

molecular ene reaction,<sup>9,10</sup> or alternatively it can also be regarded as a variant of the symmetry-allowed 1,5-hydrogen shift.<sup>11</sup> Obviously, further work is required before a final conclusion can be reached with regard to the exact mechanism.

Besides the mechanistic aspects of this unique cyclization, we are presently engaged on an examination of its synthetic utility<sup>12</sup> and on an exploration of its scope by a study of other diallenic and related systems.

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(9) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); for recent reports on ene reactions of alkylallenes with various enophiles see ref 10.

(10) H. H. Wasserman and L. S. Keller, *Chem. Commun.*, 1483 (1970); D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3322 (1970); J. C. Martin, P. L. Carter, and J. L. Chitwood, *ibid.*, **36**, 2225 (1971); H. A. Chia, B. E. Kirk, and D. R. Taylor, *Chem. Commun.*, 1144 (1971); H. Gotthardt, *Tetrahedron Lett.*, 2343 (1971); D. R. Taylor and D. B. Wright, *J. Chem. Soc., Perkin Trans. 1*, 956 (1973).

(11) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(12) It is of interest to note that while it is quite difficult to obtain thiophene 1,1-dioxides by oxidation of thiophenes,<sup>13</sup> the present method may afford an easy route for their synthesis. Subsequent reduction can also afford variously substituted thiophenes.

(13) L. A. Paquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968, p 106; C. D. Hurd, *Quart. Rep. Sulfur Chem.*, **4**, 90 (1969).

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### Photodecarbonylation of 3-Cyclopentenones. Triplet Pericyclic Reactions<sup>1</sup>

Sir:

An interesting mechanistic feature of the pericyclic fragmentations of 3-cyclopentenones (e.g., **1a** and **1b**) results from the prediction of orbital symmetry<sup>2a</sup> theory that both linear sigmasymmetric or nonlinear axisymmetric decarbonylation are "allowed" in ground state. To the best of our knowledge, no experimental test of these ideas has been reported for any simple member of the 3-cyclopentenone family of structures **1**.<sup>3</sup> However, in other pertinent cases, Lemal has reported that diazines such as **2** (which are isoelectronic with 3-cyclopentenones) lose nitrogen by a *sigmasymmetric* pathway.<sup>4</sup> In the *closest* example related to the work to be reported here, Saltiel<sup>5</sup> has found that benzene sensitized decomposition of the sulfones, **3**, exhibit preferential *axisymmetric* reactivity. These results can be interpreted in terms of the expected reversal of stereospecificity of a *linear* cycloreversion as one proceeds from a thermal fragmentation to a ( $\pi, \pi^*$ ) photochemical fragmentation.<sup>2a</sup>

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(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

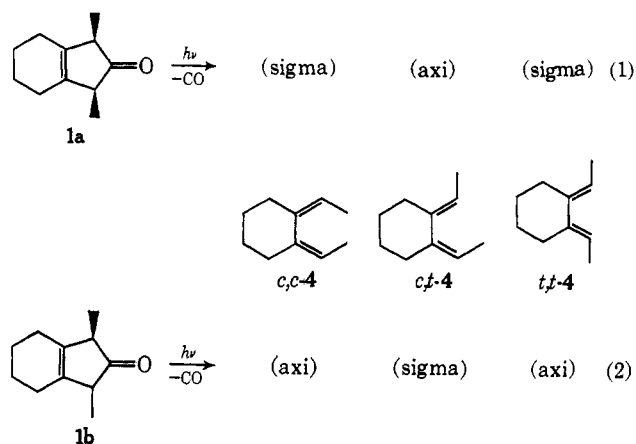
(3) Quinkert observed decarbonylation and subsequent 1,4 closure of the initial photoproducts during the irradiation of 2,5-diphenyl-3,4-benzocyclopentanone: *Angew. Chem., Int. Ed. Engl.*, **10**, 196 (1971).

(4) (a) S. D. McGregor and F. M. Lemal, *J. Amer. Chem. Soc.*, **88**, 1335 (1966); (b) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966).

(5) J. Saltiel and L. Metts, *J. Amer. Chem. Soc.*, **89**, 2232 (1967).

On the other hand, it appears that the orbital correlation of the  $n, \pi^*$  state of cyclopentenone may not establish favorable preservation or orbital symmetry during fragmentation. Some question exists if such an example falls under the jurisdiction of conventional orbital symmetry rules. Lemal<sup>4a</sup> has suggested that 3-cyclopentenones might decarbonylate in a *sigmasymmetric* fashion not only in the ground state but in a  $n, \pi^*$  state as well. Baldwin<sup>4b</sup> has pointed out that simple MO correlation diagrams do not give a direct prediction of allowedness for  $n, \pi^*$  decarbonylations. So far, no specific predictions relevant to the effect of spin multiplicity have been made in the literature. We report here our results on the photochemistry on the 3-cyclopentenones **1a** and **1b** and show that our data can be interpreted in support of a *dual linear and nonlinear concerted pathway for decomposition via a 3-cyclopentenone triplet*.

Irradiation of **1a** and **1b** in benzene at room temperature results (eq 1 and 2) in efficient loss of carbon



monoxide and quantitative formation of the 1,3-dienes *c,c-4*, *t,c-4*, and *t,t-4*. The yields of 1,3-dienes listed in Table I are extrapolated values which refer to zero con-

Table I

Ketone	$\phi^a$	$k_q\tau^b$	Relative % yields <sup>c</sup>		
			<i>c,c-4</i>	<i>t,c-4</i>	<i>t,t-4</i>
<b>1a</b>	0.49	4.3	0.18	0.22	0.60
<b>1b</b>	0.50	2.3	<0.04	0.48	0.52

<sup>a</sup> The quantum yields were measured at 313 nm in benzene for the total diene production. <sup>b</sup> The values were obtained for 1,3-pentadiene quenching in benzene at 25°. <sup>c</sup> Extrapolated to 0% conversion, see text.

version as an appropriate correction for sensitized dienes isomerization. Stern-Volmer quenching of reactions 1 and 2 by 1,3-pentadienes occurs but results in *no change* in the relative diene yields of *c,c-4*, *c,t-4*, and *t,t-4*. Stern-Volmer plots were linear to 0.2 M quencher concentration which yield  $k_q\tau$  values equal to 4.3 and 2.3  $M^{-1}$  for **1a** and **1b**, respectively. Comparable 1,3-pentadiene quenching has been reported for cyclopentenone **1c**.<sup>6</sup>

In an effort to determine the role of the singlet state in these reactions, the fluorescence lifetimes of **1b** and the tetramethyl ketone **5** were determined (Table II).

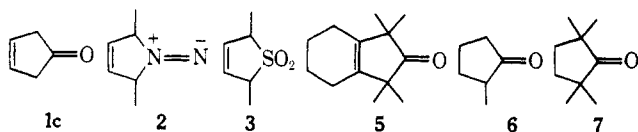
(6) P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, 5181 (1969).

**Table II.** Fluorescence Lifetimes of Some Cyclopentanones and Cyclopentenones

Ketone	$\tau_F^a$ (sec)	Ketone	$\tau_F^a$ (sec)
<b>1b</b>	3.0	<b>5</b>	9.9
<b>6</b>	2.7	<b>7</b>	8.7

<sup>a</sup> The lifetimes were measured directly using the single photon counting technique.

Neither shows any striking peculiarities when compared to saturated models **6** and **7**. The short lifetime of **1b**



( $3 \times 10^{-9}$  sec)<sup>7</sup> precludes involvement of significant singlet participation in reaction 2 since even at 0.2 M 1,3-pentadiene only a small fraction of the fluorescence of **1b** is quenched, but under these conditions reaction 2 is strongly quenched.

The striking features of the data in Table I are (a) the very high contribution of *c,c*-**4** from **1a**, (b) an overall high yield of sigmasymmetric products (*c,c*-**4** and *t,t*-**4**), and (c) a nearly 50:50 mix of *t,c*-**4** and *t,t*-**4** from **1b**, the former corresponding to a sigmasymmetric and the latter an axisymmetric product.

These results contrast sharply with those for saturated  $\alpha,\alpha'$ -dialkyl cyclic ketones for which a common triplet biradical intermediate appears to be involved starting from either trans or cis starting material.<sup>8</sup> A common triplet biradical intermediate capable of significant stereochemical loss is clearly incompatible with our data. Partially hindered rotation in specific, biradical conformers also does not appear to be involved. Substantial methyl-methyl, methyl-hydrogen, and methyl-ketyl radical interactions should severely restrict even selective rotations in the ketyl-allylic diradical. Moreover, during the initial stage of formation of the diradical isomer leading to the *cis-cis* diene, extreme repulsive interactions are encountered before allylic stabilization can be achieved. The relatively high yield of *c,c*-**4** molecule from **1a** suggests to us that we should better consider concerted pathways to explain the data.

Starting from **1a**, the competing sigmasymmetric pathways show relatively little specificity (*t,t*-**4**/*c,c*-**4**  $\sim$  3), a result which suggests a small dependence of the nonbonded  $\text{CH}_3 \cdots \text{CH}_3$  interaction in the transition state for formation of *c,c*-**4**. This in turn suggests to us that a *linear*, sterically less demanding symmetric extrusion of CO occurs to keep the  $\text{CH}_3 \cdots \text{CH}_3$  interactions from becoming important until the molecule is close to or beyond the transition state. The contrasting much greater degree of stereoselectivity in the competing axisymmetric process from **1b** (*t,t*-**4**/*c,c*-**4**  $\sim$  13) suggests that a *nonlinear* axisymmetric process is occurring, with a concomitantly high degree of nonbonded interactions occurring in the approach to the transition state.

The higher ratio of sigma/axi products from **1a** ( $\sim$ 4/1) relative to the ratio of sigma/axi products from

(7) The observed singlet lifetimes of **1a** and **1b** would necessitate quenching rates from 20 to 40 times those commonly encountered for typical ketone singlets.

(8) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Baltrop, and J. D. Coyle, *J. Amer. Chem. Soc.*, **93**, 7213 (1971).

**1b** ( $\sim$ 1/1) is also consistent with a *nonlinear* axisymmetric process, since from **1a** axisymmetric fragmentation must lead to a  $\text{CH}_3 \cdots \text{H}$  nonbonded interaction whereas for **1b** only a  $\text{H} \cdots \text{H}$  nonbonded interaction occurs in the *nonlinear* axisymmetric fragmentation. Thus for **1b**, the axisymmetric process can compete with the inherently less sterically sensitive *linear* sigmasymmetric process (eq 1 and 2). Finally, we point out the failures of these decarbonylation reactions to conform to the usual nonconcerted, biradical triplet reactions of  $n,\pi^*$  states of ketones may be related to other concurrent electronic-spin coupled processes which have been recently proposed to explain pericyclic reactions.<sup>9,10</sup> By this we mean that the spin-orbital coupling may be inherent in the "twist motions" of the orbitals involved in the retrocycloaddition reported here and that the reduction of the prohibition of spin flipping is sufficiently reduced so that a *concerted* triplet reaction leading *directly* to singlet products becomes possible.

In conclusion, we report that the unexpected stereochemical results for the triplet,  $n,\pi^*$  retrocycloaddition reactions of **1a** and **1b** can be explained in terms of a *linear* sigmatropic process which is less sterically sensitive than a competing *nonlinear* axisymmetric process.

(9) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **95**, 264 (1973); P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *ibid.*, **95**, 3025, (1973); N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *ibid.*, **95**, 2035 (1973).

(10) The cycloaddition of sulfur monoxide ( $^3\Sigma^-$ ) to *trans,trans*-2,4-hexadiene and *cis,trans*-2,4-hexadiene displays a remarkably high degree of stereoselectivity. See P. Chao and D. M. Lemal, *J. Amer. Chem. Soc.*, **95**, 920 (1973).

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## Chemical Syntheses with a Quenched Flow Reactor. Hydroxytrihydroborate and Peroxynitrite

Sir:

The technique of mixing two streams of reactant solutions in a reaction tube with downstream injection of a solution containing a quenching reagent has been used for studying the kinetics of fast reactions<sup>1</sup> but does not seem to have been applied to laboratory synthesis. The method is ideal for a synthesis involving the formation of an intermediate species which (1) must be prepared under conditions such that its half-life is in the range between a millisecond and several seconds and (2) can be stabilized by rapid reaction with a quenching reagent. We now report the successful use of this method for preparing solutions of two different compounds in high yield, sodium hydroxytrihydroborate and sodium peroxynitrite. Each synthesis involves the formation of an unstable intermediate species which is stabilized by deprotonation with hydroxide ion.

The apparatus consists of a Lucite rod bored to a depth of 10 cm with a 3-mm hole. Two 1.5-mm holes for the introduction of the reactants enter from the side of the rod, joining the 3-mm tube tangentially at its

(1) F. J. W. Roughton, "Technique of Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissberger, Ed., Interscience, New York, N. Y., 1953, Chapter 10, Parts 1 and 4.