# The Norrish Type II Photofragmentation of Esters Induced by Intramolecular Electron Transfer

Dayal P. DeCosta,[†] Amy K. Bennett, and James A. Pincock*

Department of Chemistry, Dalhousie University
Halifax, Nova Scotia, Canada B3H 4J3
Received November 23, 1998

The classic Norrish Type II photofragmentation reaction of aromatic ketones played a significant role in the development of both mechanistic and theoretical organic photochemistry; several reviews are available.[1] The established reaction mechanism proceeds by intramolecular **hydrogen atom** transfer to the carbonyl oxygen from the γ carbon to form a 1,4-biradical that then fragments to the observed products,[2] eq 1, X = CH$_2$. When the
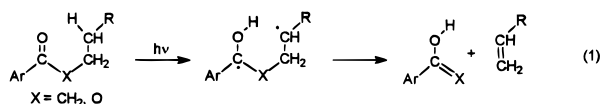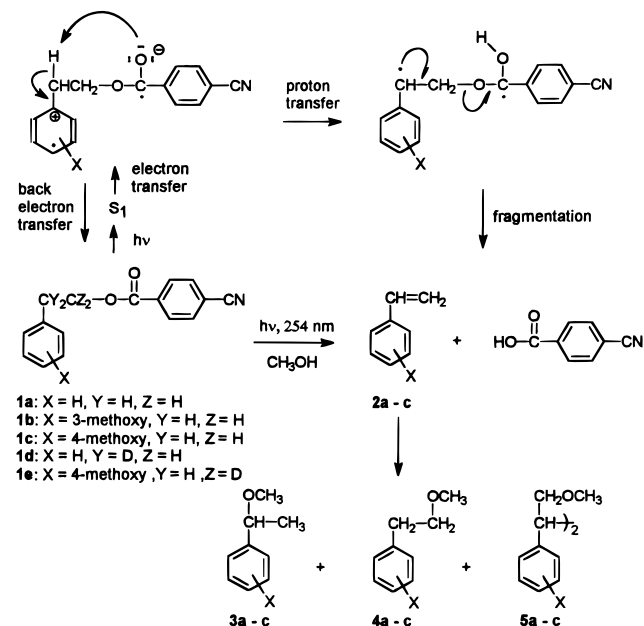
lowest energy excited state is of the n,π* triplet configuration, the efficiency for biradical formation is essentially 100%.

In contrast, for aromatic esters, eq 1, X = O, the reaction proceeds with very low efficiency. For instance, irradiation of a number of alkyl benzoates in acetonitrile does result in Norrish Type II fragmentation from both the π,π* singlet and triplet state, but the quantum yields average about 0.01 for the singlets and 0.001 for the triplets with the variation depending on the substituents on the aromatic ring.[3] Moreover, this inefficiency is not a result of preferential disproportionation of the intermediate 1,4-biradical back to starting material because a pair of diastereomers photoequilibrate in acetonitrile or pentane with a quantum yield (Φ = 0.008) that is even lower than that for fragmentation (Φ = 0.01).[4] This difference in reactivity between ketones and esters is ascribed to the fact that the esters have lowest energy π,π* states so that their carbonyl oxygen atoms are expected to be much less reactive toward hydrogen atom abstraction. We now report that the Norrish Type II fragmentation of esters can occur by intramolecular **proton transfer** if intramolecular electron transfer to form a radical ion pair occurs as the primary photochemical event.

As an extension of earlier work on arylmethyl ester (ArCH$_2$−O$_2$CR) photochemistry,[5] we have begun to examine arylethyl compounds with leaving groups (ArCH$_2$CH$_2$-LG) in the hope of obtaining a better understanding of β-cleavage reactions, a few of which have been observed previously.[6−11] To our surprise, the esters, **1**, reacted more efficiently than expected[12,13] on irradiation at 254 nm in methanol to give as the major[14] volatile (GC) products[15] those shown in Scheme 1 along with 4-cyanobenzoic

Scheme 1. Products (bottom) and Proposed Mechanism (top) for Photolysis of 4-Cyanobenzoate Esters, **1**, in Methanol

1a: X = H, Y = H, Z = H
1b: X = 3-methoxy, Y = H, Z = H
1c: X = 4-methoxy, Y = H, Z = H
1d: X = H, Y = D, Z = H
1e: X = 4-methoxy, Y = H, Z = D

acid. The yields, Table 1, indicate that at low conversions the styrenes, **2a**−**c**, are the major photoproduct and that the mass balance is good. However, at higher conversions, the styrenes, which are more strongly absorbing than **1**, rapidly disappear by secondary photochemistry and the mass balance drops, correspondingly.[16] These observations suggest (particularly for **1b**) that the styrenes and 4-cyanobenzoic acid are the major and perhaps only primary photoproducts. This conclusion is reinforced by irradiation, to complete conversion, of 2,2-diphenylethyl 4-cyanobenzoate, which gave 1,1-diphenylethylene in 80% yield, along with 1,1-diphenylethane (6%) and the Markovnikov (8%) and *anti*-Markovnikov (5%) ethers.

The secondary photolysis observed for the styrenes is of three types: (1) Markovnikov addition of methanol to give **3**, presumably by the photochemical acid-catalyzed addition to alkenes[17] with 4-cyanobenzoic acid, the other primary photoproduct, serving as the acid catalyst;[18] (2) *anti*-Markovnikov addition of methanol to give **4** and **5**, presumably by the PET mechanism[19] through the radical cation of the styrene, with either 4-cyanobenzoic acid or the starting ester, **1**, serving as the electron acceptor;[20] and (3) photooligomerization to nonvolatile products.

As summarized in Scheme 1, the primary photoproducts for these reactions are analogous to those expected from the Norrish

[†] Present address: University of Colombo, Sri Lanka.
(1) (a) Wagner, P. J. In *CRC Handbook of Organic Photochemistrty and Photobiology*; Horspool, W. M., Song, P.-S., Eds; CRC Press: New York, 1995; pp 449−470 and references therein. (b) Wagner, P. J.; Park, B.-S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcal Dekker: New York, 1991; Vol. 11, pp 227−366 and references therein.
(2) The enol is usually isolated as the ketone tautomer but can often be observed spectroscopically. The fragmentation products are often accompanied by cyclobutanols (the Yang reaction).
(3) Barltrop, J. A.; Coyle, J. D. *J. Chem. Soc. (B)* **1971**, 251−255.
(4) Gano, J. E. *Chem. Commun.* **1971**, 1491−1492.
(5) Pincock, J. A. *Acc. Chem. Res.* **1997**, *30*, 43−49.
(6) Jaeger, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6401−6402.
(7) Jaeger, D. A.; Bernhardt, E. A. *Tetrahedron. Lett.* **1983**, *24*, 4521.
(8) Cristol, S. J.; Mahfuza, B. A.; Sankar, I. V. *J. Am. Chem. Soc.* **1989**, *111*, 8207−8211 and references therein.
(9) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398−2408.
(10) Bhalerao, V. K.; Nanjundiah, B. S.; Sonawane, H. R.; Nair, P. M. *Tetrahedron* **1986**, *42*, 1487−1496.
(11) Abdel-Wahab, A. A.; Ismail, M. T.; Mohamed, O. S.; Khalaf, A. A. *Gazz. Chim. Ital.* **1985**, *115*, 591−594.

(12) The quantum yield for disappearance of **1a** was 0.05, between 5 and 50 times higher than the previously reported values for the Norrish Type II reaction of esters.
(13) The corresponding acetates of the 2-phenylethanols were photochemically inert.
(14) Minor amounts of ethylbenzenes, 3-aryl-1-propanols, and 1-aryl-2,2-dimethoxyethanes were also formed.
(15) The structures were determined either by isolation of products from the reaction mixtures or by independent synthesis. All compounds gave satisfactory spectral analysis.
(16) The styrenes are also formed in acetonitrile, but they rapidly disappear to form nonvolatile products, presumably oligomers.
(17) McEwen, J.; Yates, K. *J. Phys. Org. Chem.* **1991**, *4*, 193−206.
(18) The relative reactivity of styrenes by this pathway is 3-methoxy:4-methoxy:hydrogen = 72:26:0.8 and therefore **3** is formed most efficiently from **1b**.
(19) Neunteufel, R. A.; Arnold, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 4080−4081.
(20) The radical cations of styrenes react by this pathway with a relative reactivity of 4-methoxy:H = 0.03:180; the 3-methoxy compound is expected to react at a rate similar to that of the unsubstituted one. Therefore, the yield of **4** and **5** from **1c** is low.

Table 1. Yields of Products from the Photolysis of Esters **1** in Methanol

compd	% conv	product yields (%)[a]				
		2	**3**	**4**	**5**[b]	total
1a: X = H	11	52		16	7	75
	24	26		24	7	57
	85	2		22	9	33
1b: X = 3-OCH$_3$	7	84	2	3	2	91
	27	34	15	33	6	88
	66	18	21	48	5	92
1c: X = 4-OCH$_3$	4	44	10	1	7	62
	20	7	14	3	5	29
	75	0	13	5	6	24

[a] For instance, for **1a**, at 11% disappearance of starting material, the products **2**–**5** account for 75% of that 11%. [b] Mixture of two diastereomers in about equal amounts.

Type II photofragmentation of ketones.[1] Our proposed mechanism begins with excitation to S$_1$ followed by intramolecular electron transfer to give a radical ion pair with the 4-cyanobenzoate group being the electron acceptor. As expected for substrates that undergo rapid intramolecular electron transfer in S$_1$, compounds **1a**−**c** do not fluoresce efficiently in methanol.[21,22] The oxidation[23] and reduction[24] potential for esters **1a**−**c** along with the singlet excitation energy of 95 kcal/mol[25] allow an estimate of the free energy of electron transfer.[26] These values are exergonic; −2, −17, and −19 kcal/mol for **1a**, **1b**, and **1c**, respectively. The formation of the radical cation will increase the acidity of the benzylic hydrogen (pK_a ca. −12[27]) and radical anion formation will increase the basicity of the carbonyl oxygen (pK_a of the conjugate acid ca. 8[28]). The thermodynamic driving force for proton transfer is therefore 20 pK_a units, apparently enough to overcome the kinetic barrier for proton transfer from carbon. Exergonic back electron transfer is likely the dominant pathway in competition with proton transfer. The resulting 1,4-biradical then fragments to the two primary photoproducts.[29] Heats of formation for **1a** (−52 kcal/mol[30]), styrene (+23 kcal/mol[31]), and benzoic acid (−56 kcal/mol[31]) allow an estimate for the overall enthalpy of the reaction at +19 kcal/mol. Consequently, the reaction itself is endothermic but, after the initial excitation to S$_1$, the mechanism proceeds through a cascade of exothermic steps.[32]

A mechanism analogous to the one above has been proposed for a number of other carbonyl compounds but, to our knowledge, not for esters. For instance, both aryl alkyl ketones[33] and *N*-alkyl phthalimides[34] with oxidizable substituents, such as amino, hydroxy, and aryl groups on the alkyl chain, also react by an electron transfer followed by proton transfer pathway.

(21) For instance, in methanol, the relative fluorescence emmission intensity at 283 nm for toluene (Φ_F = 0.13):**1a** is 175:1. In addition, **1a** has a weak, long-wavelength, exciplex emission band. We are in the process of obtaining absorbance and both steady-state and time-resolved fluorescence spectra on these compounds as a function of solvent polarity. Electron transfer in analogous pyrenyl esters has been studied in some detail by fluorescence measurements but no reaction of the esters was reported.[22]

(22) Kawakami, J.; Iwamura, M. *J. Phys. Org. Chem.* **1994**, *7*, 31−42.

(23) Reversible, in volts versus SCE: 1.72 and 1.62 for **1b** and **1c**, respectively. A value of 2.4 V for **1a** is estimated from the value given for toluene: Eberson, L. In *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987; p 44.

(24) Irreversible, in volts versus SCE: −1.65, −1.66, and −1.66 for **1a**, **1b**, and **1c**, respectively.

(25) The long-wavelength absorption is mainly the 4-cyanobenzoate chromophore, particularly for **1a**.

(26) The Coulombic term, which will make the values more negative, was not included because its magnitude will depend on the conformation adopted for the radical ion pair. See ref 22.

(27) Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(28) Hayon, E.; Simic, M. *Acc. Chem. Res.* **1974**, *7*, 114−121. This estimate of 8 for the pK_a is made on the basis of the value of 5.5 reported for the conjugate acid of the radical anion of methyl benzoate and a plot of the change in pK_a as a function of reduction potential.

(29) GC/MS analysis revealed two very weak peaks (∼1% yield) isomeric with the starting ester. These are possibly products resulting from cyclization of the 1,4-biradical.

(30) Estimated from Benson's rules.

(31) Calculated from the heat of combustion.

Also relevant, in contrast to **1**, are the photocleavage reactions of several 2-phenethyl derivatives which have been studied previously. A good example is reported by Jaeger[6] for the photolysis of the mesylate, **6a**, in aqueous methanol, eq 2. Moreover, pho-

6a: Y = H, Z = H
6b: Y = H, Z = D
6c: Y = D, Z = H

(2)
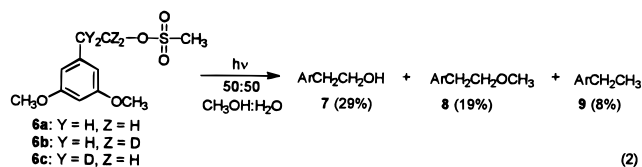
tolysis of the deuterated isomer, **6b**, demonstrated that although the starting material had only partially isomerized to **6c** (ratio of **6b**:**6c** = 6.1:1), the products **7** and **8** had the −CD$_2$− group essentially equally distributed between the two possible sites. These results were rationalized by proposing competing photoinduced cleavage to give **10** (major) and **11** (minor), or by **10** being a transition state between equilibrating open 2-arylethyl cations. An extension of this work by Cristol and co-workers[8] using analogous diastereomeric mesylates demonstrated that diastereomeric scrambling had occurred in the formation of the products. The contrast in reactivity between the 4-cyanobenzoates, **1**, and the mesylate presumably results from two facts: the poorer leaving group in **1** and the higher basicity of the 4-cyanobenzoate radical anion.
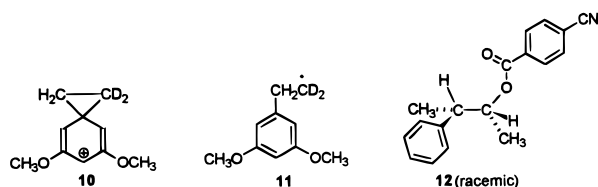
Three other experiments have contributed to the development of the proposed electron transfer mechanism for **1**. (1) Irradiation of **1d** gave products deuterated only on the carbons expected for the mechanism in Scheme 1. No scrambling was observed as required if intermediates such as **10** or equilibrating open cations were involved. (2) Compounds **1c** and **1e** reacted with relative efficiencies of 1.3:1. This small isotope effect is reasonable if the exothermic proton transfer in the intramolecular charge transfer complex is at least partially rate determining. (3) Photolysis in methanol of **12**, prepared from the known racemic (2*S*,3*R*): (2*R*,3*S*)-3-phenyl-2-butanol,[35] indicated inefficient formation of its diastereomer.[36] Therefore, fragmentation of the biradical in methanol is much faster than disproportionation back to starting material. The same is true for ketones in protic solvents.

In conclusion, we have discovered that a classic photochemical reaction, the Norrish Type II fragmentation, can occur for suitably substituted esters. Future experiments will be directed at exploring the scope and efficiency of this process.

(32) Preliminary results for the corresponding intermolecular reaction support this proposed mechanism. For instance, irradiation in methanol of 4-methoxyphenylethane and methyl 4-cyanobenzoate resulted in even more rapid disappearance of the former than for **1c**. The products, derived from the intermediate intermolecular radical pair, include 4-methoxystyrene, **2c** (and its Markovnikov methanol addition product), and three radical coupling products, methyl 4-(4-methoxyphenyl-1-ethyl)benzoate and the two diastereomers of 2,3-bis(4-methoxyphenyl)butane.

(33) Reference 1b, p 337.

(34) Griesbeck, A. G.; Henz, A.; Hirt, J.; Platschek, V.; Engel, T.; Loffler, D.; Schneider, F. W. *Tetrahedron*, **1994**, *50*, 701−714. We thank a referee for informing us of this work.

(35) Cram, D. J. *J. Am. Chem. Soc.* **1952**, *74*, 2129−2137.

(36) At 84% conversion, the ratio of disappearance of **12** to formation of the diastereomer was about 50:1.