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Photocyclization to Cyclopropanols and Exciplex Emission of β-Arylpropiophenones

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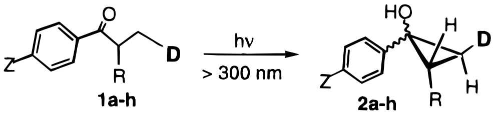
Charge transfer (CT) interactions between photoexcited benzoyl chromophores and both amines and substituted benzenes are well-known.[1] When intermolecular, these CT interactions lead to rapid hydrogen transfer from the α-carbons of amines[2] and the benzylic carbons of alkylbenzenes[3] to the carbonyl oxygen, resulting in hemipinacol radicals and their coupling products. When the charge transfer is intramolecular, its extent and that of any subsequent product formation depend on the nature of the donor substituent and its position relative to the carbonyl.[1,4] Thus, both β-(dialkylamino)propiophenones[4,5] and β-phenylpropiophenones[6−8] undergo very rapid triplet decay due to internal CT quenching; the former produce 2-aminocyclopropanols in high yields,[9,10] whereas the latter form no photoproducts.[6−8] We report here that propiophenones with more electron rich β-aryl groups, especially *N*,*N*-dimethylanilino, not only photocyclize to cyclopropanols but also display exciplex emission.

The compounds we studied are listed in Table 1. Like **1a**,[9,11] the α-substituted **1b** and **1c** photocyclize in both benzene and methanol. Upon irradiation in the near UV, the β-(*p*-aminophenyl) ketones **1d−g** also form cyclopropanols in benzene but not in polar solvents. Chemical and quantum yields are listed in Table 1. The cyclopropanols could not be isolated because of their sensitivity to trace acid, base, and oxygen.[10−12] Prolonged irradiation of **1h** and α,β-diphenylpropiophenone in benzene results only in slow photofragmentation, as anticipated.[6−8] However, in methanol **1h** cyclizes in good yield but with low efficiency. Quantum yields were measured at 366 nm to prevent competitive absorption by the aniline group.



Product identification consisted of 500 MHz NMR analysis of solutions originally ~0.01 M in **1a−h** that had been irradiated in NMR tubes, with methyl benzoate as an internal standard. The methine and methylene protons at the C(2) and C(3) ring atoms could be clearly identified by their chemical shifts and coupling patterns.[13] The magnitude of the coupling constants indicates that substituents R and D are arranged in a trans configuration.[10,14] NOESY experiments on **2e−g** confirmed the trans configuration of the hydrogens at C(2) and C(3). For **2e−g**, the OH proton signals could be assigned by H/D exchange. The NOESY spectrum of **2f** showed a crosspeak between the OH proton and the *ortho*-protons of the anilino group. We conclude that the hydroxy group is situated cis to the C(2)-anilino group and trans to the C(3)-benzyl group. The stereochemistry at C(1) and C(2) could not be assigned for **2e** and **2g** because the doublets for the C(2)- and C(3)-protons could not be differentiated. For **1c** and **1f**, cyclization takes place only at the amino- or anilino-substituted methylene groups, as indicated by ^{13}C NMR/DEPT experiments on **1c**/**2c** and the NOESY experiment on **2f**.

Table 1. Yields of Cyclopropanols **2** from >300 nm Irradiation of Various β-Substituted Propiophenones[a]

			benzene		methanol	
reactant	R	ϵ^b	yield (%)	Φ^c	yield (%)	Φ^c
			D = NMe_2			
1a[d]	H	14	95	0.59	0.15	
1b	Ph	51	73	0.27	42	0.20
1c	$PhCH_2$	15	24	0.41	68	0.37
			D = *p*-Me_2N-Ph			
1d	H	38	50	0.25	<5	
1e	Ph	133	88	0.22	<5	
1f	$PhCH_2$	104	65	0.065		
1g[a]	Ph	62	56	0.078	<5	
			D = *p*-MeO-Ph			
1h	Ph	49			50	0.008

[a] Z = *p*-MeO in **1g**, H in others. [b] At 366 nm. [c] Irradiation at 366 nm. [d] Reference 11.

UV absorption of the ketone and the aniline chromophores are superimposed below 350 nm for ketones **1d−g**. At longer wavelengths only an enhanced n,π* absorption of the benzoyl group occurs; extinction coefficients at 366 nm are listed in Table 1.

Figure 1 demonstrates the solvent dependence of the 77 °K emission of **1d−f**: only normal n,π* phosphorescence in hydrocarbon solvents but mainly broad, structureless emission at 470 nm in more polar solvents. We assume that the broad emission is due to a triplet exciplex, since a chopper was used to block any fluorescence. Similar exciplex emission spectra have been reported for benzophenone/aniline systems[15] and for (ω-(dimethylamino)alkyl)styrenes.[16] An exciplex energy of 2.69 eV can be estimated for **1d−f** from the redox potentials (*vs* SCE) of acetophenone (−2.14 V)[3] and *N*,*N*-dimethyltoluidine (0.70 V)[17] by assuming nearly full electron transfer in the exciplex. This value is consistent with the observed emission λ_{max} of 470 nm.

Ketones **1d−h** represent the first examples of β-aryl ketones that undergo the rarely observed photoinduced β-hydrogen abstraction. Scheme 1 depicts a mimimal mechanism, as a progression from exciplex to biradical to **2**. Hydrogen transfer clearly is actuated by prior charge transfer from the β-aryl group to the excited benzoyl group, as occurs in **1a**.[4,5] However, more is required for intramolecular reaction than simple exciplex

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[13] ^{1}H-NMR δSPCLN **2e** (C_6H_6) 1.61 (s, 1H), 2.41 (s, 6H), 3.22 (d, 1H, J = 7.8 Hz), 3.30 (d, 1H, J = 7.9 Hz), 6.47 (d, 2H, J = 9 Hz), 7.0 (d, 2H, J = 9 Hz), 7.05−7.45 (m, 10H); **2f** 1.74 (s, 1H), 2.05 (ddd, 1H, J = 7.4, 7.4, 13.8 Hz), 2.37 (s, 6H), 2.49 (d, 1H, J = 7.3 Hz), 3.09 (dd, 1H, J = 6.4, 14.8 Hz), 3.13 (dd, 1H, J = 7.5, 14.8 Hz), 6.32 (d, 2H, J = 8.8 Hz), 6.77 (d, 2H, J = 8.8 Hz), 6.88−7.17 (m, 8H), 7.34 (d, J = 7.5 Hz, 2H).

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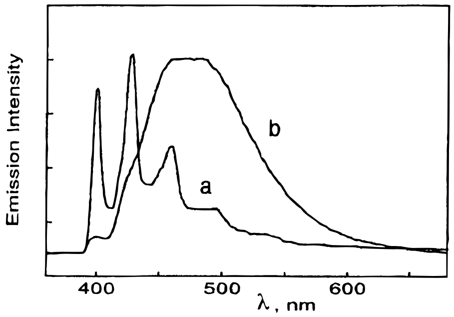
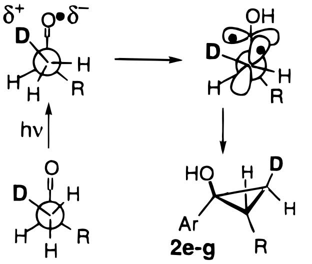


Figure 1. The 77 K emission of **1d** in (a) methylcyclohexane and (b) 2-methyltetrahydrofuran. Those of **1e** and **1f** are nearly identical.

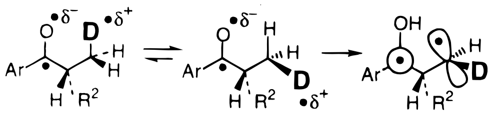
Scheme 1



formation, otherwise β-phenylpropiophenone (**3**) would form products as efficiently as **1a**−**h**. The order of quantum yields (**1a**−**c** > **1d**−**f** > **1h** ≫ **3**) implicates the degree of electron transfer in the internal CT process as a major determinant of reaction efficiency. ΔG values calculated from the Weller equation[18] indicate that electron transfer from the β-donors to the triplet benzoyl group is 10 kcal/mol less endothermic for **1h** than for **3** and exothermic for **1a**−**g.** These values reflect the anticipated differences in the degree of electron transfer within the intramolecular exciplexes formed from these bichromophores, as well as the ease with which these exciplexes can proceed to bis(radical ions). The regioselective cyclizations of **1f** and **1c** provide independent, intramolecular examples of the greater degree of charge transfer to the photoexcited benzoyl chromophore from a β-amino or -anilino group than from a β-phenyl group.

Quantum yields for photocyclization of **1f** and **1g** are lower than those for **1a**−**e**. The low efficiency for **1g** does not reflect the usual triplet deactivation by methoxy substitution,[8,19] since quenching of **1g** by piperylene indicated a triplet lifetimeof ∼0.2 ns. The rapid triplet decay of **1g**, despite its π,π^* lowest triplet, is consistent with the fact that amines are known to react with both n,π^* and π,π^* ketone triplets.[20] Scaiano's work[5,8,21] suggests that the triplets of all of these β-aryl ketones undergo, with comparable subnanosecond rapidity, internal CT quenching by the β-aryl group as their only reaction. Therefore, product quantum yields reflect how well the ensuing hydrogen transfer competes with radiationless decay by the exciplex and/or reverse electron transfer by radical ion pairs and how well cyclization competes with disproportionation by the 1,3-biradical. The low value for **1f** could indicate CT quenching by the β-phenyl group in competition with formation of a chemically active exciplex between the photoexcited benzoyl and the anilino group as well as conformational effects on proton transfer or biradical behavior.[19,22]

More complete mechanistic studies will be described in a full paper, but there are three effects that warrant brief discussion here: the correlation between ΔG values and quantum yields, the solvent effect on quantum yields, and the diastereoselectivity of cyclization. The accepted picture for the intramolecular exciplex from **3** assumes an eclipsed conformation about the α- and β-carbons to provide maximum overlap between the β-aryl π-system and the carbonyl n orbital.[8,21] This geometry holds both β-hydrogens too far away from the carbonyl oxygen for hydrogen transfer to occur. The rotation about the $C_\alpha - C_\beta$ bond required for H-transfer apparently occurs only when D is a much stronger electron donor than phenyl. As the extent of electron transfer increases, Coulombic attraction apparently reduces the importance of orbital overlap. For **1h**, this may produce a "looser", more extended exciplex geometry;[16] for **1d**−**g**, it probably represents actual formation of a radical ion pair.



Photocyclizations to **2b, 2c**, and **2e**−**h** proceed stereoselectively (de ≥ 90%), whereas two diastereomeric cyclopropanols are formed in a 2:1 ratio from the α-unsubstituted **1d**. α-Substituents induce a highly regioselective hydrogen transfer and control ring closure of the resulting 1,3-hydroxy biradical, as shown in Scheme 1. On the basis of earlier experiments,[10,23] we would anticipate the major cyclopropanol to be the one formed by least motion ring closure of a short-lived 1,3-hydroxy biradical, in which D maintains its anti relationship with R and its syn relationship with OH, both inherited from the exciplex geometry. This geometry was confirmed by the NOESY experiment on **2f**.

Finally, the negative effect of polar solvents on the photoreactivity of these anilino ketones is the opposite of what was found for ω-dialkylamino ketones[24] but parallels that found for the photocyclization of aminostyrenes.[16] Polar solvents should promote full electron transfer and thus could promote proton transfer by increasing conformational mobility; however, they also increase rates of reverse electron transfer.[16b] Positive charge would be more delocalized in the anilino group than in the amino group in both exciplex and radical ion pair. The weaker solvation of the more diffuse charge may minimize conformational relaxation sufficiently to impede proton transfer.

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