Effect of a Polar Substituent on Olefin Triplet Lifetime

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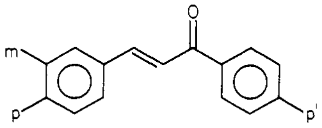
The lifetimes of olefin triplets are important parameters for the study of the vast number of olefin triplet-state isomerizations[1] and cycloadditions.[2] They also serve as models for intersystem crossing rates in flexible organic triplet biradicals and biradicaloids, intermediates of much current interest.[3] Several structural factors are expected to influence intersystem crossing in and thus the lifetimes of such species:[4] interterminal distance, relative orientations of the orbitals bearing the unpaired electrons, and the degree of ionic character in the singlet wave function. We have sought systems that can test the importance of these factors one by one. We now report the triplet lifetimes of chalcones with a wide range of polar substituents, presumably a valid test of the last factor. We observe essentially no effect, in contrast to what might have been expected.[4]



The chalcones were chosen for study because of their ease of preparation,[5] because precedent suggested both that α,β-unsaturated ketones underwent rapid and essentially quantitative intersystem crossing[2a,2e] and that their triplets thus were attractive candidates for transient spectroscopy[6] and because the excited triplet was likely to prefer the twisted structure[6a] (Figure 1). In this structure, triplet and ground-state singlet are thought to be nearly degenerate and the system thus resembles a "1,2-biradical". Intersystem crossing in this geometry may thus model that in other biradical/biradicaloids.

We have observed transient absorptions in the 5–500-ns time regime (Table I) by flash photolysis with a modelocked YAG laser (fourth harmonic, 266 nm, 1.75-ns FWHM for excitation/response function, ca. 10 mJ/pulse). The transients are responsible for efficient geometric isomerization (Table II) as evidenced by consonance of isoprene quenching of the isomerization and of the transient lifetime (cf. last column of Table II). Isomerization would be expected from acyclic olefin triplets. That the transients are indeed triplets and not singlets follows from the absence of the fluorescence which would certainly have been appreciable from ketone singlets with these lifetimes. Dimerization of chalcones is known[7] and has been assigned a triplet mechanism[7] in accord with the expectation of efficient, even quantitative[2e] intersystem crossing in α,β-unsaturated ketone photochemistry.[2a,b,e] We too observe photodimerization. We cannot conceive a reasonable alternative assignment of the transients that would be consistent with the absence of fluorescence, with their demonstrated involvement in the isomerization, and with the fact that a known triplet reaction (photodimerization) in addition to geometric isomerization is also observed. Longer-lived transients amounting to 5–15% of the total signal were observed but have not been studied.

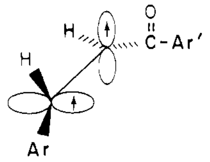


Figure 1. Twisted structure for chalcone triplets.

Table **I.** Properties of Chalcone Triplets

substituent	$^3\tau$, ns[a] CH$_3$OH	$^3\tau$, ns[a] C$_7$H$_{16}$	λ_{max}, nm[b]
p-Me$_2$N	*c*	500	550
p-MeO	29	23	480 (525[d])
p-Me	15.5	17	
H	12	13	430
p-Cl	14.5	15	
p-Br	5	5	
p-CN	19	20	360
m-Br	13	11	
m-MeO	17	16	
p'-MeO	22	15	
p'-Br	13	16	
p'-CN	13	15	

[a] Estimated ±5% or ±1 ns, whichever is greater. Obtained by deconvolution from the excitation/response function. [b] Estimated ±15 nm. In heptane except as noted. [c] No signal. [d] In methanol.

Table **II.** Isomerization and Isoprene Quenching of Chalcone Triplets

substituent	$\phi_{t\to c}$[a]	$k_q\tau$-(isoprene), M^{-1} [b]	k_q(isoprene), M^{-1} s^{-1} [c]
p-CH$_3$O	0.45	4.2	1.5×10^8 (1.1×10^8)
H	0.41	3.5	2.9×10^8 (3.1×10^8)
p-CN	0.58	5.0	2.6×10^8 (2.2×10^8)

[a] By HPLC. Estimated precision ±3%. [b] By fit of isomerization quenching as a function of isoprene concentration. [c] Values given first derived from $k_q\tau$ by the use of $^3\tau$ values from Table I. Values in parentheses obtained by dependence on isoprene concentration of the flash spectroscopically measured triplet lifetimes.

Demonstration that the chalcone triplets adopt the twisted structure as suggested by Bonneau[6a] for other enones is less direct but still cogent. Most significant is that the lifetimes are in the range observed for other twisted triplets,[8-13] or even somewhat shorter, with the exception of *p*-(dimethylamino)chalcone (for which the lowest triplet may be planar around the double bond

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(1) See: Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. III, p 25ff.

(2) (a) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123–225 and numerous references therein. (b) See the numerous references in the chapters by: Horspool, W. M. *Photochemistry* **1970–1983**, *1–present*. (c) Chapman, O. L. *Org. Photochem.* **1967**, *1*, 283. (d) Trecker, D. J. *Ibid.* **1969**, *2*, 63. (e) Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090–5097. (f) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. Loutfy, R.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559. Liu, R. S. H.; Hammond, G. S. *Ibid.* **1967**, *89*, 4936. Rosenberg, H. M.; Serve, P. J. *Ibid.* **1970**, *92*, 4746.

(3) (a) Michl, J. *Photochem. Photobiol.* **1977**, *25*, 141. (b) See also: Michl, J., Ed. "Biradicals. Tetrahedron Symposium in Print #4"; *Tetrahedron* **1982**, *38*, issue 6. (c) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533–6542 and references therein. (d) Schmidt, S. P.; Pinbar, A. R., Hammons, J. H., Berson, J. A. *Ibid.* **1982**, *104*, 6822. (e) Kelley, D. F.; Rentzepis, P. M.; Mazus, M. R.; Berson, J. A. *Ibid.* **1982**, *104*, 3764. (f) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *Ibid.* **1982**, *104*, 3768. (g) Goldberg, A. H.; Doubherty, D. A., *Ibid.* **1983**, *105*, 284.

(4) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.*, **1972**, *11*, 92.

(5) By condensation of appropriately substituted benzaldehydes and acetophenones: Adams, R., Johnson, J. R., Wilcox, C. F. "Laboratory Experiments in Organic Chemistry", 6th ed.; Macmillan: New York, 1970; p 361.

(6) (a) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816–3822. (b) Chan, C. B.; Schuster, D. I. *Ibid.* **1982**, *104*, 2928, report an additional experiment by Bonneau.

(7) (a) Stobbe, H.; Bremer, K. *J. Prakt. Chem.* **1929**, *123*, 1. (b) Wynberg, H.; Gruen, M. B.; Kellogg, R. M. *J. Org. Chem.* **1970**, *35*, 2828–2830. (c) Montando, G.; Caccamese, S. *Ibid.* **1973**, *38*, 710–716. (d) We have observed several new photodimers and will report on them separately.

(8) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174–6180.

(9) Bonneau, R. *J. Photochem.* **1979**, *10*, 439–449.

(10) Gorner, H.; Schulte-Frohlinde, D. *J. Am. Chem. Soc.* **1979**, *101*, 4388.

(11) Gorner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1978**, *82*, 2653.

(12) Gorner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835.

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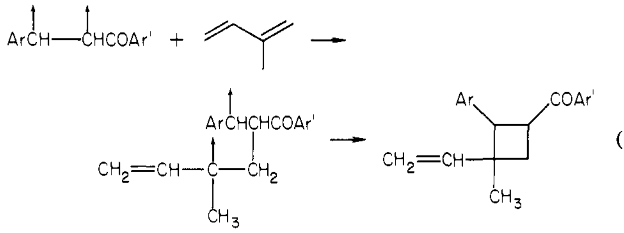
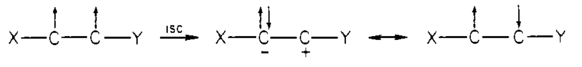
and of the CT or TICT[14,15] type). Increased planarity is always associated with a longer triplet lifetime for an olefin,[8,12,16] and the present cases are even somewhat shorter than the styrenes for which a twisted structure is generally accepted.[8,9] They may be compared to the lifetime of cyclohexenone triplet (30 ns).[2e,6a] Second, the quenching by isoprene, which is largely or wholly chemical and affords predominantly cycloadducts best rationalized as involving the most stable allylic/benzylic biradical (eq 1) is



(1)

nearly unaffected in rate by a polar para substitutent (Table II). This suggests attack on the isoprene by a "benzoylmethylene" terminus largely unaffected by conjugation with the polar substituent, a situation best rationalized by the orthogonal structure of the figure. Third, there is a profound bathochromic shift in the T-T absorption (Table I) as the ability to support charge transfer by polar substituent increases. This requires that the lower triplet be less affected by CT than the upper. We therefore suggest that the lowest triplet is probably largely unaffected by CT, as would be expected for the twisted triplet. It seems safe to conclude that the lifetimes in Table I pertain to the twisted structure, with the probable exception of *p*-(dimethylamino)chalcone. Previous studies[11,17] of stilbene triplets bearing polar substituents have been complicated by planar-twisted equilibria.

The present study is the first in which the effect of polar substituent on intersystem crossing at the twisted geometry is dominant. As can be seen from Table I, that effect is nearly nonexistent. Salem and Rowland[4] include twisted ethylene in their discussion of intersystem crossing in diradicals. They further point out that spin-orbit coupling will in general be proportional to the degree of ionic character in the singlet wave function. We expect that this would be enhanced by substituents X or Y that enhance the ionic resonance form of the singlet below.



These considerations would suggest a faster isc rate and thus a shorter lifetime for the cases with a higher ionic contribution in the (twisted) ground singlet. The carbonyl-bearing terminus is clearly the electron-deficient one. The shortest lifetime would thus have been expected for the compounds with donor groups in the para position. In fact, the p-Me$_2$N and *p*-MeO compounds show the longest lifetimes, probably as the result of a planar contribution that dominates for the former and is moderate for the latter. While one might ascribe the decrease in lifetime in the series *p*-CN > *m*-MeO, *p*-Cl > H to the anticipated polar effect, the lifetime decrease in this series is only some 35% in either solvent.

A heavy-atom effect can clearly be observed for *p*-bromochalcone, consistent with substantial spin density at the para position of the chalcone triplet. Neither *m*-Br nor *p'*-Br shows a significant effect, consistent with low spin density in the triplet at these positions.

The results provide at best scant support for the analysis of polar effects on olefin triplet lifetimes by the treatment of Salem and Rowland.[4] We have previously[8,18] anticipated that nuclear motions, which were not considered by Salem and Rowland, may be important.[19]

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Registry No. *p*-(Dimethylamino)chalcone, 1030-27-9; *p*-methoxychalcone, 959-33-1; *p*-methylchalcone, 4224-87-7; chalcone, 94-41-7; *p*-chlorochalcone, 956-04-7; *p*-bromochalcone, 1774-66-9; *p*-cyanochalcone, 5724-55-0; *m*-bromochalcone, 29816-74-8; *m*-methoxychalcone, 5470-91-7; *p'*-methoxychalcone, 959-23-9; *p'*-bromochalcone, 2403-27-2; *p'*-cyanochalcone, 31083-73-5; isoprene, 78-79-5.

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(14) Grabowski, Z. R.; Rotkiewicz, K.; Rubaszewska, W.; Kirkor-Kaminska, E. *Acta. Phys. Pol. A* **1978**, *A54*, 767.

(15) Grabowski, Z. R., Rotkiewicz, K.; Siemiarczuk, A., *J. Lumin.*, **1979**, *18/19*, 420.

(16) Stilbene triplets constrained by rigid glasses from twisting can have lifetimes increased over fluid solution lifetimes by many orders of magnitude. In addition to ref 11; see: Heinrich, G.; Blume, H.; and Schulte-Frohlinde, D. *Tetrahedron Lett.* **1967**, 4693. Saltiel, J.; Khalil, G.-E.; and Schanze, K. *Chem. Phys. Lett.* **1980**, *70*, 233.

(17) Bent, D. V.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1974**, *78*, 451-454.

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Azo Precursors to a Putative Biradical in Arene Meta Photoadditions: Evidence for a Novel Concerted Nitrogen Expulsion

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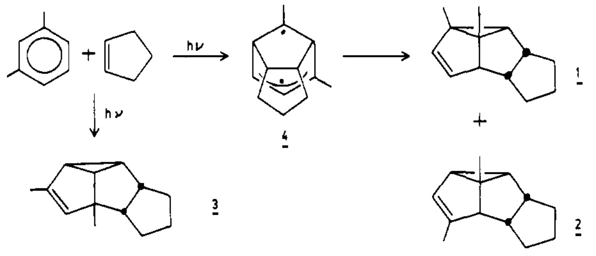
Cyclic azo compounds or 1,2-diazenes have become popular as precursors to organic biradicals.[2] The mechanisms of nitrogen loss in these molecules, however, are not well understood. In particular, subtle questions of concerted vs. stepwise decomposition have proved challenging to experimentalists and theoreticians.[2] We now wish to report a novel concerted nitrogen elimination reaction in two azo compounds corresponding to a retrohomo-Diels-Alder reaction.

Irradiation (254 nm) of an equivolume mixture of *m*-xylene and cyclopentene gave predominantly three products: the endo meta photoadducts **1** and **2**, which have been previously described,[3] and a compound to which we tentatively assign the structure **3**,[4]



which has not been reported. Biradicals such as **4** have been suggested as possible intermediates in arene-olefin photoadditions.[5] To explore this possibility we sought to generate **4** independently.

Reaction of **1** (from preparative GC) with 3-methyltriazoline-2,4-dione (MTAD) gave two major products, **5** (21%) and **6** (49%),[6] which were separated by flash chromatography.

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[1] Recipient of a Camille and Henry Dreyfus Foundation Grant for Newly Appointed Young Faculty in Chemistry.

(2) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(3) Cornelisse, J.; Merritt, V. Y.; Srinivasan, R. *J. Am. Chem. Soc.* **1973**, *95*, 6197.

(4) Tentative assignment based on ^{1}H NMR.

(5) Sheridan, R. S. *Tetrahedron Lett.* **1982**, *23*, 267. Gilbert, A. *Pure Appl. Chem.* **1980**, *23*, 2669 and references cited therein.

(6) Structural assignment is based on ^{1}H NMR, IR, and exact mass spectra; see supplementary material for data.

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