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Photolysis of 10,10-difluorophenanthren-9(10*H*)-one. Evidence for solvent-assisted α -cleavage

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Abstract—The photolysis of 10,10-difluorophenanthren-9(10*H*)-one **1** in different solvents shows that the major competing reaction of the diradical formed by α -cleavage: recombination and hydrogen atom abstraction depends on the hydrogen atom donating ability of the solvent. Photolysis of **1** in cyclohexane in the presence of air or oxygen leads mainly to α -cleavage while photoreduction with the formation of 10-fluoro-9-phenanthrol occurs when the solution is deaerated prior to irradiation. In acetonitrile, a poor hydrogen donor, recombination of the diradical back to starting compound **1** is the sole process. © 2003 Elsevier Science Ltd. All rights reserved.

The α -cleavage of ketones¹ was first described in 1907 and is generally known as the Norrish Type I process. α -Cleavage is a fundamental reaction of electronically excited carbonyl compounds and for several systems the reactivity of the triplet ($n\pi^*$) state is greater than that of the corresponding singlet excited state by some orders of magnitude.

In cyclic ketones, the reaction pathways available to the acyl-alkyl diradicals,^{2,3} resulting from the α -cleavage, are recombination to give the original compound, a second α -cleavage (decarbonylation), internal disproportionation and rearrangements to an oxacarbene.

As may be expected, the rate coefficients of the individual processes have an appreciable effect on which of the pathways is preferred. Since the competing reactions require different diradical conformations, sufficiently long lifetimes of the triplet-derived diradicals, that allow them to attain conformational equilibration prior to reaction must also be considered. The diradicals produced from cyclic ketones usually follow more efficient modes of reaction than the second α -cleavage.⁴

Generally, the diradicals formed by α -cleavage undergo either recombination or internal disproportionation reactions. The disproportionation processes depend on the ring size of the cyclic ketone, and position and size of alkyl substituents that influence diradical partition-

ing by perturbing the population of the equilibrated conformers. This means that some individual transition-state geometries are more favoured than others.⁴

Several investigators have observed solvent effects^{5–7} on the α -cleavage reactions. Quantum yields and often chemical yields are very low in benzene, whereas they are respectable to good in alcohols. No explanation for this poorly understood effect is currently known. It is possible that further decomposition of untrapped ketenes is responsible for low yields.

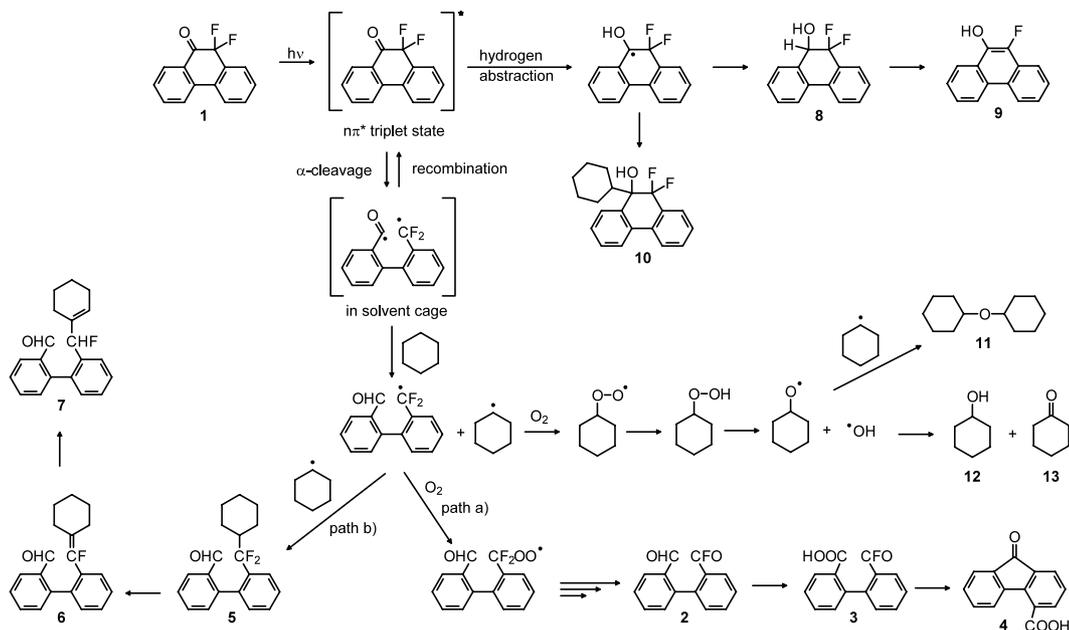
In cycloalkanones, the major competing triplet reaction is photoreduction by the solvent;^{8,9} this proceeds with a pseudounimolecular rate constant of 10^6 s^{-1} in hexane¹⁰ and 10^7 s^{-1} in ethanol. The value is somewhere between that of methanol¹¹ and is surprisingly low in acetonitrile ($k < 10^4 \text{ s}^{-1}$).

In this letter we present the results of the photolysis of 10,10-difluorophenanthren-9(10*H*)-one **1**¹² in cyclohexane and acetonitrile, showing that the efficiency of α -cleavage is not simply affected by solvent polarity, but is rather controlled by the hydrogen atom donor ability of the solvent.

There are two main reasons for our choice of 10,10-difluorophenanthren-9(10*H*)-one for these studies.

- The internal disproportionation of the diradical formed by α -cleavage is not possible.
- There is no active hydrogen atom for internal hydrogen atom abstraction from the $n\pi^*$ triplet state of the carbonyl group.

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Scheme 1. Photoproducts obtained after irradiation of **1**.

To determine the effect of the solvent, we used cyclohexane as a nonpolar solvent with good hydrogen atom donor ability and the polar acetonitrile as a weak hydrogen atom donor.

Results

Irradiation of a 0.013 M solution of 10,10-difluorophenanthren-9(10H)-one **1** (Scheme 1) for 4 h in cyclohexane at $\lambda = 360$ nm (λ_{max} of **1** in cyclohexane = 345.5 nm) resulted in a 10% conversion to a mixture of products: **2**, **3**, **4**, **6**, **7**, **9** and **10**. The crude reaction mixture was analyzed by GC/MS and ^{19}F NMR.¹³ The product distributions and the relative % yields are given in Table 1.

The structures of the products were determined on the basis of their mass and the ^{19}F NMR spectra of the crude reaction mixture, which shows besides the signal at $\delta = -103.80$ ppm, that corresponds to the *gem* difluoromethylene group of starting compound **1**, five

additional signals at $\delta = 28.68$, 27.67, -124.72 , -157.03 and -180.31 ppm.

The signals at 27.67 and 28.68 ppm correspond to the fluorine atom of acyl fluorides **2** and **3**, the signal at -124.72 ppm corresponds to the fluorine atom bonded to the sp^2 carbon of compound **6**, the signal at -157.03 is in agreement with the known chemical shift for the fluorine atom¹⁴ in compound **9**, while a doublet with the coupling constant $^2J_{\text{FH}} = 45$ Hz at -180.31 ppm corresponds to the fluorine atom in compound **7**. The relative ratio of fluorine signals for the mentioned compounds is very similar to the ratio of products obtained by GC analysis.

When the photolysis of **1** was carried out as a cyclohexane solution saturated with oxygen (acting as triplet quencher), lower conversion (3%) with the formation of products formed by α -cleavage was observed. On the other hand, when a cyclohexane solution of **1** was deaerated before irradiation, compound **9** was formed

Table 1. Conversion and product distribution^a in the photolysis^b of **1** in cyclohexane

Cyclohexane/ Conditions	Conversion of 1 (%)							
air, not degassed	10	6	32	17	22	11	12	Trace
Ar, degassed	9	-	-	-	9	-	91	-
Saturated O ₂	3	9	-	38	46	7	-	-

^a Relative yields in % determined by GC/MS. ^b Irradiation time: 4 hours; $\lambda = 360$ nm; concentration of substrate: 0.013M.

as the main product by hydrogen atom abstraction on the $\pi\pi^*$ triplet state of the carbonyl group.

With longer irradiation time (24 h) the conversion of **1** increases up to 50% but at the same time the reaction mixtures become more complex.

Irradiation of **1** in acetonitrile for 4 h at $\lambda=360$ nm resulted in no conversion. The ^{19}F NMR spectrum of the crude reaction mixture showed only a signal corresponding to the *gem* CF_2 group of starting compound **1**. GC analysis using diphenylacetylene as an internal reference showed no additional signals. We also determined that compound **1** is photostable in acetonitrile at longer irradiation times (24 h and 72 h).

Discussion

The $\pi\pi^*$ excited state of **1**, formed after absorption of one photon, can further react by two competing processes: (1) α -cleavage and (2) abstraction of a hydrogen atom.

α -Cleavage produces a diradical in a solvent cage that is capable of C–C bond rotation about the biphenyl bond and equilibrium of different rotational conformers is established. The calculated enthalpy of formation (ΔH_f) for the planar structure is -148.7 kJ mol $^{-1}$ and -160.4 kJ mol $^{-1}$ for a twisted conformer where the phenyl rings are orthogonal to each other¹⁵ (Fig. 1).

In cyclohexane, a good hydrogen donor, the triplet diradicals formed by α -cleavage can be first transformed by intersystem crossing into singlet diradicals¹⁶ that recombine to form the starting compound **1**. We believe that the process proceeds as a result of the planar conformation of the diradicals since the distance

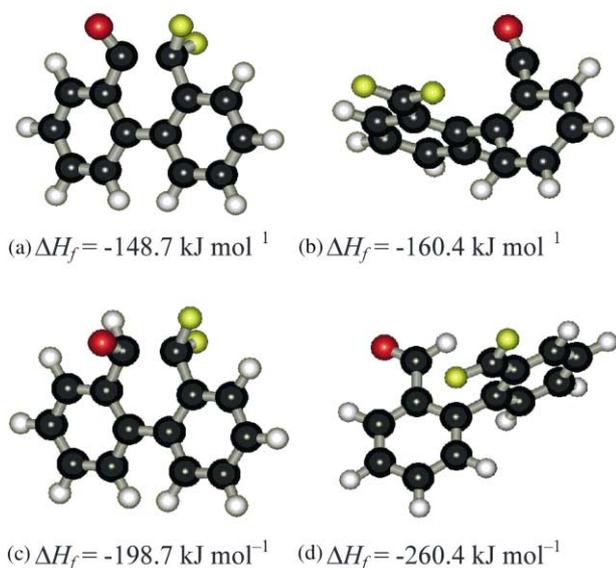


Figure 1. Ball-and-stick models for (a) planar and (b) twisted diradical; (c) planar and (d) twisted difluorobenzyl radical.

between the carbonyl carbon and that of the difluoromethylene group is very short ($r(\text{CO}:\text{CF}_2) = 1.57$ Å). On the other hand, the acyl group of the triplet diradical can abstract a hydrogen atom from the solvent thus forming a difluorobenzyl radical derivative (abstraction is much more convenient from the twisted conformer of the diradical), which diffuses from the solvent cage and reacts with cyclohexyl radicals (path b) and with oxygen (path a) when the photolysis was carried out in the presence of air or when the reaction mixture was purged with O_2 . In the latter case the peroxy radicals formed are transformed into acyl fluoride **2**, which is readily further oxidized into carboxylic acid **3**. After a Friedel–Crafts type intramolecular acylation of **3** the product **4** was formed. The reaction is probably catalyzed by hydrogen fluoride liberated during the formation of product **2** and the conversion of **5** to **6** and **8** to **9**. The relative % yield of product **4** in comparison with product **3** increased by increasing the irradiation time.

Reaction of a cyclohexyl radical with the difluorobenzyl radical derivative results in the formation of product **5**, which after the elimination of hydrogen fluoride generates compound **6**. An acid catalyzed rearrangement of the double bond in **6** produces the compound **7**.

Hydrogen atom abstraction also proceeds from the $\pi\pi^*$ excited state of the carbonyl group of starting ketone **1** and therefore, competes with α -cleavage, but is less expressed in aerated solutions (12%, Table 1) and is completely suppressed in solutions purged with O_2 . On the other hand, when the reaction solution was degassed this reaction became more favourable and the major product **9** was obtained by elimination of hydrogen fluoride from the first formed reduced product **8** (91%).

Photolysis in acetonitrile, a poor hydrogen atom donor, led to no conversion of starting compound **1**. The only process that took place even over prolonged time ($t=72$ h) was recombination of initially formed diradicals. It is possible that the solvent polarity has an influence on the formation of the $\pi\pi^*$ and the $\pi\pi^*$ triplet states. In non-polar cyclohexane the reactive $\pi\pi^*$ triplet is formed because it is lower in energy than the unreactive $\pi\pi^*$ triplet. In polar acetonitrile the position of the two triplet states is reversed. Here an unreactive $\pi\pi^*$ triplet is formed. To prove or eliminate this possibility we tested another polar solvent methanol, which also acts as a good hydrogen donor. Preliminary results on the photolysis of **1** in methanol show a similar reaction pathway to that observed in cyclohexane. The products are derived from α -cleavage but the overall conversion is higher than in cyclohexane (20%).

Conclusion

The results obtained in the photolysis of **1** in different solvents show that the major competing reactions of the diradical formed by α -cleavage recombination and hydrogen atom abstraction, depend on the hydrogen donor ability of the solvent. A higher chemical yield of products was obtained from the diradical in methanol in comparison with that in cyclohexane. This is likely to

be an effect of the lower C–H bond strength in methanol.¹⁷ Another factor may be the different populations of the equilibrated diradical conformers mediated by solvent molecules leading to recombination or hydrogen atom abstraction.

In acetonitrile, a poor hydrogen atom donor, recombination of the diradical back to starting compound **1** is the sole process.

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References

1. Wagner, P. J. *Top. Curr. Chem.* **1976**, 66, 1–52.
2. Wagner, P. J. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980.
3. Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, pp. 339–466.
4. Gilbert, A.; Baggott, I. In *Essentials of Molecular Photochemistry*; Wagner, P. J., Ed.; Blackwell Scientific Publications: Oxford, 1991; pp. 295–297.
5. Wagner, P. J. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vols. 42–43, p. 388.
6. Dalton, J. C.; Daves, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, 93, 7213–7221.
7. Dalton, J. C.; Turro, N. J. *Annu. Rev. Phys. Chem.* **1970**, 21, 499–560.
8. Scaiano, J. C. *J. Photochem.* **1973**, 2, 81–118.
9. Horspool, W. M. *Photochemistry in Organic Synthesis*; Coyle, J. S., Ed.; The Royal Society of Chemistry, Special Publication, 1986; Vol. 57, pp. 61–79.
10. Wagner, P. J. *J. Am. Chem. Soc.* **1966**, 88, 5672–5673.
11. (a) Charney, D. R.; Dalton, J. C.; Hautala, R. R.; Snyder, J. J.; Turro, N. J. *J. Am. Chem. Soc.* **1974**, 96, 1407–1410; (b) Yip, R. W.; Siebrand, W. *Chem. Phys. Lett.* **1972**, 13, 209–212.
12. Zupan, M.; Iskra, J.; Stavber, S. *Bull. Chem. Soc. Jpn.* **1995**, 68, 1655–1660.
13. **2**: $\delta_F = 27.67$ ppm; 228 (M^+ , 18); 200 (23); 199 (28); 182 (18); 181 (100); 180 (16); 171 (16); 170 (31); 153 (16); 152 (28); 151 (16); 104 (19); 76 (24). **3**: $\delta_F = 28.68$ ppm; 244 (M^+ , 17); 228 (13); 227 (71); 226 (22); 225 (100); 212 (19); 199 (30); 199 (18); 197 (88); 181 (39); 180 (23); 172 (22); 170 (44); 152 (14); 151 (15); 82 (23); 67 (32). **4**: 224 (M^+ , 25); 181 (21); 180 (100); 152 (54); 151 (24); 150 (14); 126 (13); 76 (29). **6**: $\delta_F = -124.72$ ppm; 294 (M^+ , 5); 213 (15); 212 (100); 183 (27); 164 (5); 163 (5); 55 (7); 41 (6). **7**: $\delta_F = -180.31$ ppm; 294 (M^+ , 2); 213 (15); 212 (100); 165 (3); 164 (3); 163 (3); 55 (9); 41 (7). **9**: $\delta_F = -157.03$ ppm; 212 (M^+ , 100); 184 (16); 183 (68); 164 (23); 163 (23); 106 (13); 92 (13); 81 (8). **10**: $\delta_F = -103.26$ ppm; 314 (M^+ , 6); 232 (17); 231 (31); 213 (20); 212 (100); 211 (30); 183 (42).
14. Zupan, M.; Iskra, J.; Stavber, S. *Croatica Chem. Acta* **1996**, 69, 1437–1447.
15. Enthalpies of formation were calculated on MP3 semi-empirical level, on full-optimized geometries, using the program HYPERCHEM 6.02.
16. Step, E. N.; Buchachenko, A. L.; Turro, N. J. *J. Org. Chem.* **1992**, 57, 7018–7024.
17. C–H bond strength in cyclohexane is 399 ± 5 kJ mol⁻¹ and 389 ± 5 kJ mol⁻¹ in methanol.