dπ* or ππ* parentage. As a result, photochemical processes in fluid solutions above 0°C cannot be anticipated from low temperature spectroscopic results. The determination of the range of applicability of these selection rules for radiationless transitions to other transition metal complexes awaits more definitive studies of the wavelength dependence of photoluminescence quantum yields and lifetimes (vide supra). Studies of this type, when coupled with time-resolved spectroscopy throughout the temperature region between −196 and 25°C, will help to determine whether efficient population of the lowest set of thermally equilibrated excited levels regardless of orbital parentage is general, as previously postulated,[1,2] or whether the selection rules we have proposed are generally applicable. A firm experimental substantiation of the general pathways for radiationless deactivation in metal complexes is fundamental to understanding the photophysics and photochemistry of these molecules.

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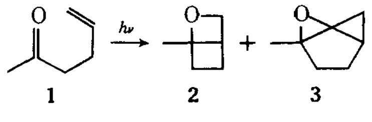
Mechanistic Photochemistry of γ,δ-Unsaturated Ketones. Discovery of a Photo-Cope Reaction of β-Oxa-γ,δ-enones and Its Implications for the Mechanism of Intramolecular Photocycloaddition

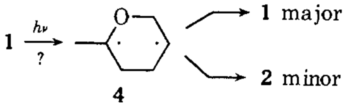
Sir:

Irradiation of γ,δ-unsaturated ketones and aldehydes most often results in formation of 2-oxabicyclo[2.2.0]hexanes and/or 5-oxabicyclo[2.1.1]hexanes (eq 1).[1] The quantum yields for these intramolecular photocycloaddition reactions are usually low, particularly for acyclic γ,δ-enones.[1a,b,l] Srinivasan has reported, for example, a quantum yield of 0.006 for formation of oxetane **2** on irradiation of ketone **1**.[1a]

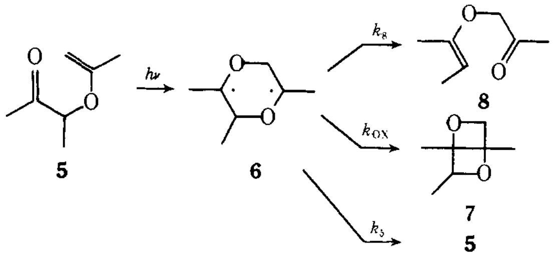


1 **2** **3** (1)

One of the possible causes of the considerable inefficiency in formation of 2-oxabicyclo[2.2.0]hexanes on photolysis of γ,δ-enones is the intermediacy of a cyclic 1,4-biradical, e.g., **4**, which undergoes β-cleavage to regenerate the starting γ,δ-enone more efficiently than closure to the 2-oxabicyclo[2.2.0]hexane (see eq 2).[1,2] If such biradical partitioning does occur, then irradiation of a suitably labeled β-oxa-γ,δ-enone such as **5** should yield photo-Cope products, e.g., **8**,[3] since in this case the cyclic 1,4-biradical, **6**, is "symmetrical" and has two possible β-cleavage pathways to yield γ,δ-enones (see eq 3).[4] By measuring the quantum yields



4 (2)



5 **6** **8** **7** **5** (3)

for intramolecular photocycloaddition (**5** → **7** and **8** → **7**) and for photo-Cope reactions in both directions, i.e., **5** → **8** and **8** → **5**, the relative values of k_8, k_5, and k_{ox} can be determined. This establishes an upper limit on the extent to which cyclic 1,4-biradical **6** undergoes β-cleavage and allows the role of β-cleavage from **6** in contributing to the inefficiency of intramolecular photocycloaddition of β-oxa-γ,δ-enones to be evaluated.[5]

With these thoughts in mind, we have studied the photochemistry of γ,δ-enones **5**[6] and **8**.[7] Irradiation of a pentane solution (0.08 *M*) of 3,5-dimethyl-4-oxa-5-hexen-2-one (**5**) at 313 nm for 5 hr results in 32% loss of **5** and a 27% yield of two new compounds, an intramolecular photocycloaddition product, **7**,[8] and the photo-Cope product, **8**, in a ratio of 2.5:1 (eq 4).[9] Prolonged irradiation leads to disappearance of both the starting γ,δ-enone **5** and the photo-Cope product **8**, and formation of 1,4,6-trimethyl-2,5-dioxabicyclo[2.2.0]hexane (**7**) as the major product. Quantum yields for formation of **7** and **8** from photolysis of **5** in hexane to less than 5% conversion are found to be 0.12 and 0.04, respectively.[10] Similar irradiation of a pentane solution (0.08 *M*) of 5,6-dimethyl-4-oxa-5-hexen-2-one, **8**, for 4 hr leads to a 27% loss of **8** and a 20% yield of oxetane **7** and photo-Cope product **5** formed in a 3.1:1 ratio (see eq 5).[11]

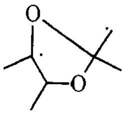
$$\mathbf{5} \xrightarrow[\text{pentane}]{h\nu} \underset{\Phi = 0.12}{\mathbf{7}} + \underset{\Phi = 0.04}{\mathbf{8}} \qquad (4)$$

$$\mathbf{8} \xrightarrow[\text{pentane}]{h\nu} \underset{\Phi = 0.13}{\mathbf{7}} + \underset{\Phi = 0.05}{\mathbf{5}} \qquad (5)$$

Quantum yields for formation of **7** and **5** from photolysis of **8** in hexane to less than 5% conversion are measured to be 0.13 and 0.05, respectively.[10] Thus we note that β-oxa-γ,δ-enones **5** and **8** undergo competitive intramolecular photocycloaddition and photo-Cope reactions. Although still overall an inefficient process, the efficiencies of intramolecular photocycloaddition for **5** and **8** are considerably greater than the efficiencies reported for other acyclic γ,δ-enones.[1a,b,l]

The formation of photo-Cope products upon irradiation of β-oxa-γ,δ-enones **5** and **8** is consistent with the intermediacy in these photolyses of 1,4-biradical **6**, which partitions between closure to bicyclo[2.2.0]hexane **7** and cleavage to β-oxa-γ,δ-enones **5** and **8** in a ratio of approximately

3:1.2:1.[12] The low values of the quantum yields for formation of photo-Cope products ($\Phi_{5\rightarrow8} = 0.04$, $\Phi_{8\rightarrow5} = 0.05$) make it clear that the bulk of the inefficiency in intramolecular photocycloaddition of these β-oxa-γ,δ-enones is *not* due to β-cleavage of 1,4-biradical intermediate **6**. Since kinetic studies indicate that the intramolecular oxetane formation is an S_1 reaction and that trapping of the ketone $^1n,\pi^*$ state of **5** or **8** by the internal olefin is efficient,[13] the low quantum yields for oxetane formation must result from inefficient reaction from some intermediate on the pathway to **7** other than the γ,δ-enone $^1n,\pi^*$ state or biradical **6**. The obvious candidate is an exciplex formed by interaction of the electrophilic half vacant oxygen atom of the n,π^* state and the electron-rich γ,δ-double bond. Analogous exciplexes have been postulated as intermediates in intermolecular and intramolecular photocycloaddition reactions of ketones and electron-rich olefins.[1l,2b,14] Our quantum yield measurements indicate that the efficiency of formation of biradical **6** from both exciplexes is at most 20%.[15] The inefficiency in proceeding from the exciplex to **6** could result from direct decay of the exciplexes to the ground state of the starting γ,δ-enone and/or from competitive formation from the exciplexes of 1,4-biradicals in which oxygen is bonded to the γ-carbon, e.g., **9**. Since our mass balances are high (>70%), formation of biradicals such as **9** followed by closure to a 2,5-dioxabicyclo[2.1.1]hexane cannot be a major pathway for decay of the exciplexes.[16] Thus if biradicals with oxygen bonded to the γ-carbon are formed they must primarily undergo cleavage to regenerate starting γ,δ-enones.



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In summary, we have shown that acyclic β-oxa-γ,δ-enones **5** and **8** undergo photo-Cope reactions in competition with inefficient intramolecular photocycloaddition to form dioxabicyclo[2.2.0]hexanes. Both photoreactions most likely proceed through a common 1,4-biradical intermediate, **6**. The bulk of the inefficiency in production of 1,4,6-trimethyl-2,5-dioxabicyclo[2.2.0]hexane is attributed to inefficient formation of biradical **6** from an exciplex initially generated by interaction of the carbonyl $^1n,\pi^*$ state with the internal olefin.

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(2) 1,4-Biradicals analogous to **4** have also been postulated as intermediates in the intermolecular photocycloaddition of carbonyl compounds to electron-rich olefins. See, for example, (a) N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, **92**, 320 (1970); (b) N. C. Yang and W. Eisenhardt, *ibid.*, **93**, 1277 (1971); (c) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).

(3) Although it is a priori possible that the γ,δ-enone analogous to **8**, but with the methyl groups trans, could also be formed, only **8** is observed (vide infra).

(4) See ref 1g for an earlier example of a photo-Cope reaction of a γ,δ-enone in which the γ,δ-double bond is allenic.

(5) We observed formation of 2,5-dioxabicyclo[2.2.0]hexanes but no photo-Cope product on irradiation of 3-methyl-4-oxa-5-hexen-2-one. In this case, however, the photo-Cope product would be an aldehyde which might not be stable under the reaction conditions. See ref 1o.

(6) γ,δ-Enone **5** was prepared in 15% yield by a transetherification reaction between 3-hydroxy-2-butanone and isopropenyl methyl ether using mercuric acetate as the catalyst. See H. Yuki, K. Hatacha, K. Nagata, and K. Jajiyama, *Bull. Chem. Soc. Jpn.*, **42**, 3546 (1969).

(7) γ,δ-Enone **8** was obtained by dehydrohalogenation of *erythro*-6-iodo-5-methyl-4-oxahexan-2-one or the corresponding bromo compound. The erythro iodo was prepared by reaction of *trans*-2-butene, acetol, mercuric oxide, and iodine while the erythro bromo compound was prepared by reaction of acetol, *N*-bromoacetamide, and *trans*-2-butene. See (a) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughn, *J. Am. Chem. Soc.*, **60**, 440 (1938); (b) P. J. Stang and M. G. Mangum, *ibid.*, **97**, 1459 (1975).

(8) **7**: ^{1}H NMR (CCl$_4$, δ, 100 MHz) 1.22–1.28 (9 H, includes 1.28 (s), 1.22 (s), and 1.28 (d, $J = 8$ Hz)), 4.7–5.0 (3 H, includes 4.7 (ABq), and 4.96 (q, $J = 8$ Hz)); ν_{max} (CCl$_4$, cm^{-1}) 955 (oxetane); MS (*m/e*, relative intensity, 20 eV) 128 (M$^+$, 3), 85 (4), 72 (5), 71 (10), 70 (9), 58 (13), 55 (21), and 43 (100).

(9) Product ratios were determined by GLPC using internal standards. Products were isolated by removal of solvent followed by preparative GLPC.

(10) Quantum yields were measured using the photoreduction of benzophenone by benzhydrol as an actinometer. See W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, **84**, 1368 (1962).

(11) Small, but variable, yields of 3-methyl-2,5-hexanedione and 2-butanone are also observed on irradiation of **8**. These products most likely arise via acetonyl radicals formed by β-cleavage of **8**.

(12) The photo-Cope products could also be formed by β-cleavage of the β-oxa-γ,δ-enones to acetonyl radicals, followed by recoupling to rearranged β-oxa-γ,δ-enones. This mechanism seems quite unlikely, however, since photolysis in piperylene partially quenches formation of hexanediones, believed to be formed via β-cleavage to acetonyl radicals,[11] but does not quench formation of photo-Cope or 2,5-dioxabicyclo[2.2.0]hexane products. A concerted photo-Cope reaction from **5** or **8** is also unlikely both on the basis of orbital symmetry considerations and because of restrictions placed on the transition state for intramolecular photocycloaddition by the stereoelectronic requirements for electrophilic attack by the carbonyl oxygen on the γ,δ-double bond (see, for example, N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5**, 92 (1972)). It is also possible that photo-Cope products could be formed by unimolecular decomposition of hot ground state 2,5-dioxabicyclo[2.2.0]hexane (**7**) formed by closure of biradical **6**. Bond energy and ring strain considerations suggest that **7** is formed from **6** with approximately 35 kcal/mol of excess vibrational energy. Vibrational relaxation of vibrationally excited **7**, however, should be much faster than cleavage to γ,δ-enones, a process whose activation energy can be estimated to be on the order of 36 kcal/mol using bicyclo[2.2.0]hexane as a model. See C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).

(13) Formation of **7** and photo-Cope product upon irradiation of **5** or **8** is not quenched in neat 1,3-pentadiene. Unlike normal alkanones ($\Phi_f \sim 10^{-3}$), but like other acyclic γ,δ-enones,[1l,1o] both **5** and **8** show no measurable fluorescence ($\Phi_f < 10^{-4}$) indicating that the singlet lifetime, τ_f, is much shorter for these γ,δ-enones than for normal alkanones.[1l,1o] This provides strong evidence for efficient trapping of the alkanone $^1n,\pi^*$ state by the γ,δ-double bond.

(14) See, for example, (a) R. A. Caldwall, G. W. Sovocool, and R. P. Gajewski, *J. Am. Chem. Soc.*, **95**, 2549 (1973); (b) I. E. Kochevar and P. J. Wagner, *ibid.*, **94**, 3859 (1972); (c) N. E. Schore and N. J. Turro, *ibid.*, **97**, 2482 (1975); (d) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971).

(15) This requires the reasonable assumption that the only pathways for decay of biradical **6** are β-cleavage or closure.

(16) This requires the reasonable assumption that 2,5-dioxabicyclo[2.1.1]hexanes do not decompose to the starting β-oxa-γ,δ-enone. Careful examination by NMR and GLPC yields no evidence for the presence of 2,5-dioxabicyclo[2.1.1]hexanes in the photolysis mixtures.

(17) Shell Fellow, 1974–1975.

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Synthesis and Characterization of a New Series of First Row Element Tetrahedral Mercaptide Complexes

Sir:

Tetrahedral, monomeric complexes of halide and pseudohalide ions with first row transition elements are well docu-