J. Mass Spectrom. Ion Phys., **18,** 65 (1975).

(8) An increase in the bond energy of an association complex has been shown to enhance the kinetics of its formation; see E. Herbst, *J. Chem. Phys.*, **70,** 2201 (1979), and A. Good, *Trans. Faraday Soc.*, **67,** 3495 (1971). The rate constants in Table I exceed, for example, the value of 2.5×10^{-28} cm^6 $molecule^{-2}$ s^{-1} reported for the association of OH^- with H_2O to form the strongly proton-bound (24 kcal mol^{-1}) species $HO^- \cdots H^+ \cdots {}^-OH$: F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **61,** 3181 (1974); J. D. Payzant, T. Yamdagni, and P. Kebarle, *Can. J. Chem.*, **49,** 3308 (1971). They also greatly exceed the rate constants determined for the association of the other anions discussed later in the text.

(9) We could not rule out the production of HCO^- by proton abstraction under our experimental operating conditions. An ion with *m/e* 29 was observed to be produced in small quantities and shown in separate experiments to react with NH_3.

(10) As noted by one of the referees, another exothermic pathway is available for the production of H^-:

$$RHN^- + \;{>}C{=}O \longrightarrow RNH_2 + CO + H^-$$

(11) The formation of H^- could not be precluded under our experimental operating conditions because of its known associative detachment reaction with O_2 which was present in the reaction region; see D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, **53,** 987 (1970).

(12) For reactions of O^- with other carbonyl compounds, see A. G. Harrison and K. R. Jennings, *J. Chem. Soc., Faraday Trans. 1*, **72,** 1601 (1976).

(13) The electron affinity of the oxygen atom is only 1.5 eV. Electron affinities were taken from the compilation by H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6** (1977).

(14) An extensive study of nucleophilic displacement reactions with other carbonyl compounds at low pressures has very recently been reported by O. I. Asubiojo and J. I. Brauman, *J. Am. Chem. Soc.*, **101,** 3715 (1979).

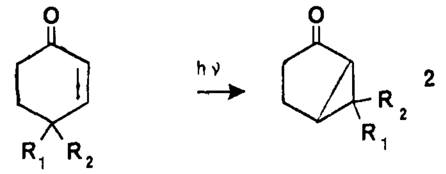
D. K. Bohme,* G. I. Mackay, S. D. Tanner
Department of Chemistry, York University
Downsview, Ontario M3J 1P3, Canada

Received May 21, 1979

Photochemistry of Ketones in Solution. 57.[1] Synthesis and Photochemistry of a Constrained 2-Cyclohexenone[2]

Sir:

The excited-state properties of 2-cyclohexenones continue to interest organic, physical, and theoretical chemists.[3] We have previously argued that the very low quantum efficiency ($\phi \leq 0.01$) of the so-called "lumiketone rearrangement" of 4,4-dialkyl enones, **1** → **2**,[4] cannot be adequately explained on

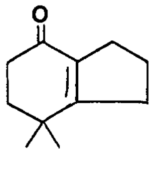


1 **2**

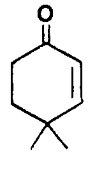
the basis of a mechanism involving C—C bond scission to form diradical or zwitterionic intermediates which revert to starting material in competition with progress to product.[5]

We have suggested[3c,5] that the planar enone triplet, formed in unit efficiency from the excited singlet state(s), relaxes rapidly by twisting around the C=C bond to give a twisted species which serves as an ideal "funnel" for crossing to the ground state (S_0) potential surface from T_1, since the difference in energy of S_0 and T_1 is minimized at this geometry.[5,6] A partitioning on the S_0 surface between return to starting material and conversion into rearrangement products is postulated, the latter being the minor decay pathway.

One corollary of this description is that enones which are constrained from twisting around the C=C bond should be unable to undergo the lumiketone rearrangement and might display photochemical and photophysical properties atypical of "normal" unconstrained enones. This has now been confirmed in the case of bicyclic enone **3**, a structural analogue of an enone (**4**) which displays prototypic enone photoreactivity



3

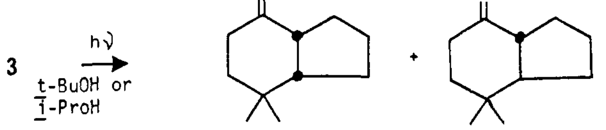


4

[i.e., inefficient rearrangement to lumiketone and cyclopentenone isomers via short-lived triplet states in *tert*-butyl alcohol (*t*-BuOH) and photoreduction in hydrogen-donor media such as 2-propanol (*i*-PrOH)].[3,7,8]

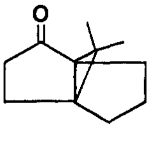
The synthesis of **3** is modeled in its initial stages on work of Raphael et al.[9] The structure of **3** is evident from spectral data, most notably λ_{max}^{EtOH} 249 nm (log ε 4.07); *m/e* 164 (M), 149 ($M^+ - CH_3$), 136 ($M^+ - CO^+$), 122 (base, $M^+ - C_3H_6$); IR (CCl_4) 1665, 1625, 1385, 1365 cm^{-1}; NMR δ 1.15 (sharp s, 6 H), 1.5–2.7 (m, 10 H), absence of vinyl H.

Irradiation of **3** in degassed *t*-BuOH through Pyrex at 300 nm led in low quantum efficiency to the formation of two major products, which were isolated chromatographically and identified as the *cis*- and *trans*-dihydro ketones **5** and **6** on the basis of spectral characteristics and independent synthesis from **3** using various hydrogenation methods.[10] The trans ketone **6** could be epimerized to the cis ketone **5** by treatment with $NaNH_2$-pyridine-Me_2SO-d_6.[11] A gas chromatography/mass spectroscopic analysis of the complete photolysate in this and all other solvents studied indicated the absence of any product isomeric with the starting enone but the presence of a minor product corresponding to an adduct of **3** and *t*-BuOH, probably **8**.[12-15] Enol **9**, synthesized independently from **3** by reduction with Dibal in toluene,[18] was not detected among the photolysis products of **3** in any solvent studied.

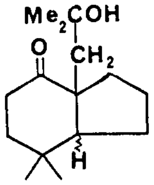


5 **6**

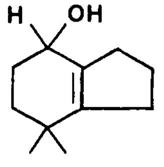
Φ = 0.00016 in t-BuOH
Φ = 0.041 in i-PrOH



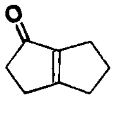
7



8



9



10

Irradiation of **3** in 2-PrOH under similar conditions again gave **5** and **6** in greater quantum efficiency and no photoisomers. The reaction was readily quenched in the presence of 1,3-cyclohexadiene (E_T = 53 kcal/mol)[19] with $k_q\tau_T$ = 63 M^{-1}, corresponding to a lifetime of the reactive triplet excited state of ~20 ns, assuming that triplet quenching is approximately diffusion controlled at 3×10^9 M^{-1} s^{-1} in *i*-PrOH.[19] Photoreduction is also observed in acetone, leading to **5**, **6**, and 2,5-hexanedione.

The photochemical behavior of **3** is qualitatively in accord with our expectation that typical enone molecular rearrangements should be inhibited in this case because of structural rigidity. However, the triplet lifetime of **3** is not particularly enhanced relative to that of cyclohexenone[6b] and simple substituted cyclohexenone[3,4,7] triplets which are not constrained from twisting around C=C.[20] Indeed, there is now strong

0002-7863/80/1502-0409$01.00/0

evidence from laser flash irradiation of several cyclic enones (including cyclohexenone itself, acetylcyclohexene, and testosterone) for the generation of transient triplet and ground-state species with twisted geometries.[23] Although some other cyclohexenones, most notably the 2-methyl and 3-methyl analogues of enone **4**, have been reported as unreactive toward the lumiketone rearrangement for reasons not at all clear at the present time,[8] there are two properties of **3** which appear to be unique in cyclohexenone photochemistry. One is that photoreduction of **3** at the C=C bond, strongly indicative of a reactive π,π^* triplet state,[3c,13,14,24,25] occurs even in *t*-BuOH and acetone, which are known to be unreactive as H donors toward n,π^* ketone triplets.[26] Thus, photorearrangement of **3** is slower than H abstraction even under conditions where the latter is expected to be unfavorable, contrary to the behavior of "normal" cyclic enones.[3,4,7,8,14] Secondly enone **3** exhibits fluorescence in fluid solution at room temperature, the first observation of such emission from a cyclohexenone.[27]

The fluorescence of enone **3** at room temperature in cyclohexane, methanol, and acetonitrile has a maximum at 385 nm; the excitation spectrum coincided with the UV absorption of **3**.[28] The fluorescence lifetime as determined by single photon counting was 0.26 ns. The emission was not quenched by CHD at concentrations sufficient to obliterate all photochemical reactivity. Loutfy and Morris[29] previously reported fluorescence from bicyclo[3.3.0]octenone **10**, attributed to an unusually large $^1n,\pi^*$-$^3\pi,\pi^*$ energy gap which inhibits intersystem crossing. We ascribe the observation of fluorescence of **3** to structural rigidity around the C=C bond, which inhibits rapid radiationless decay to a distorted geometry by twisting around the C=C bond, a decay process which can operate in unconstrained cyclohexenones. Thus, this suggests that unconstrained cyclohexenones may undergo intersystem crossing preferentially in nonplanar rather than planar geometries, contrary to usual assumptions.

We propose that the photochemical and photophysical properties of **3** are most readily understood in terms of the structural rigidity of **3** compared with that of other cyclohexenones studied to date. However, the surprisingly rapid nonproductive decay of the lowest triplet state of **3** needs to be explained, as well as the reason for the lack of reactivity toward rearrangement of some cyclohexenones[8] which appear to be unconstrained with respect to twisting around the C=C bond. These problems, as well as detailed studies of other constrained enones, are now under investigation in our laboratory.

Acknowledgement. This research was supported in part by the National Science Foundation under Grant CHE-76-09566, for which support we are most grateful. We appreciate the assistance of Mr. Walter Davidson of Halcon, Inc., with the GC/MS analyses and of Mr. Oscar Roberto with the fluorescence lifetime measurements. We are indebted to P. J. Wagner for critical comments beyond the call of editorial duty.

References and Notes

(1) Part 56: D. I. Schuster and J. Eriksen, *J. Org. Chem.*, in press.
(2) Presented before the Organic Division at the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 1979, ORGN 383.
(3) For recent reviews of this subject, see (a) O. L. Chapman, and D. S. Weiss, *Org. Photochem.*, **3**, 197 (1973); (b) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976, Chapter 7; (c) D. I. Schuster in "Molecular Rearrangements in Ground and Excited States", P. de Mayo, Ed., Academic Press, New York, in press.
(4) For reviews of the contrasting situation in dienone photochemistry, where rearrangements proceed with high efficiency, see ref 3a and 3b, as well as P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967); D. I. Schuster, *Acc. Chem. Res.*, **11**, 65 (1978); K. Schaffner and M. Demuth in ref 3c.
(5) D. I. Schuster, R. H. Brown, and B. M. Resnick, *J. Am. Chem. Soc.*, **100**, 4504 (1978), and earlier papers cited.
(6) (a) J. Michl, *Mol. Photochem.*, **4, 243**, 257 (1972); (b) P. J. Wagner and D. I. Buchek, *J. Am. Chem. Soc.*, **91**, 5090 (1969).
(7) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963); G. Wampfler, Ph.D. Dissertation, Iowa State University, 1970; B. M. Resnick, Ph.D. Dissertation, New York University, 1974.
(8) Dauben and co-workers previously reported that the 2-methyl and 3-methyl analogues of enone **4** fail to undergo the lumiketone rearrangement, a result attributed to some sort of steric effect. Photoreduction in these systems also seems to be suppressed. Quantitative data were not given. No studies were reported on 2,3,4,4-tetramethyl-2-cyclohexenone, perhaps a better structural analogue of enone **3:** W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).
(9) G. A. MacAlpine, R. A. Raphael, A. Shaw, A. W. Taylor, and H.-J. Wild, *J. Chem. Soc., Perkin Trans. 1*, 410 (1976); *J. Chem. Soc., Chem. Commun.*, 834 (1974).
(10) Hydrogenation of **3** over PtO_2/C in EtOH gave only **5**, while a similar reaction over Pd/C gave a mixture of **5** and **6**. The former conditions are known to favor clean cis hydrogenation of C=C bonds, while the latter often afford apparent trans hydrogenation owing to migration of the double bond in the presence of palladium catalysts prior to reduction: R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, 1965.
(11) See A. J. Wexler, J. A. Hyatt, P. W. Reynolds, C. Cottrell, and J. S. Swenton, *J. Am. Chem. Soc.*, **100**, 512 (1978).
(12) Spectral data and details of secondary photochemical transformation of **8** will be reported separately.
(13) This assignment is consistent with H abstraction at C_β and radical coupling at C_α. For related reactions in enone photochemistry, see ref 14.
(14) S. Wolff, W. L. Schreiber, A. B. Smith III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972); S. Ayral-Kaloustian, S. Wolff, and W. C. Agosta, *ibid.*, **99**, 5984 (1977); B. Byrne, C. A. Wilson II, S. Wolff, and W. C. Agosta, *J. Chem. Soc., Perkin Trans. 1*, 1550 (1978); D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).
(15) Nucleophilic addition of alcohols to enones to give ethers is a well-known photoreaction[8,16,17] but does not seem to occur in this system.
(16) W. C. Agosta and A. B. Smith III, *J. Am. Chem. Soc.*, **93**, 5513 (1971).
(17) E. Dunkelblum, H. Hart, and M. Jeffares, *J. Org. Chem.*, **43**, 3409 (1978), and earlier reports cited therein.
(18) See K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970).
(19) Estimated from data on related alcohols given by P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).
(20) Although the typical cyclohexadiene (CHD) dimers were detected, indicating that transfer of triplet excitation had occurred,[21] we can not exclude the possibility that quenching of intermediate radicals by CHD was also taking place to some extent.[22] Also, the assumption of diffusion-controlled quenching requires further confirmation.
(21) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).
(22) See D. I. Schuster and G. C. Barile, *Tetrahedron Lett.*, 3017 (1976); D. I. Schuster, G. C. Barile, and K. Liu, *J. Am. Chem. Soc.*, **97, 4441** (1975).
(23) R. Bonneau, J. Joussot-Dubien, J. Yarwood, and J. Pereyre, *Tetrahedron Lett.*, 235 (1977); R. Bonneau, P. Fornier de Violet, and J. Joussot-Dubien, *Nouv. J. Chim.*, **1**, 31 (1977); R. Bonneau and P. Fornier de Violet, *C. R. Acad. Sci. Paris, Ser. C*, **284**, 631 (1977); T. Goldfarb, *J. Photochem.*, **8**, 29 (1978).
(24) A. Devaquet, *J. Am. Chem. Soc.*, **95**, 5160 (1972); *Top. Curr. Chem.*, **54**, 1 (1975).
(25) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968). *Helv. Chim. Acta*, **51**, 1890 (1968); *J. Am. Chem. Soc.*, **93**, 3129 (1971).
(26) For rare investigations of H abstraction from *t*-BuOH by ketones, see D. S. Kendall and P. A. Leermakers, *J. Am. Chem. Soc.*, **88**, 2766 (1966); D. W. Alexander, A. C. Pratt, and A. E. Tipping, *Tetrahedron Lett.*, 2893 (1976).
(27) Enone **3**, also readily undergoes photocycloaddition to alkynes and alkenes to give [4.3.2]propellane derivatives, which is not surprising since analogous photocycloadditions to the enone lacking the *gem*-dimethyl groups have been reported by R. L. Cargill and J. W. Crawford, *J. Org. Chem.*, **35**, 356 (1970), and N. P. Peet, R. L. Cargill, and D. F. Bushey, *ibid.*, **38**, 1218 (1973).
(28) The identical fluorescence was seen using samples of **3** prepared at different times and subsequently purified by repeated column and gas–liquid partition chromatography to a purity of >99.8%, according to GLC analysis.
(29) R. O. Loutfy and J. M. Morris, *Chem. Phys. Lett.*, **19**, 377 (1973).

David I. Schuster,* Saadat Hussain
Department of Chemistry, New York University
Washington Square, New York, New York 10003

Received January 15, 1979

Electron-Beam-Induced Wolff Rearrangement

Sir:

The Wolff rearrangement[1] has attracted much interest both academically[2,3] and industrially.[4-6] For the most part this is due to the high reactivity of α-diazo ketones and the relative ease with which products may be chemically or spectroscopically analyzed. Mechanistic studies for electron-beam exposure

0002-7863/80/1502-0410$01,00/0