10^{-2}.[10] Such a relatively efficient reaction, especially at the concentrations used,[11] requires a moderately long-lived excited-state species.[12] The only long-lived complex excited state would presumably have to be the triplet state. Triplet states of square-planar d^8 complexes are almost certainly tetrahedral and can be expected to cross over rapidly into the ground state.[13] It would thus seem that photoexcited quinone is the logical candidate for the active partner in the reaction. This would explain our observation that the reactivity or unreactivity of particular quinones is the same in reaction 1 and in the cyclosulfate synthesis.

Studies of the chemistry of **2** and **4** under various conditions and attempts to expand this synthesis to thiolenes and to other metal complexes will be reported soon.[14]

[10] Estimated at 365 nm relative to the quantum yield for photochemical decomposition of $[(NH_3)_4Co(NH_2,O_2)Co(NH_3)_4]^{4+}$ in 0.1 *M* $HClO_4$ solutions. *Cf.* J. Valentine and D. Valentine, *J. Amer. Chem. Soc.*, in press.

[11] These concentrations produced optimum yields; at higher concentrations separation problems were encountered.

[12] We assume explicitly that neither geometrical isomerization of **1** nor expulsion of a ligand would lead to the observed products.

[13] See ref 1b for further exposition of this point.

[14] We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

[15] National Science Foundation Summer Fellow, 1969.

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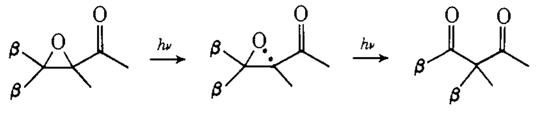
Photoisomerization of Phenalen-1-one Oxide. A New Course of Light-Induced α,β-Epoxy Ketone Rearrangement[1]

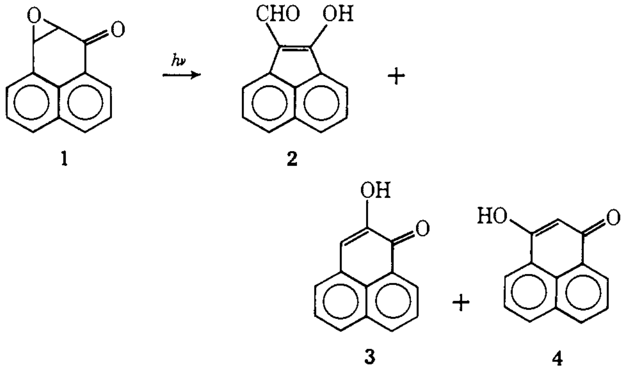
Sir:

The photoisomerization of α,β-epoxy ketones to β-diketones is a subject of considerable interest.[2] A characteristic feature of this reaction is the lack of phenyl migration, which has been interpreted in terms of the mechanism in eq 1, whereby there is complete or pronounced bond breaking at the β carbon prior to rebonding of the migrating group at the α position.[2a,c] On investigating the generality of this feature, we have discovered a new course of photorearrangement of an α,β-epoxy ketone system, which is described herein.



(1)

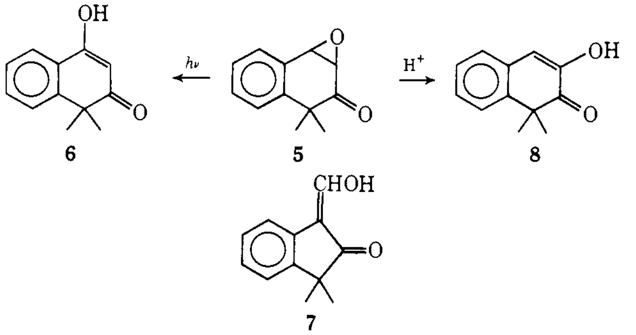
Irradiation[3] of a 0.5% solution of phenalenone oxide **1**[4] in acetonitrile followed by silica gel chromatography provided three products identified as acenaphthen-1-one-2-carboxaldehyde (**2**),[5] 2-hydroxyphenalen-1-one (**3**),[4] and 3-hydroxyphenalen-1-one (**4**)[6] by direct comparison with the known compounds. The products **2**, **3**, and **4** were obtained in 16, 30, and 5% yields, respectively.



The results provide a distinct point of departure from previous findings. Based on the mechanism of eq 1, formation of product **2** requires an aryl migration, which has not been observed previously. The β-diketone **4**, predicted to be the major product, was actually produced in minor amount. Furthermore the formation of **3** apparently represents the first example of an α,β-epoxy ketone photorearrangement to an α-diketone, a process which is not readily explicable in terms of eq 1.

These findings suggested that epoxy ketone **1** follows an alternative course of photorearrangement, which was considered either (a) to be unique for this naphthyl carbonyl system, or (b) to reflect a general feature of the system, such as incorporation of the β-aromatic substituent into the cyclic epoxy ketone framework which might reasonably facilitate aryl migration. Thus, it was of interest to investigate 1,1-dimethyl-2-(1H)-naphthalenone oxide (**5**),[7] which retains the latter feature.

Irradiation[8] of **5**[8] in acetonitrile yielded a single crystalline product, mp 199–200°, in 21% yield. Although isomeric with **5**, the photoproduct was not identical with either the acid-catalyzed rearrangement product of **5**, mp 101–102°, formulated as the β-diketone **6**,[7] or the previously unreported formyl ketone **7**,



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[1] Taken in part from the Ph.D. Thesis of R. M. G., Emory University, Atlanta, Ga., 1969. The preparation of this thesis and the terminal research of R. M. G. were directed by Dr. Leon Mandell.

[2] (a) H. E. Zimmerman, B. R. Cowley, C-Y. Tseng, and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 947 (1964), and earlier reports; (b) H. Wehrli, C. Lehmann, P. Keller, J. Bonet, K. Schaffner, and O. Jeger, *Helv. Chem. Acta*, **49**, 2218 (1966), and earlier reports; (c) C. S. Markos and W. Reusch, *J. Amer. Chem. Soc.*, **89**, 3363 (1967), and earlier reports; (d) J. P. Pete and M. L. Villaume, *Tetrahedron Lett.*, 3753 (1969); (e) for an interesting vinylogous system, see M. Debono, R. M. Molloy, D. Bauer, T. Iizuka, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **92**, 420 (1970); (f) for a review, see A. Padwa in "Organic Photochemistry," Vol. I, Marcel Dekker, New York, N. Y., 1967, pp 93–100.

[3] A Hanovia 450-W medium-pressure Hg lamp was utilized together with a Corex filter (λ > 280 nm).

[4] L. F. Fieser and L. W. Newton, *J. Amer. Chem. Soc.*, **64**, 917 (1942).

[5] E. Ghigi, A. M. Drusiani, and L. Plessi, *Ann. Chim. (Rome)*, **53**, 266 (1963); *Chem. Abstr.*, **59**, 15225*a* (1963).

[6] K. Fleischer and E. Retze, *Chem. Ber.*, **55**, 3280 (1922).

[7] N. H. Cromwell and R. D. Campbell, *J. Org. Chem.*, **22**, 520 (1957).

[8] (a) The epoxy ketone was obtained crystalline, mp 35–38°; (b) experimental details will be presented in full report.

mp 119–120°, which was prepared straightforwardly.[8b] However, a comparison of the nmr spectra of the acid-catalyzed and photorearrangement products of **5** clearly indicates that the latter is **6**, while the former should be reformulated as the α-diketone **8**.

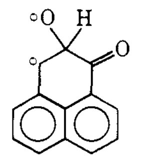
It is known that the H_β resonance of an α,β-unsaturated ketone system is shifted to higher field on replacement of H_α by a hydroxyl group,[9] as observed in the phenalenone system; *cf.* H_β of phenalen-1-one (**9**) and the α-diketone **3** in Table I. Replacement of H_β by OH results in an analogous upfield shift of H_α in this system; *cf.* H_α of **9** and β-diketone **4**. In the naphthalenone series, in addition to aromatic, methyl, and hydroxyl resonances, the acid-catalyzed and photorearrangement products exhibit sharp singlets, each attributable to one hydrogen, at τ 3.12 and 4.30, respectively. With reference to the spectrum of the parent 1,1-dimethyl-2(1H)-naphthalenone (**10**), these spectra clearly classify the photoproduct as the β-diketone **6**, and the acid product as the α-diketone **8**. Furthermore, the latter formulation has been confirmed by an unambiguous synthesis.[8b]

Table I. Nmr Spectra[a]

Compd	Solvent	τ (multiplicity) (*J*, Hz)	
		H_α	H_β
9	$CDCl_3$	3.38 (ABq) (10)	2.40[b] (ABq) (10)
9	DMSO-d_6	3.27 (ABq) (10)	1.95[b] (ABq) (10)
3	$CDCl_3$		2.86 (s)
4	DMSO-d_6	3.97 (s)	
10	$CDCl_3$	3.95 (ABq) (10)	2.68 (ABq) (10)
6[c]	DMSO-d_6	4.30 (s)	
8[d]	DMSO-d_6		3.12 (s)
8[d]	CCl_4		3.20 (s)

[a] Spectra were obtained on a Varian A-60A spectrometer. [b] These chemical shifts were determined by spin decoupling for which we thank Mr. Richard Zaylskie, Metabolism and Radiation Research Laboratories, USDA, Fargo, N. D. [c] Photoproduct. [d] Acid-catalyzed rearrangement product.

The results are noteworthy for the following reasons. First, the postulated[7] formation of β-diketone **6** on acid-catalyzed rearrangement of epoxy ketone **5** represents an unexpected course for this transformation. Reformulation of the product as the α-diketone **8** removes this ambiguity and establishes an analogy with the corresponding transformation of epoxy ketone **1** to α-diketone **2** in the phenalenone series.[4] Secondly, the photochemical rearrangement of epoxy ketone **5** to β-diketone **6** provides an example of the lack of aryl migration in a system for which this course appears to be structurally more attractive than in previous cases examined. This finding further substantiates the earlier proposals.[2a,c] Thirdly, the epoxy ketone **1** is shown to undergo a unique photochemical rearrangement. These results are reasonably interpreted in terms of the intermediacy of biradical **11**, which may partition into the major products **2** and **3** by an acyl and hydrogen migration, respectively. This possibility is in accord with the proposal that excitation is "localized" in the aromatic chromophore of the lowest energy triplet state (π,π*) of naphthyl carbonyl systems, a model based on phosphorescence data[10] and supported by a low photoreactivity of these systems in typical n,π* carbonyl reactions.[11] The present results may constitute direct chemical evidence for the spectroscopic model.



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[9] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, pp 93–94.

[10] (a) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949); (b) V. Ermolaev and A. Terenin, *J. Chim. Phys.*, **55**, 698 (1958).

[11] (a) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962); (b) N. C. Yang, M. Nussium, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964); (c) for a review, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 99 (1968).

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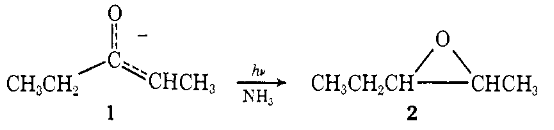
Ketone Enolate Photochemistry

Sir:

In connection with a survey of carbanion irradiations,[1-3] we have now examined the photochemical behavior of a typical monocarbonyl enolate, pentan-3-one anion, apparently the first such case to have been studied. Although almost obscured by precedented photoinduced reduction and coupling processes, a novel, but predicted, valence bond isomerization was detected: the transformation, with protonation, of excited ketone enolate **1** to epoxide **2**.



Sodium enolate was prepared from dry, freshly distilled 3-pentanone by reaction with sodium hydride in THF.[4] Either in the presence or absence of dry *tert*-butyl alcohol,[5] the anion in solution was irradiated[6] for 4 hr in a 450-W Hanovia quartz apparatus. After hydrolysis, no epoxides and only the reduction products of 3-pentanone were formed in isolable amounts. Major products were 3-pentanol (**3**), 3-(2-tetrahydrofuryl)-3-pentanol (**4**), and di-2-tetrahydrofuryl (**5**). However,

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[1] E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **87**, 4964 (1965); **89**, 5073 (1967).

[2] J. I. Brauman, J. Schwartz, and E. E. van Tamelen, *ibid.*, **90**, 5328 (1968).

[3] J. Schwartz, *Chem. Commun.*, 833 (1969).

[4] Solutions of the enolate were prepared under an atmosphere of dry, prepurified nitrogen and were transferred to the irradiation apparatus under nitrogen pressure. The ketone was dried by distillation from calcium hydride, and the solvent was distilled under nitrogen from benzophenone ketyl.

[5] Vpc analysis of an aliquot of this reaction mixture which was treated with excess methyl iodide showed the presence of less than 20% ketone and greater than 80% of the enolate to be present in this reaction mixture.

[6] The enolate in THF displays an ultraviolet spectrum featuring λ_{max} 287 mμ (ε 11,200).