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**.

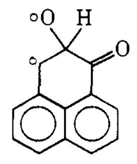
It is known that the H_β resonance of an α,β-unsaturated ketone system is shifted to higher field on replacement of H_α by a hydroxyl group,[9] as observed in the phenalenone system; *cf.* H_β of phenalen-1-one (**9**) and the α-diketone **3** in Table I. Replacement of H_β by OH results in an analogous 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	τ (multiplicity) (*J*, Hz) 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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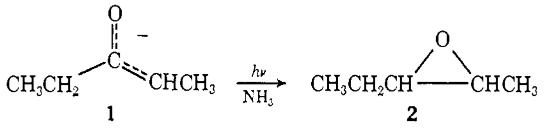
Ketone Enolate Photochemistry

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**.



$$CH_3CH_2\overset{\overset{O}{\|}\ -}{C}{\cdots}CHCH_3 \xrightarrow[NH_3]{h\nu} CH_3CH_2\overset{O}{CH{-}{-}CHCH_3}$$

1 **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).

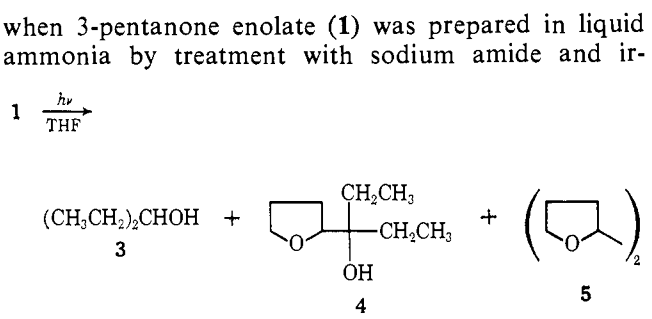
(3) J. Schwartz, *Chem. Commun.*, 833 (1969).

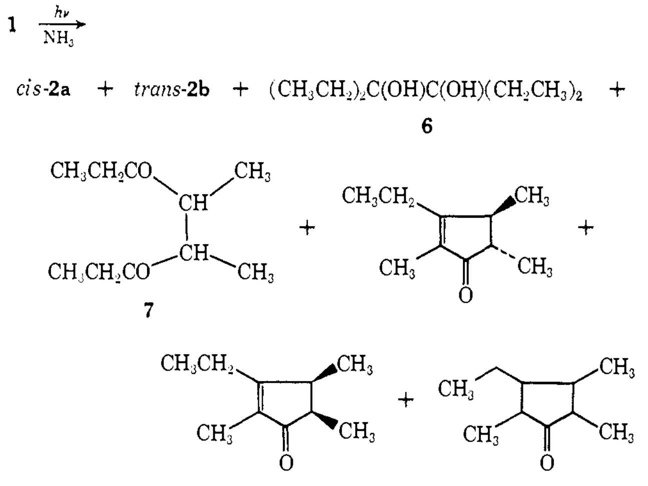
(4) Solutions of the enolate were prepared under an atmosphere of dry, prepurified nitrogen and were transferred to the irradiation apparatus under nitrogen pressure. The ketone was dried by distillation from calcium hydride, and the solvent was distilled under nitrogen from benzophenone ketyl.

(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).

when 3-pentanone enolate (**1**) was prepared in liquid ammonia by treatment with sodium amide and irradiated at 2537 Å for 8 hr, followed by addition of 1 equiv of ammonium chloride, yields of 2% *cis*-pentene-2,3-oxide (**2a**) and 0.2% *trans*-pentene-2,3-oxide (**2b**) were realized. The products were collected by preparative vpc,[7] and identification was made by means of vpc, nmr, and mass spectral comparison with authentic material. The major products in the liquid ammonia irradiation were shown to be the pinacol **6** and the base-catalyzed cyclization products of the ketone dimer **7**. Attempts to sensitize the reaction were unsuccessful. No change in the yield of epoxides was observed when either benzophenone or naphthalene was employed as a triplet sensitizer.





Past investigations have revealed[2,3] that photochemically activated carbanions may experience enhanced basicity. In view of this possibility, we thought it especially noteworthy that the excited state of the enolate anion undoubtedly bears a substantial amount of negative charge on the carbonyl carbon.[8] Thus, in the presence of an acid too weak to protonate it in the dark, an enolate, on irradiation, could protonate at the carbonyl carbon to yield with ring closure, the corresponding epoxide. Alternatively, concerted cyclization of the enolate would produce the epoxide anion directly, a pathway analogous to the photochemical formation of oxaziranes from nitrones.[9] Epoxide anions have not been observed to ring open to enolates, but undergo slow α elimination of alkoxide to yield carbene-derived products.[10,11]

Formation of the less thermodynamically stable cis epoxide in tenfold excess over the trans isomer may be the result of preferred geometrical factors operative in the ground state or in the transition state for cyclization. Substituted allylic anions are believed to be more stable in the cis configuration,[12] and this may also be true for enolates. In regard to orbital symmetry factors, concerted photochemical cyclization could give either epoxide from either ground state, since there is no stereochemical label at the oxygen atom.

The production of epoxides thus provides evidence for the photochemical valence bond isomerization of enolates. This potentially synthetically useful reaction, then, reveals a mechanistic path available to carbonionic species, different from those outlined previously. Further work is in progress to ascertain the reasons for the predominance of the cis product.

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[7] An F and M thermal conductivity vpc with a 10 ft × $^3/_8$ in. column of 10% FFAP on Chromosorb P was used in these studies (72° oven for volatile components, 160° oven for high-boiling products).

[8] See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1967, Chapter 8.

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[10] J. K. Crandall and L. C. Lin, *J. Amer. Chem. Soc.*, **89**, 4526, 4527 (1967).

[11] Treatment of an epoxide with strong base, when a hydrogen β to oxygen is present, results in the formation of the corresponding allylic alcohol: J. K. Crandall and L. C. Lin, *J. Org. Chem.*, **33**, 2378 (1968).

[12] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 193, for an extensive discussion.

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Geometric Isomerization *vs.* Cycloreversion in the Pyrolysis of Tetramethylcyclobutane-d_6. Ponderal and Energetic Effects on the Competition Ratio in a Series of "1,4-Butanediyls"[1]

Sir:

Both thermodynamic[2] and quantum mechanical[3] arguments have been used to rationalize and predict the behavior of the high-energy species produced as intermediates or transition states in the unimolecular pyrolysis reactions of simple small-ring compounds. As part of an effort to provide experimental tests of these ideas, we report here the preparation and pyrolysis of *cis*-, racemic *trans*-, and optically active *trans*-1,1,2,2-tetramethylcyclobutane-d_6.

Stereospecific syntheses of the labeled hydrocarbons from the known[4] compounds *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylic acid and *cis*-1,2-dimethylcyclobutane-1,2-dicarboxylic anhydride followed procedures similar to those used[5] for the corresponding tetramethylcyclopropane-d_6 isomers. Optical activation of

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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[3] (a) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (b) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, in press; (c) L. Salem, *Bull. Soc. Chim. Fr.*, in press. (d) We thank Professors Hoffmann and Salem for preprints of the latter two papers.

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