Polar effects are significantly more prominent in 4-methoxy-β-phenylpropiophenone **1j** and derivatives than in parent β-phenylpropiophenone **1a**.[3,5] The relatively small influence of substituents in the β-phenyl ring observed for **1a** and derivatives has been attributed to the antiperiplanar → gauche interconversion being the rate-determining step for BPQ in **1a**, while the less reactive **1j** shows more selectivity due to its π,π* character.[3]




1a

In this contribution, I introduce an alternative mechanism for BPQ that is consistent with the experimental data, see Scheme 1. On the basis of computational chemistry investigations, I assume that BPQ occurs by addition of the carbonyl oxygen to the ipso (preferred) or ortho (less favorable) carbon atoms of the β-phenyl ring, yielding intermediary triplet biradicals **2** and **3**. The triplet and singlet energies are nearly degenerate for **2** and **3**, thus allowing for efficient intersystem crossing to the singlet manifold. On the singlet hypersurface, neither **2** nor **3** are minima at the levels of theory employed in this study.

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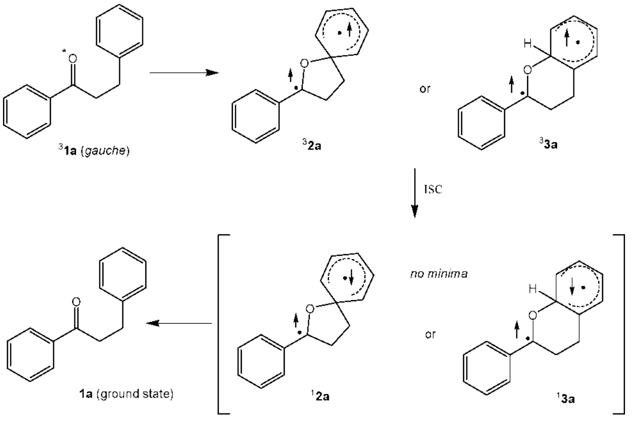
SCHEME 1: Addition−ISC−Relaxation Mechanism for BPQ



Relaxation to the ground-state singlet ketones **1** thus is expected to be a very rapid process once the singlet manifold is reached. It is noted that the structure of **3a** has previously been discussed in work on BPQ but that its possible role in BPQ was dismissed based on the failure to observe it experimentally.[1a]

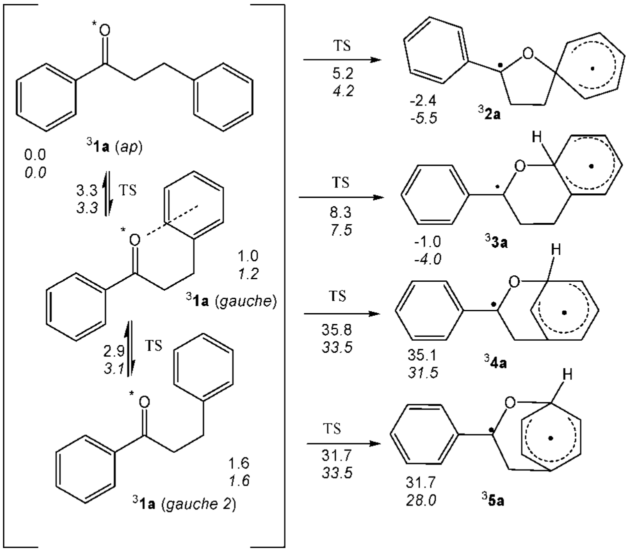
Results

***β*-Phenylpropiophenone 1a.** In the antiperiplanar (ap) conformation of ^{3}**1a**, no interaction between the triplet ketone moiety and the β-phenyl ring is expected as the distance between the two reacting subunits of the molecule is rather large ($r_{(O-C1)}$ = 4.53 Å). For that reason, *ap*-^{3}**1a** was taken as reference point and set to a relative enthalpy of 0.0 kcal mol^{-1}. In the gauche-1 (g1) conformation of ^{3}**1a**, on the other hand, clear evidence of interaction between the carbonyl oxygen and the π system of the β-phenyl ring is obtained, as $r_{(O-C1)}$ = 2.64 Å. This value is significantly shorter than the sum of the van der Waals radii of carbon and oxygen (3.25 Å). At the level of theory generally used in this study (UB3LYP/cc-pVTZ single points based on UB3LYP/6-31G(d) geometries), *g1*-^{3}**1a** is predicted to be higher in energy by 1.0 kcal mol^{-1} than *ap*-^{3}**1a**. The activation enthalpy for interconversion of the two rotamers is calculated as $\Delta H^{\#}$ = 2.3 kcal mol^{-1} from *g1*-^{3}**1a** and $\Delta H^{\#}$ = 3.3 kcal mol^{-1} from *ap*-^{3}**1a**. In a second gauche conformer (*g2*-^{3}**1a**), the carbonyl moiety points away from the β-phenyl ring. This conformer is predicted to be higher in energy than *ap*-^{3}**1a** by 1.6 kcal mol^{-1} and converts into *g1*-^{3}**1a** via a small (1.3 kcal mol^{-1}) barrier.

Triplet **1a** can in principle undergo addition of the carbonyl oxygen atom to any of the four ring positions (ipso, ortho, meta or para) of the β-phenyl ring. Not unexpectedly, activation enthalpies for addition to the meta or para positions are predicted to be prohibitively high ($\Delta H^{\#}_{\mathrm{meta}}$ = 35.8 kcal mol^{-1} and $\Delta H^{\#}_{\mathrm{para}}$ = 35.2 kcal mol^{-1} relative to *ap*-^{3}**1a**). The resulting biradicals are highly strained *meta*- or *para*-[4]cyclophanes that are energetically much higher than the triplet ketone (ΔH_{meta} = 35.1 kcal mol^{-1}, ΔH_{para} = 31.7 kcal mol^{-1}). Addition to the ipso and ortho positions of the β-phenyl ring is predicted to be much more favorable (ΔH_{ipso} = −2.4 kcal mol^{-1}, $\Delta H_{\mathrm{ortho}}$ = −1.0 kcal mol^{-1}), with much lower activation enthalpies ($\Delta H^{\#}_{\mathrm{ipso}}$ = 5.2 kcal mol^{-1}, $\Delta H^{\#}_{\mathrm{para}}$ = 8.3 kcal mol^{-1}). It is also seen that the barriers for the conformational changes in ^{3}**1a** are predicted to be smaller than the barriers for any of the addition reactions. For that reason, it does not matter from which conformer of ^{3}**1a** an addition step will take place, as they will be in rapid equilibrium anyways.

To test the validity of these results, further geometry optimizations were performed employing the UB3PW91/6-31G(d) method, which were followed by single-point energy calculations at the UB3PW91/cc-pVTZ level of theory. The results are in excellent agreement with the results obtained at the UB3LYP level of theory; see Scheme 2.

SCHEME 2: Energies, Relative to *ap*-^{3}1a = 0.0 kcal mol^{-1}, of Stationary Points Relevant to BPQ in Parent Triplet *β*-Phenylpropiophenone ^{3}1a, as Calculated at the UB3LYP/cc-pVTZ//UB3LYP/6-31(d) (Top) or UB3PW91/cc-pVTZ//UB3PW91/6-31G(d) (Bottom, Italicized) Levels of Theory



From the results presented so far, I may conclude that the mechanism for BPQ as outlined in Scheme 1 appears plausible. The activation enthalpy predicted for addition of the carbonyl oxygen atom to the ipso carbon atom of the β-phenyl ring is small and consistent with a lifetime of ^{3}**1a** in the sub-nanosecond range.

Figure 1 shows the calculated geometries of the stationary points shown in Scheme 2, with the exceptions of the pathways resulting in meta or para addition.

The $C_{\mathrm{ipso/ortho}}-O_{\mathrm{carbonyl}}$ distances $R1$ in the two relevant transition states resulting in addition to the ipso or ortho positions of the β-phenyl ring are very similar, with $R1_{\mathrm{ipso}}$ = 1.938 Å and $R1_{\mathrm{ortho}}$ = 1.946 Å. The angle from which the carbonyl oxygen attacks the plane of the β-phenyl ring, however, is different in the ipso and ortho addition reactions. This angle $A1$ ($A1_{\mathrm{ipso}}$ = O−C$_{\mathrm{ipso}}$−C4, $A1_{\mathrm{ortho}}$ = O−C$_{\mathrm{ortho}}$−C5) amounts to $A1_{\mathrm{ipso}}$ = 103.8° for ipso attack and $A1_{\mathrm{ortho}}$ = 111.1° for ortho attack. In the triplet biradicals ^{3}**2a** and ^{3}**3a**, the C−O distances are $R1_{\mathrm{ipso}}$ = 1.482 Å (^{3}**2a**) and $R1_{\mathrm{ortho}}$ = 1.469 Å (^{3}**3a**). These values are slightly longer than the typical value of 1.43 Å for a C sp^3−O sp^3 bond.[10]

Derivatives of *β*-Phenylpropiophenone 1a. The BPQ reaction sequence was further calculated for a series of substituted derivatives of triplet β-phenylpropiophenone, employing the UB3LYP/cc-pVTZ//UB3LYP/6-31G(d) methodology. Table 1 lists the electronic energies obtained.[11a]

From the set of data obtained, the following conclusions may be drawn:

(1) As far as the effect of para substitution on the ketone benzene ring is concerned, methoxy substitution is predicted to have little effect, while substitution by a dimethylamino group is predicted to significantly decelerate BPQ. This holds for both ipso and ortho attack.

(2) Para substitution on the β-phenyl ring is predicted to have a pronounced effect on ipso attack, while ortho attack is little

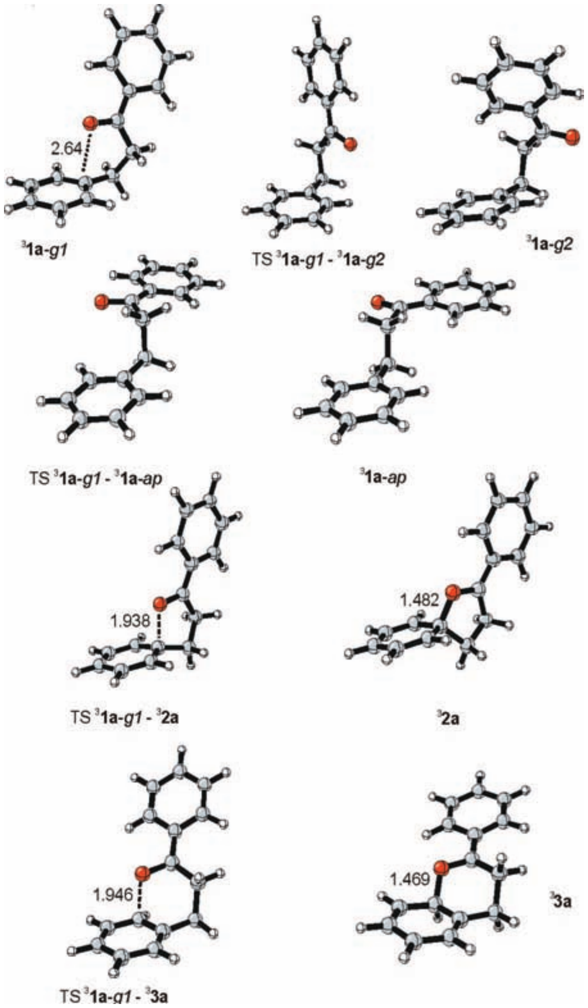
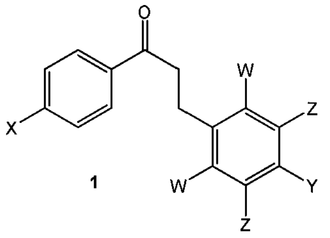


Figure 1. Optimized geometries (UB3LYP/6-31G(d)) of stationary points relevant to BPQ of triplet β-phenylpropiophenone. Some relevant C−O distances are given (in angstroms).



1

influenced. Ipso attack is facilitated, if Y is electron donating and slowed down, if Y is electron withdrawing. The activating effect is particularly pronounced if Y = $-N(CH_3)_2$.

(3) Meta, meta disubstitution on the β-phenyl ring decelerates BPQ, if Z is electron withdrawing (Z = $-CF_3$ or $-NO_2$). If Z is electron donating (Z = $-N(CH_3)_2$), ortho attack is greatly facilitated and in fact is predicted to become the prevailing mode of reaction, while the barrier for ipso attack is essentially unchanged.

(4) Ortho, ortho disubstitution on the β-phenyl ring was investigated in order to examine the importance of steric effects on the two modes of BPQ. Methyl substitution (**1h**) is predicted to facilitate ipso attack, while exerting little influence on the ortho mode of BPQ. While this result is expected due to the electron-donating character of the methyl group, the fact that *t*-butyl substitution (**1i**) is predicted to facilitate both ipso and ortho attack is counterintuitive. For a possible explanation, see the discussion.

(5) According to the calculations, the relative stability of the g1 and ap conformers of the triplet ketones is a function of the substituent properties. In general, the presence of electron-donating substituents in the β-phenyl ring stabilizes the g1 conformer. It is destabilized by *para*-dimethylamino substitution in the aryl ketone chromophore and by the presence of electron-withdrawing groups in the β-phenyl ring.[11b]

Intrinsic Reaction Coordinates (IRC). Starting from the geometries and force constants obtained for the transition states for both the ipso and ortho attacks of ^{3}**1a**, ^{3}**1j**, and ^{3}**1o** (X = H, OCH_3, and $N(CH_3)_2$, respectively, Y, Z, W = H in all cases), IRC calculations were performed at the UB3LYP/6-31G(d) level of theory. A series of intermediary points along the reaction coordinate was thus obtained. At each geometry, a single point energy calculation was performed at the UB3LYP/cc-pVTZ level of theory for both the triplet and the singlet spin manifold.[12] A number of molecular properties was extracted from the data. Besides the singlet and triplet energies, the spin density at the carbonyl oxygen atom and the degree of charge transfer from the β-phenyl ring to the aryl ketone moiety (R−CO) was calculated for the triplet states.[13] In the cases of **1j** and **1o**, the Mulliken charges at the methoxy and dimethylamino substituents were additionally calculated. Finally, for **1o** the dihedral angle CNCC defined by one of the methyl carbon atoms of the DMA group, the nitrogen atom and two carbon atoms (C4 and C3) of the aryl ketone benzene ring was taken as parameter. As the X axis, the $C_{(ipso/ortho)}-O_{carbonyl}$ distance was chosen as it changes monotonically along the reaction coordinate. Figure 2 shows a plot of the singlet and triplet energies as function of the C−O distance.

Figure 2 clearly shows that the energy gap between singlet and triplet hypersurface is significantly reduced when moving along the reaction coordinates for both ipso and ortho attack, reaching a value of close to zero for the triplet biradicals ^{3}**2a** and ^{3}**3a**. Given this near degeneracy of the triplet and singlet spin states of **2a** and **3a**, rapid ISC can be expected. As all attempts at an optimization of ^{1}**2a** and ^{1}**3a** resulted in relaxation to the ground state of **1a**, formation of ^{3}**2a** and ^{3}**3a** very likely represents an efficient way for relaxation of ^{3}**1a**. For **1j** and **1o**, the corresponding plots are similar to Figure 2 (see Figures S1 and S2 of the Supporting Information).

BPQ has been reported to proceed with a significant degree of charge transfer.[3,5] Figure 3 shows a plot of the degree of charge transfer (in elementary units) vs C−O distance for BPQ of ^{3}**1j**.

Figure 3 shows that both the ipso and ortho attack on the β-phenyl ring occur with significant charge transfer, which amounts to about a quarter of an elementary charge in the maximum. This maximum degree of charge transfer is reached at a C−O distance of ca. 1.85 Å, and it occurs slightly earlier along the reaction coordinate in case of the ipso attack than in the ortho attack. The methoxy group is calculated to act as a net electron acceptor rather than as electron donor, with a negative charge of ca. 0.1 elementary units in case of the ipso addition. For ^{3}**1a**, a plot of the charge at the aryl ketone moiety vs C−O distance is similar to the plot shown for ^{3}**1j**, see Figure S3.

If an analogous plot is generated for BPQ in case of ^{3}**1o**, significant differences to the behavior of ^{3}**1j** are observed (Figure 4).

According to Figure 4, the dimethylamino substituent acts as a weak electron acceptor, if the addition occurs in the ipso position, while it is an electron-donor substituent in case of the ortho attack. Moreover, the degree of charge transfer to the aryl

TABLE 1: Relevant Electronic Energies (in kcal mol^{-1}) Calculated (UB3LYP/cc-pVTZ//UB3LYP/6-31G(d)) for BPQ of Derivatives of ^{3}1 (As Reference Points (0.0 kcal mol^{-1}), the Energies of the ap Conformers of the Triplet Ketones Are Taken)

compound	X	Y	Z	W	*E*(*g1*)[a]	*E*(TS$_{ipso}$)[b]	*E*(^{3}BR$_{ipso}$)[c]	*E*(TS$_{ortho}$)[d]	*E*(^{3}BR$_{ortho}$)[e]
1a	H	H	H	H	1.0	5.2	−2.4	8.3	−1.0
1b	H	OH	H	H	−0.6	1.8	−4.1	8.3	−2.1
1c	H	$N(CH_3)_2$	H	H	−2.8	−1.3	−5.3	7.7	0.9
1d	H	NO_2	H	H	0.6	6.5	−4.3	10.1	0.1
1e	H	CF_3	H	H	1.2	6.5	−2.6	9.3	−0.8
1f	H	H	$N(CH_3)_2$	H	−4.3	5.6	0.0	−1.8	−4.1
1g	H	H	CF_3	H	1.1	7.0	−2.3	9.3	0.8
1h	H	H	H	CH_3	0.7	2.6	−5.8	8.2	−0.9
1i	H	H	H	$C(CH_3)_3$	2.0	5.0	−10.8	6.5	−9.6
1j	OCH_3	H	H	H	0.6	5.2	−2.9	7.8	−1.8
1k	OCH_3	OCH_3	H	H	−1.0	1.6	−4.7	6.0	−2.6
1l	OCH_3	$N(CH_3)_2$	H	H	−2.4	−0.9	−5.5	7.6	0.4
1m	OCH_3	CF_3	H	H	0.8	6.8	−2.8	9.1	−1.4
1n	OCH_3	H	CF_3	H	0.7	7.5	−2.3	9.2	0.6
1o	$N(CH_3)_2$	H	H	H	2.7	12.3	3.4	13.9	4.2
1p	$N(CH_3)_2$	OCH_3	H	H	2.5	8.3	1.3	13.8	5.4
1q	$N(CH_3)_2$	$N(CH_3)_2$	H	H	2.6	4.1	−1.2	11.7	4.1
1r	$N(CH_3)_2$	NO_2	H	H	2.4	14.1	2.8	14.1	6.6
1s	$N(CH_3)_2$	CF_3	H	H	2.6	14.5	4.1	15.5	5.2
1t	$N(CH_3)_2$	H	$N(CH_3)_2$	H	1.0	11.3	4.5	3.2	−0.3
1u	$N(CH_3)_2$	H	CF_3	H	2.4	15.5	4.9	15.2	4.9
1v	$N(CH_3)_2$	H	NO_2	H	1.7	10.9	5.5	11.8	3.1

[a] Enthalpy of the g1 conformer. [b] Enthalpy of the transition state leading to ipso attack. [c] Enthalpy of the triplet biradical (**2**) formed by ipso attack. [d] Enthalpy of the transition state leading to ortho attack. [e] Enthalpy of the triplet biradical (**3**) formed by ortho attack.

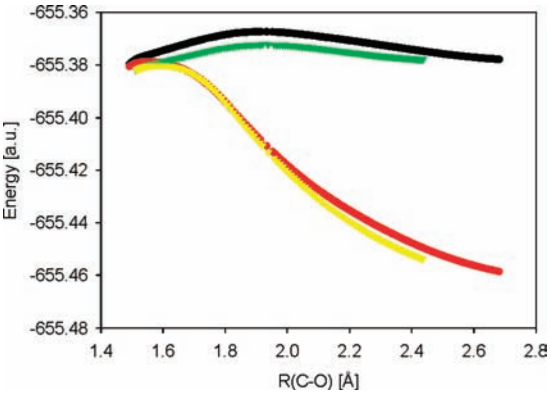


Figure 2. Plot of the energy (in atomic units) vs the O (carbonyl)−C (ortho/ipso) distance, as calculated for ^{3}**1a** at the UB3LYP/cc-pVTZ//UB3LYP/6-31G(d) level of theory. Green: triplet energy, IRC for ipso attack. Yellow: singlet energy at triplet geometry, IRC for *ipso* attack. Black: triplet energy, IRC for ortho attack. Red: singlet energy at triplet geometry, IRC for ortho attack. The transition state of the reactions is indicated by the data points at $R \approx 1.95$ Å having two larger gaps on each side.

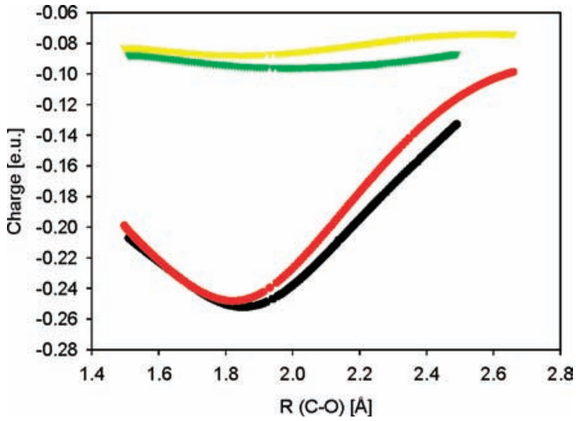


Figure 3. Plot of the negative charge on the methoxy group alone and on the aryl ketone moiety (including the methoxy group) vs C−O distance in BPQ of ^{3}**1j**. Black: negative charge on the aryl ketone moiety, ipso attack. Red: negative charge on the aryl ketone moiety, ortho attack. Green: negative charge on the methoxy group, ipso attack. Yellow: negative charge on the methoxy group, ortho attack. The transition state of the reactions is indicated by the data points at $R \approx 1.95$ Å having two larger gaps on each side.

ketone moiety is significantly more pronounced for the ipso attack than for the ortho attack.

Figure 5 shows a plot of the Mulliken spin density at the carbonyl oxygen atom vs the C−O distance, again calculated at the UB3LYP/cc-pVTZ//UB3LYP/6-31G(d) level of theory, for BPQ of ^{3}**1o**.

According to Figure 5, the spin density on the carbonyl oxygen atom increases coming from the triplet ketone, reaches a maximum, and then decreases to finally reach the small value for the triplet biradical. While this statement holds for both ipso and ortho attack, the degree of build-up of spin density is much less pronounced in the case of the ortho addition. Analogous plots for ^{3}**1a** and ^{3}**1j** are given in Figures S4 and S5. In these systems, no maximum value of the carbonyl-O spin density S is reached. The plot of S vs R_{OC} is sigmoidal, and S approaches the values for the unperturbed triplet ketones for long R_{OC}.

The final parameter of importance to this study is the degree of twisting of the dimethylamino group along the reaction coordinate of BPQ of ^{3}**1o**. Again, the O−C$_{ipso/ortho}$ distance is taken as a measure for progress of the reaction; see Figure 6.

While the DMA group remains essentially coplanar with the ketone phenyl ring along the reaction coordinate of the ortho addition, it is twisted to a significant degree (ca. 52°) along most of the reaction coordinate of ipso addition. Only at a very early stage of the reaction in an increase of the CNCC dihedral noted. In contrast, the analogous dihedral COCC, including the methoxy carbon and oxygen atoms as well as C4 and C3 of the aryl ketone phenyl ring, remains essentially unchanged ($\theta = 0 \pm 2.5°$) along the entire reaction coordinate of BPQ in ^{3}**1j**; see Figure S6.

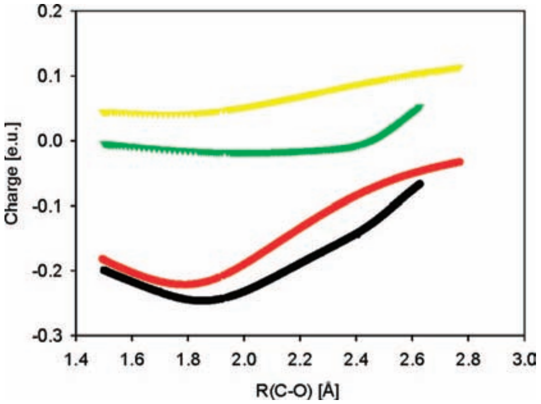


Figure 4. Plot of the negative charge on the dimethylamino group alone and on the aryl ketone moiety (including the dimethylamino group) vs C−O distance in BPQ of ^{3}**1o**. Black: negative charge on the aryl ketone moiety, ipso attack. Red: negative charge on the aryl ketone moiety, ortho attack. Green: negative charge on the dimethylamino group, ipso attack. Yellow: negative charge on the dimethylamino group, ipso attack. The transition state of the reactions is indicated by the data points at $R \approx 1.95$ Å having two larger gaps on each side.

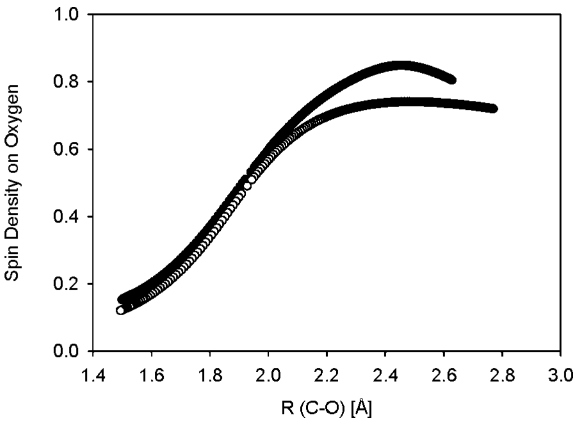


Figure 5. Plot of the spin density at the carbonyl oxygen atom of ^{3}**1o** vs the O−C$_{\text{ipso/ortho}}$ distance. Black circles: ipso attack. Light circles: ortho attack. The transition state of the reactions is indicated by the data points at $R \approx 1.95$ Å having two larger gaps on each side.

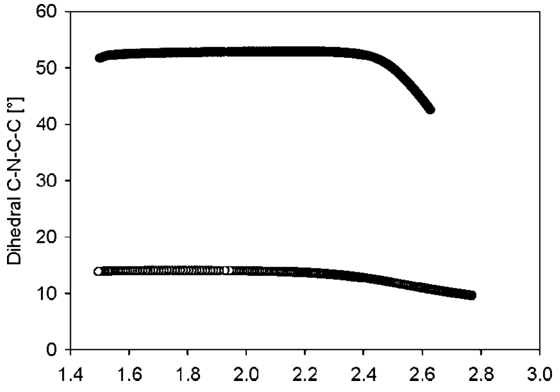


Figure 6. Plot of the dihedral CNCC defined by one of the methyl carbon atoms of the DMA group, the nitrogen atom, and two carbon atoms (C4 and C3) of the aryl ketone benzene ring of ^{3}**1o** vs the O−C distance. Black circles: ipso addition. Light circles: ortho addition.

Discussion

The first triplet excited state of parent β-phenyl-propiophenone **1a** has been reported to be of ($n \rightarrow \pi^*$) character, while 4-methoxy-β-phenyl-propiophenone **1j** has a lowest ($\pi \rightarrow \pi^*$) triplet excited state.[3,5,8a] In both cases, the energy gap between the two types of triplet excited states has been reported to be very small, of the order of <3 kcal mol^{-1}.[3] This degree of accuracy is unlikely to be achieved employing the computational methodology used throughout this study. The calculations predict a ($n \rightarrow \pi^*$) lowest triplet excited-state for **1a** and **1j**, while **1o** is predicted to have a ($\pi \rightarrow \pi^*$) T$_1$ state.[14] Evidence for this is provided by the calculated Mulliken spin densities at the carbonyl oxygen atoms in the *ap*-conformers of the triplet ketones. This parameter amounts to $S = 0.986$ for *ap*-^{3}**1a**, $S = 0.850$ for *ap*-^{3}**1j**, but $S = 0.357$ for *ap*-^{3}**1o**. A crude value for the energy gap between the ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) triplet states of ^{3}**1o** can be obtained by performing a time-dependent density functional theory calculation on its *ap*-conformer (UB3LYP/6-31+G(d)//UB3LYP/6-31G(d)). At this level of theory, the ($\pi \rightarrow \pi^*$) triplet state is lower in energy by 13.8 kcal mol^{-1}. The prediction that a significantly higher value of S is reached along the reaction coordinate of BPQ of ^{3}**1o** implies that ($n \rightarrow \pi^*$) character must be built up during BPQ. In case of *ipso*-BPQ, this is partially achieved by rotating the dimethylamino group, whose presence otherwise stabilizes the ($\pi \rightarrow \pi^*$) T$_1$ state, out of the plane of the aryl ketone phenyl ring, see Figure 6. By this, the overlap of the nitrogen lone pair with the π system of the aryl ketone moiety is reduced, and the ($n \rightarrow \pi^*$) triplet state becomes more accessible. In *ortho*-BPQ of ^{3}**1o**, however, the degree of DMA twisting is predicted to be much less pronounced, and the nitrogen lone pair still will thus interact significantly along all of the reaction coordinate. Hence, it must mostly be the approach of the carbonyl oxygen atom to the β-phenyl ring that results in a reorganization of the spin density toward the carbonyl oxygen atom or to a gradual development from ($\pi \rightarrow \pi^*$) to ($n \rightarrow \pi^*$) character. The calculations presented in this work suggest that BPQ involves surface crossing along the reaction coordinate rather than a prereaction equilibrium between unperturbed ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) triplet states, as has been postulated before.[3] In fact, at least in case of the system **1t**, which is deactivated in the ketone moiety by a *para*-dimethylamino group and activated in the β-phenyl ring by 2-fold dimethylamino-substitution, the prereaction equilibrium mechanism seems improbable based on the data presented. There is no obvious reason why the energy gap between the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) triplet states of **1t** should be much smaller than the corresponding energy gap in **1o**. It should thus be much larger than the activation enthalpy for BPQ by *ortho*-addition ($\Delta H^{\#} = 3.2$ kcal mol^{-1}).

The data on substituent effects presented in Table 1 can be compared with experimental data published for a number of derivatives of **1j**, substituted in the β-phenyl ring.[5] Table 2 presents the comparison. In addition, Table 2 gives the calculated entropies of activation, and the triplet lifetimes estimated from eq 1

$$k = (kT/h)\exp(\Delta S^{\#}/R)\exp(-\Delta H^{\#}/RT) \qquad (1)$$

Table 2 clearly shows that a qualitative agreement exists between the activation enthalpies predicted and the rate constants actually measured. Quite as clearly, this agreement is not quantitative. The lifetime of **1k** is underestimated by the calculations, while the lifetime of the deactivated substrates **1m** and **1n** is overestimated. The latter may be due to alternative pathways of triplet decay (other than BPQ) that were not taken into account in this estimate. The underestimation of the triplet lifetime of **1k**, on the other hand, is likely due to the fact that the overestimation of the stability of the ($n \rightarrow \pi^*$) state by the calculations has the most pronounced effect on the estimated triplet lifetime if the activation enthalpy for BPQ is small anyways, as is the case in *ipso*-BPQ of **1k**.

TABLE 2: Comparison of LFP Data of BPQ in Derivatives of 1j with Calculated Activation Enthalpies and Entropies and Estimated Triplet Lifetimes for BPQ

derivative (X = OCH_3 in all cases)	τ_T (ns)[a]	$\Delta H^{\#}$(ipso, ortho) (kcal mol^{-1})[b] ($\Delta S^{\#}$(ipso, ortho) (cal mol^{-1} K^{-1}))[c]	τ_T (ns)[d](ipso, ortho)
1j (Y = H, Z = H)	57	5.2, 7.8 (−9.6, −10.5)	133, 1838
1k (Y = OCH_3, Z = H)	4	2.6, 7.0 (−6.5, −7.8)	0.35, 1214
1m (Y = CF_3, Z = H)	1160	6.8, 9.1 (−8.1, −9.6)	1001, 106197
1n (Y = H, Z = CF_3)	1830	7.5, 9.2 (−9.6, −11.1)	6993, 268541

[a] Lifetime in *n*-octane, as published in ref 5. [b] Activation enthalpy for ipso/ortho addition to the β-phenyl ring, as calculated at the UB3LYP/cc-pVTZ//UB3LYP/6-31G(d) level of theory, relative to the most stable calculated conformer of the triplet ketones, this work. [c] Activation entropy for ipso/ortho addition to the β-phenyl ring, as calculated at the UB3LYP/6-31G(d) level of theory, relative to the lowest energy conformation of the triplet ketones, this work. [d] Estimated lifetime of BPQ (ipso and ortho addition), based on eq 1, $T = 296$ K.

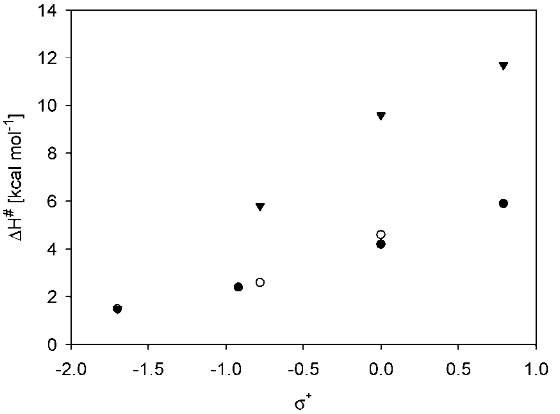


Figure 7. Plot of the calculated activation enthalpies of ipso attack vs the Hammet σ^+ constants of para substituents present in the β-phenyl ring. Dark circles: compounds unsubstituted in the ketone benzene ring (X = H). Light circles: compounds para methoxy substituted in the ketone benzene ring (X = OCH_3). Triangles: Compounds *para*-dimethylamino-substituted in the ketone benzene ring (X = $N(CH_3)_2$).

Given the partial charge transfer occurring along the reaction coordinate of BPQ, the activation of BPQ by electron-donating substituents present in the β-phenyl ring offers little surprise. The regioselectivity of BPQ is expected to follow the known rules for electrophilic attack to an arene system. The presence of an electron-donating substituent in the para position is expected to further enhance the preference for *ipso*-BPQ, while meta/meta disubstitution with the strongly electron-donating dimethylamino group is predicted to be one of the few cases where *ortho*-BPQ is preferred (**1f**, **1t**). If the calculated activation enthalpies for BPQ at the ipso position of derivatives of **1** para-substituted in the β-phenyl ring are plotted against Hammet σ^+ constants, a linear correlation is observed in all three systems (Figure 7). This observation further supports the idea of electrophilic attack at the β-phenyl ring.

Steric effects exerted by substituents present on the β-phenyl ring are expected to play a minor role only in BPQ. In case of the *ortho,ortho*-dimethyl compound **1h**, only the electron-donating character of the methyl substituent comes into the play, activating *ipso*-BPQ. Somewhat counterintuitive, however, is the fact that *t*-butyl substitution (**1i**) is predicted to facilitate both ipso and ortho attack. The formation of both triplet biradicals is calculated to be particularly favorable in this system. A possible explanation for this lies in a reduction of steric strain, if either the methylene group (ipso attack) or one of the *t*-butyl groups (ortho attack) is allowed to move out of the plane of the β-phenyl ring. In either reaction mode, the highly unfavorable ortho interaction between one (ortho attack) or both (ipso attack) *t*-butyl group(s) and the CH_2 group next to the β-phenyl ring is reduced.

Conclusion

A mechanism for β-phenyl quenching (BPQ) of β-phenylpropiophenone and derivatives is developed that explains the experimental findings and predicts qualitatively correct rate constants. It consists of addition of the electrophilic carbonyl oxygen atom of the triplet excited ketone to the ipso or ortho position of the β-phenyl ring, followed by ISC of the resulting triplet biradical. The singlet biradical is not predicted to be a minimum energy structure and undergoes retro-addition to yield the ground-state ketone.

The finding could be of more general importance as it may also provide a pathway for quenching of triplet carbonyl compounds with π-systems with relatively high triplet energies, such as quenching of triplet acetone by benzene. Earlier experimental studies had provided some evidence that biradicals might be formed in such reactions.[15]Further calculations in this direction are currently under way, as are experimental studies designed to confirm some of the predictions made in this contribution.

Computational Methods

All calculations were performed using the Gaussian03 suite of programs.[16] All energy minima and transition structures were fully optimized at the UB3LYP/6-31G(d)[17] level of theory and characterized as such by performing a vibrational analysis. On the basis of the geometries thus obtained, single-point energy calculations were performed at the UB3LYP/cc-pVTZ[18] level of theory. In case of stationary points relevant to BPQ of **1a**, the optimizations and single point energy calculations were repeated using the UB3PW91[17,19] hybrid functional, employing the basis sets mentioned before. IRC calculations were performed starting from transition structures relevant to BPQ of **1a**, **1j**, and **1o**. The reaction coordinates were followed in both directions, using the UB3LYP/6-31G(d) method. On the basis of the intermediary (nonstationary) geometries thus obtained, again single-point energy calculations were performed at the UB3LYP/cc-pVTZ level of theory. The activation and reaction enthalpies given in this work do not include a zero-point energy (ZPE) correction. Because of the low-frequency nature of the modes acquiring an imaginary force constant in the transition structures, the ZPE error is small in the systems studied.

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Supporting Information Available: Full citation of ref 16, Cartesian coordinates, and electronic energies of stationary points optimized. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) (a) The energies do not include a ZPE correction and refer to $T = 0$ K. (b) (b) The preference for the g1 π-complex conformer in β-donor-substituted derivatives is not unexpected. However, it is noted that the level of theory used is not likely to describe weak complexes well.

(12) The single-point energy calculations for the singlet spin manifold were generally performed using the Gaussian keywords guess=(mix,always). Nonzero values of S^2, however, were only obtained for biradical-like geometries much beyond the transition structure.

(13) To calculate the degree of charge transfer to the ketone moiety, the UB3LYP/cc-pVTZ//UB3LYP/6-31G(d) Mulliken charges of the atoms of the ketone half of the molecule ($R-C_6H_4-CO$, R being H, OCH_3, or NMe_2) were summed up.

(14) (a) The fact that B3LYP tends to overestimate the stability of ($n \rightarrow \pi^*$) triplet states has been observed before. Muthukrishnan, S.; Mandel, S. M.; Hackett, J. C.; Singh, P. N. D.; Hadad, C. M.; Krause, J. A.; Gudmundsdóttir, A. D. *J. Org. Chem.* **2007**, *72*, 2757. (b) Klima, R. F.; Jadhav, A. V.; Singh, P. N. D.; Chang, M.; Vanos, C.; Sankarananarayan, J.; Vu, M.; Ibrahim, N.; Ross, E.; McCloskey, S.; Murthy, R. S.; Krause, J. A.; Ault, B. S.; Gudmundsdóttir, A. D. *J. Org. Chem.* **2007**, *72*, 6372.

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