

The resulting product was treated with trifluoroacetic acid (10 min) to remove the BOC groups and 1 M aqueous piperidine at 0° (1 hr) to remove the  $\epsilon$ -TFA group.

Amino acid analysis, after digestion with aminopeptidase-M,<sup>6</sup> gave the following ratio: Asp 2.0, Ser + Asn 3.2, Glu 1.9, Gly 1.0, Ala 0.9, Ile 1.2, and Leu 1.1.

## Communications to the Editor

### A Cyclobutanol Intermediate in the Decomposition of Aldehydes under Electron Impact. A Further Photochemical Analogy

Sir:

Loss of  $C_2H_4$  from the molecular ion was reported in an early paper to be characteristic of aliphatic aldehydes in the mass spectrometer.<sup>1</sup> The assumption that this neutral product is derived from the terminal  $C_2H_5$  group<sup>1</sup> seemed plausible, but it offered no clue to a possible driving force. As part of a more extensive study of the decomposition reactions of aldehydes under electron impact, we have obtained evidence pointing to a rather different process for the loss of  $C_2H_4$ . High-resolution mass measurement on heptanal identifies the  $[M - 28]^+$  peak as a singlet and the ionic composition as  $C_5H_{10}O^+$ , in agreement with the conclusion of the earlier work,<sup>1</sup> based on <sup>18</sup>O labeling. However, the deuterium labels in heptanal-4- $d_2$ , -5- $d_2$ , and -6- $d_2$ , hexanal-4- $d_2$ , -5- $d_2$ , and -6- $d_3$ , and nonanal-1- $d$  are retained, and those in heptanal-2- $d_2$  and -3- $d_2$  are lost almost quantitatively in this process. Thus, the ethylene clearly comprises the methylene groups originally in the  $\alpha$  and  $\beta$  positions.

Especially in light of the close parallels between reactions of acyclic carbonyl compounds under electron impact and uv irradiation,<sup>2,3</sup> this finding suggests that the reaction may occur *via* a cyclobutanol intermediate, as in a photochemical reaction path of aliphatic ketones.<sup>4-7</sup> Subsequent rupture of the ring, characteristic of cyclobutane and its derivatives,<sup>8-13</sup> would then effect loss of the  $\alpha$ - and  $\beta$ -methylene groups as ethylene. To test this surmise, we compared the mass spectrum of heptanal with that of the suspected intermediate, 2-propylcyclobutanol, which was prepared by irradiation<sup>7,14</sup> of heptanal in pentane solution with a medium-intensity Hanovia lamp. Carbonyl compounds were

removed as water-soluble bisulfite salts, and 2-propylcyclobutanol was collected by gas chromatography.

The spectra of the two compounds are qualitatively similar, in accord with the proposal of such a common intermediate. They both contain metastable peaks corresponding to the primary loss of  $C_2H_4$  and competing secondary processes by which  $CH_3$  and  $H_2O$  are lost (Table I). Moreover, the intensity ratios listed in Table II (mass 86 refers to the normal peak due to the

Table I. Metastable Peaks

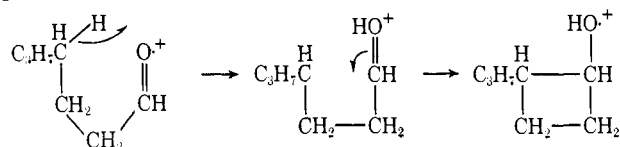
Apparent Mass	Process
64.9	$114^+ \rightarrow 86^+ + 28$ $C_7H_{14}O^+ \rightarrow C_5H_{10}O^+ + C_2H_4$
58.6	$86^+ \rightarrow 71^+ + 15$ $C_5H_{10}O^+ \rightarrow C_4H_7O^+ + CH_3$
53.8	$86^+ \rightarrow 68^+ + 18$ $C_5H_{10}O^+ \rightarrow C_5H_8^+ + H_2O$

Table II. Intensity Ratios at 70 eV

	Mass 64.9:mass 86	Mass 53.8:mass 58.6
Heptanal	0.0076 $\pm$ 0.0010	2.0 $\pm$ 0.2
2-Propylcyclobutanol	0.0081 $\pm$ 0.0008	1.9 $\pm$ 0.2

$[M - 28]^+$  ion) are nearly the same in the two spectra, as expected if the ions involved have the same structures and energy contents and distributions.<sup>15,16</sup>

Analogy with the photochemical process, which has been shown conclusively to occur, at least in large part, by a stepwise mechanism,<sup>7</sup> suggests that isomerization to cyclobutanols under electron impact is also, again at least in large part, a stepwise, rather than a concerted, process.



Moreover, this is now the third known reaction of carbonyl compounds under electron impact that appears to involve  $\gamma$ -hydrogen migration as an essential part. The first is, of course, the well-known counterpart of the Norrish type II photolysis;<sup>2</sup> the second,  $\epsilon$  cleavage of  $\Delta^2$ -enones and -enoates,<sup>3</sup> is seemingly related to the photoisomerization of the same unsaturated types.<sup>17</sup> A growing body of evidence indicates that

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- (4) N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958).
- (5) W. Davis and W. A. Noyes, *ibid.*, **69**, 2153 (1947).
- (6) P. Ausloos and R. E. Rebert, *ibid.*, **83**, 4897 (1961).
- (7) N. C. Yang, A. Morduchowitz, and D. H. Yang, *ibid.*, **85**, 1017 (1963).
- (8) P. Natalis, *Bull. Soc. Roy. Sci. Liège*, **31**, 790 (1962).
- (9) H. J. Hofmann, *Tetrahedron Letters*, 2329 (1964).
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- (12) H. Audier, J. M. Conia, M. Fétizon, and J. Goré, *Bull. Soc. Chim. France*, 787 (1967).
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- (14) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 378.

hydrogen migration in these photochemical processes occurs as a discrete step.<sup>17,18</sup> Our finding suggests that hydrogen migration under electron impact occurs similarly as a discrete primary step, which may be followed by a choice of possible secondary steps.<sup>19</sup>

The data presented in Table II were obtained with 70-eV electrons on an A.E.I. Model MS9 instrument with the source and inlet system at 250 and 100°, respectively, and the multiplier at high gain.<sup>20</sup>

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(19) For opposing views, based on molecular orbital calculations, on the stepwise *vs.* concerted nature of the process comprising  $\gamma$ -hydrogen migration and  $\beta$  cleavage, see F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 7239 (1968); R. C. Dougherty, *ibid.*, **90**, 5780 (1968).

(20) Following submission of this communication for publication, we learned of a similar study of the mass spectra of variously deuterated hexanals and heptanals by R. J. Liedtke and C. Djerassi, whose results are generally in good agreement with ours. We thank Drs. Liedtke and Djerassi for making their findings available to us before publication (R. J. Liedtke and C. Djerassi, *ibid.*, **91**, 6814 (1969)).

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### High *exo:endo* Rate Ratios in the Solvolysis of the 2-Methyl- and 2-Phenyl-*exo*-5,6-trimethylene-2-norbornyl *p*-Nitrobenzoates. Evidence for the Unimportance of $\sigma$ Participation in the High *exo:endo* Rate Ratios in Tertiary Norbornyl Derivatives

Sir:

A major difficulty in resolving the question of the factors responsible for the high *exo:endo* rate and product ratios in the solvolysis of 2-norbornyl derivatives<sup>1</sup> has been the problem of defining norbornyl systems in which  $\sigma$  participation cannot be a significant factor. An examination of the *exo:endo* rate and product ratios in such systems would soon establish whether such high ratios were simply steric properties of the norbornyl structure or were properties of  $\sigma$  participation.

Several approaches have been employed. We have examined the properties of 2-norbornyl derivatives con-

(1) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

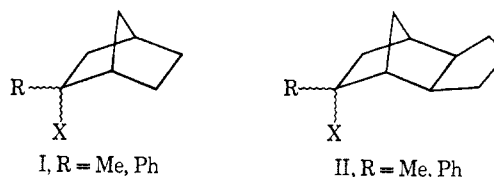
taining stabilizing substituents, such as *p*-anisyl, at the 2 position.<sup>1,2</sup> The argument is that a tertiary benzylic cation, especially one stabilized by a *p*-anisyl group, would make little demand on a neighboring saturated carbon-carbon bond for further stabilization.<sup>3</sup>

A second approach has been to introduce strongly electron-withdrawing substituents at the 7 position of the norbornyl system.<sup>4</sup> Such substituents should greatly reduce the ability of the C-1-C-6 carbon bond to donate electrons to the developing positive charge.

Another approach has been to bridge the *exo*-5,6<sup>5</sup> or the *exo*-4,5<sup>6</sup> positions of the norbornane structure by a trimethylene group. It is postulated that the increase in strain accompanying  $\sigma$  bridging will decrease  $\sigma$  participation as compared to the parent norbornyl system.

High *exo:endo* rate and product ratios are observed both for the highly stabilized tertiary norbornyl cations<sup>2</sup> and for the destabilized norbornyl derivatives carrying electron-withdrawing substituents in the 7 position. Both results indicate that  $\sigma$  participation cannot be a major factor in the high *exo:endo* rate and product ratios of normal norbornyl derivatives. On the other hand, low *exo:endo* rate ratios are observed for *exo*-5,6- and *exo*-4,5-trimethylene-2-norbornyl tosylates<sup>7</sup> and have been interpreted as indicating that  $\sigma$  participation cannot be an important factor in this system, but must be responsible for the high *exo:endo* rate ratio observed in the parent system.

This question will be considered later. However, the conclusion that the strain introduced by the trimethylene bridge acts to cancel  $\sigma$  participation would appear to make available norbornyl systems where such participation should not be a significant factor in the behavior of the compounds. Accordingly, we undertook to synthesize and to determine the rates of solvolysis of the epimeric 2-methyl- (II-Me) and 2-phenyl-*exo*-5,6-trimethylene-2-norbornyl *p*-nitrobenzoates (II-Ph) for comparison with the parent system (I-Me, I-Ph).



(2) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2691, 2693, 5268, 5270 (1968).

(3) For example, a *p*-anisyl group in the 7 position effectively cancels out the 10<sup>11</sup> rate acceleration observed in the *anti*-7-dehydronorbornyl system: P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968); P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **91**, 1545 (1969).

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(6) E. J. Corey and R. S. Glass, *J. Am. Chem. Soc.*, **89**, 2600 (1967).

(7) The titrimetric *exo:endo* rate ratios for acetolysis at 25° is 11.2 for the 5,6<sup>6</sup> and 8.6 for the 4,5<sup>8</sup> systems, as compared to 280 for the parent norbornyl system. The *exo:endo* rate ratio in secondary 2-norbornyl systems has also been reduced by strong carbonium ion stabilizing groups (an exocyclic double bond or cyclopropane ring) at C-3 (C. F. Wilcox, Jr., and R. G. Jesaites, *Tetrahedron Letters*, 2567 (1967); *Chem. Commun.*, 1046 (1967)). However, the *exo:endo* product ratio for the 3-methylene-2-norbornyl system is claimed to be very high (C. W. Jefford and W. Wojnarowski, *ibid.*, 129 (1968)), and this discrepancy between rate and product data has not yet been reconciled.