is not very informative because of the very different acidities of these ligands. The ligand, mugineic acid, is a much better complexing agent for ferrous iron than liquids which contain hydroxamate or catecholate. Thus, the great difference in redox potential would be explained by the relative stability of the ferrous complex of mugineic acid. The iron-solubilizing action of mugineic acid is strongly inhibited by the presence of cupric ion.[6] This can be explained by blockage of the Fe(III) binding to mugineic acid by Cu(II) ion, consistent with the order of the formation constant for the mugineic acid-metal complexes, Cu(II) ≥ Fe(III).

Most microbial siderophores have hydroxamate or phenolate groups as Fe(III)-ligand donors. The present phytosiderophore, mugineic acid, consists of carboxyl, amine, and hydroxyl groups as ligand functional groups. The mechanism for absorption and transport of iron in graminaceous plants involves the excretion of mugineic acid from the roots, which aids Fe(III) solubilization and reduction of Fe(III) to Fe(II).

Acknowledgment. We are grateful to Dr. Y. Maeda for Mössbauer measurements and to referees for useful comments. This study was supported in part by a grant from the Ministry of Education, Science, and Culture, Japan.

---

(21) Harris, W. R.; Weitl, F. L.; Raymond, K. N. *J. Chem. Soc., Chem. Commun.* **1979**, 177-178.

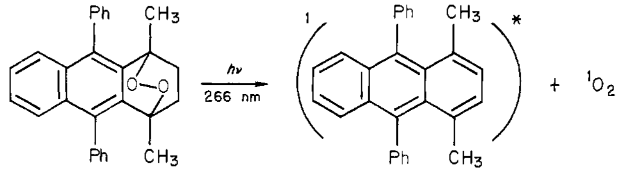
Picosecond Laser Study of the Adiabatic Photodissociation of an Endoperoxide

S.-Y. Hou, C. G. Dupuy, M. J. McAuliffe, D. A. Hrovat, and K. B. Eisenthal*

Department of Chemistry, Columbia University
New York, New York 10027

Received June 24, 1981

We wish to report the first direct evidence for the adiabatic photodissociation of an endoperoxide, the 1,4-endoperoxide of 1,4-dimethyl-9,10-diphenylanthracene (DMDPA-O_2). To establish that a photocleavage is adiabatic it is necessary to demonstrate that an excited electronic state photoproduct is produced.[1] The evidence that the photolysis of an endoperoxide is adiabatic has rested heretofore on the chemical evidence[2,3] that the oxygen fragment is produced in an excited state, $^1O_2$. In the present work we discovered a dissociation route in which the other fragment in the reaction, namely, the 1,4-dimethyl-9,10-diphenylanthracene (DMDPA), is produced in an excited singlet state rather than in the ground state. That the hydrocarbon fragment DMDPA is generated in an excited singlet state is established by observation of its fluorescence which in turn directly demonstrates that the photodissociation is adiabatic. The reaction can be written as



DMDPA-O_2 ^{1}DMDPA*

The precursor molecule, DMDPA-O_2 (1.5×10^{-4} M), in acetonitrile at room temperature, was excited with a picosecond laser pulse at 266 nm, the fourth harmonic of a Nd laser. The emission spectrum was recorded with a monochromator-optical multichannel analyzer, and the kinetics were measured with a streak camera.

We find that the fluorescence lifetime (0.5 ns) and spectrum (Figure 1) obtained on photoexcitation of the parent endoperoxide were indistinguishable from those of DMDPA, thus establishing the identity of the fragment. From the risetime of the fluorescence we found that the excited fragment DMDPA* appears in less than 5 ps. However, to demonstrate that the process is adiabatic, it is necessary to show that the observed fluorescence does not arise from a sequential two-photon process. Such a process would involve one photon exciting the endoperoxide and generating the ground-state fragment DMDPA. The DMDPA could then absorb a second photon from the same excitation pulse to produce DMDPA*, whose fluorescence we observe. Our experimental results show that the fluorescence varies linearly with the laser intensity, thus proving that this is indeed a one-photon process. We have also eliminated the possibility that DMDPA, present as an impurity in the endoperoxide sample or resulting from a buildup of the DMDPA photoproduct, is responsible for the observed fluorescence. This was done by determining that there was negligible emission following irradiation of the endoperoxide sample at 355 nm, where DMDPA adsorbs strongly but the endoperoxide does not.

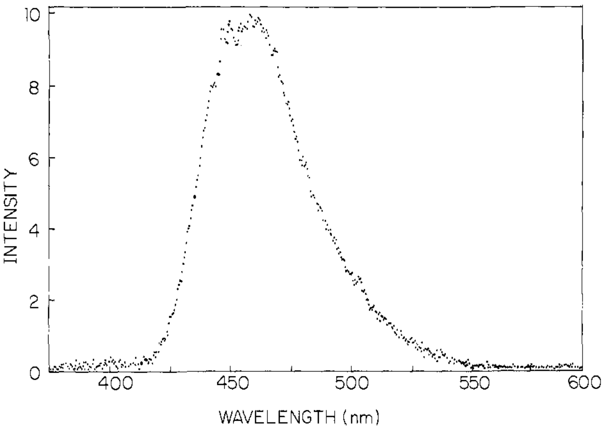


Figure 1. Fluorescence spectrum of the DMDPA* fragment following photodissociation of the precursor endoperoxide (1.5×10^{-4} M) in acetonitrile.

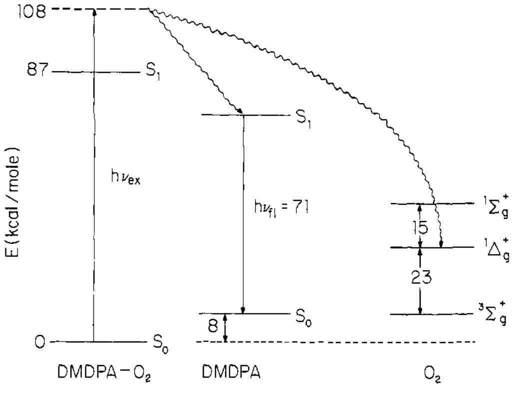


Figure 2. Energetics of endoperoxide photodissociation, $\lambda_{ex} = 266$ nm.

An interesting aspect of this photodissociative route is the particular state in which the oxygen is formed. It is reasonable to assume that the oxygen is released in an excited singlet state based on the time scale of the photolysis. We have shown that the photodissociation occurs in less than 5 ps as seen by the risetime of the ^{1}DMDPA* fluorescence. If oxygen were coming off in its triplet state the photodissociation process would be spin forbidden and highly unlikely to occur in such a short time. We can now consider the energetics of this route to decide on the particular excited state in which the $^1O_2$ is released. The two possible excited states for $^1O_2$ are the $^1\Sigma_g^+$ and the $^1\Delta_g$ separated by 15 kcal/mol. From the energy of dissociation[4-6] of DMDPA-O_2 and the energies

---

(1) Förster, Th. *Pure Appl. Chem.* **1973**, *34*, 225.

(2) Drews, W.; Schmidt, R.; Brauer, H. D. *Chem. Phys. Lett.* **1980**, *70*, 84.

(3) Turro, N. J., unpublished results on DMDPA-O_2.

(4) Turro, N. J.; Chow, M. F.; Rigaudy, J. *J. Am. Chem. Soc.* **1979**, *101*, 1300.

(5) Olmsted, J., III. *J. Am. Chem. Soc.* **1980**, *102*, 66.

0002-7863/81/1503-6982$01.25/0

of ^{1}DMDPA* and $^1O_2(^1\Delta_g)$,[7] we find that 102 kcal/mol is required to produce the excited hydrocarbon ^{1}DMDPA* and $^1O_2$ in the $^1\Delta_g$ state (Figure 2). The excitation light at 266 nm has an energy of 108 kcal/mol. Thus the process is energetically allowed with a maximum excess of 6 kcal/mol. To produce the $^1O_2$ in the $^1\Sigma_g^+$ state requires 9 kcal/mol more than that provided by the exciting light. We therefore conclude that in the newly observed adiabatic dissociation channel the $^1O_2$ is produced in the $^1\Delta_g$ state.

Acknowledgment. We thank Professor N. J. Turro for his valuable help in this work. We also thank the National Science Foundation, the Air Force Office of Scientific Research, and the Joint Services Electronics Program (DAAG-79-C-0079) for their generous support.

---

(6) From literature values of the thermochemistry of DMDPA and related endoperoxides the minimum value for the enthalpy of dissociation is used in order to determine the maximum energy available upon photodissociation.

(7) For a theoretical and experimental discussion of $^1O_2$, its spectroscopy, and reactions, see: Wasserman, H. H.; Murray, R. W., Eds. "Singlet Oxygen"; Academic Press: New York, 1979.

Substituent Effects on the Aliphatic Claisen Rearrangement. 1. Synthesis and Rearrangement of Cyano-Substituted Allyl Vinyl Ethers

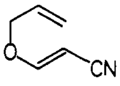
Cynthia J. Burrows and Barry K. Carpenter*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

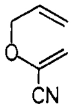
Received August 10, 1981

There has recently been a renaissance of interest in the aliphatic Claisen rearrangement both as a technique for organic synthesis[1] and as an important part of the shikimate biosynthetic pathway.[2] It is therefore somewhat surprising that there has, to our knowledge, been no systematic study of substituent effects on the rate of the reaction. In this communication we report the first stage of such an investigation. Our intentions are to provide a body of empirical data that could be employed by synthetic organic chemists and also to test the various qualitative[3] and quantitative[4] theories of substituent effects on pericyclic reactions.

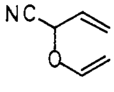
This stage of the investigation centers on the synthesis and rearrangement of the five cyano-substituted allyl vinyl ethers **1**–**5**.



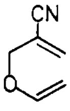
1



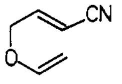
2



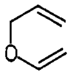
3



4



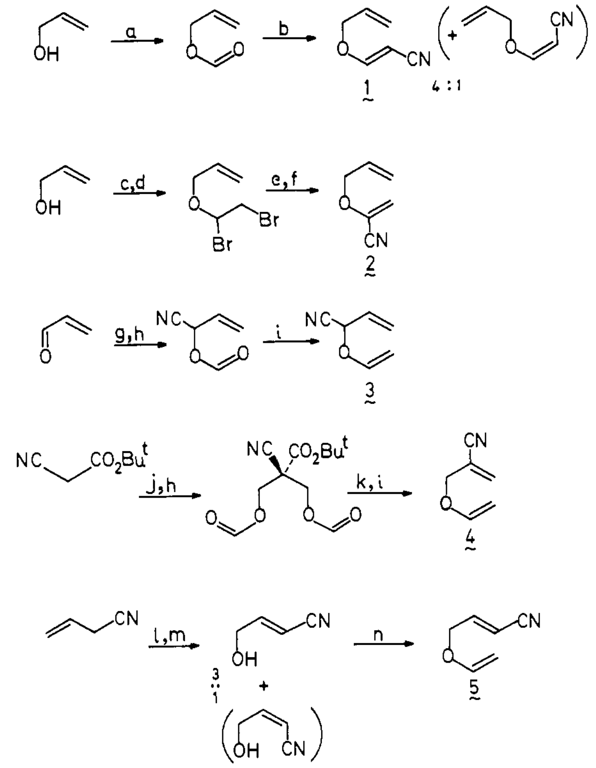
5



6

Of special interest is the comparison of the activation parameters for their [3,3]-sigmatropic rearrangement with those for the parent compound **6**. The cyano substituent was chosen as a sterically small π acceptor, although its radical stabilizing properties[5] might also be important for some theoretical interpretations.[4] The *E* configurations of compounds **1** and **5** were also selected to minimize steric effects in the transition state for the rearrangement.[1a] The syntheses of **1** → **5** are summarized in Scheme I.

Scheme I^a



^{a} Reagents: (a) $HCO_2H/CaCl_2$; (b) $Ph_3P{=}CHCN$; (c) $(EtO)_2CHCH_2Br/TsOH$; (d) BBr_3; (e) $Et_4N^+CN^-$; (f) Et_3N; (g) $NaCN/CH_3CO_2H$; (h) HCO_2H/DCC; (i) $Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Al(CH_3)_2$; (j) $H_2CO/H_2O/K_2CO_3$; (k) TsOH/PhH/Δ; (l) MCPBA; (m) $i\text{-}Pr_2N^-Li^+$ −78 °C; (n) $EtOCH{=}CH_2/Hg(O_2CCF_3)_2$.

Table I. Kinetic Data for Compounds 1–6

compd	temp range, °C	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(mol K)	k_{rel}, 100 °C
1	124–174	27.08 ± 0.09	−11.6 ± 0.2	0.90
2	66–115	22.84 ± 0.19	−13.4 ± 0.5	111
3	55–101	22.33 ± 0.20	−13.0 ± 0.6	270
4	90–140	22.58 ± 0.26	−18.0 ± 1.3	15.6
5	135–185	28.76 ± 0.54	−11.2 ± 1.2	0.11
6	113–173	25.40 ± 0.65	−15.9 ± 1.5	(1)

A few points in these syntheses require comment. The conversion of allyl formate to **1** by a Wittig reaction was inspired by the work of LeCorre[6a] and Subramanyam et al.[6b] We confirmed the observation of these investigators that unstabilized phosphorus ylides would not undergo an analogous reaction, although the reasons for this are not clear.

We were unable to convert acrolein cyanohydrin to **3** by either Hg^{2+} or Pd^{2+} catalyzed exchange with ethyl vinyl ether[7] although this procedure was successful in the synthesis of **5**. The use of the Tebbe reagent,[8] allowing preparation of **3** and **4** from the formates of the corresponding allylic alcohols, followed the precedent of Pine et al.[9]

The synthesis of compound **4** was by far the most difficult, primarily because the corresponding allylic alcohol (3-hydroxypropene-2-carbonitrile) was extremely susceptible to polymeri-

---

(1) (a) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227–232. (b) Bennett, G. B. *Synthesis* **1977**, 589–606. (c) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1974**, *22*, 1–252.

(2) Ganem, B. *Tetrahedron* **1978**, *34*, 3353–3383.

(3) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877–1884.

(4) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142–148.

(5) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(6) (a) LeCorre, M. *Bull. Chim. Soc. Fr.* **1974**, 2005–2008. (b) Subramanyam, V.; Silver, E. H.; Soloway, A. H. *J. Org. Chem.* **1976**, *41*, 1272–1273.

(7) Burgstahler, A. W.; Nordin, I. C. *J. Am. Chem. Soc.* **1961**, *83*, 198–206.

(8) Tebbe, F. N.; Parshall, G. W.; Reddy G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.

(9) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270–3272.

0002-7863/81/1503-6983$01.25/0 © 1981 American Chemical Society