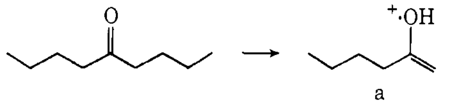
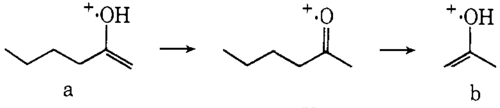
Mechanism of the Double McLafferty Rearrangement

Sir:

The electron impact induced double McLafferty rearrangement of aliphatic ketones might *a priori* proceed through three distinct pathways: (1) ketonization of the intermediate enol ion a, followed by hydrogen transfer to the carbonyl oxygen (eq 2); (2) hydrogen transfer to the enolic oxygen atom (eq 3); (3) hydrogen transfer to the carbon–carbon double bond (eq 4). Ion cyclotron resonance studies have demonstrated that those ions with lifetimes of *ca.* 10^{-3} sec which undergo ion–molecule reactions are formed through the third pathway (eq 4).[1] Similarly, metastable ion studies have demonstrated that those ions fragmenting with rate constants of *ca.* 10^{-5} sec^{-1} are formed *via* the same pathway.[2] However, the fragment ions observed in a conventional mass spectrum are formed in less than 10^{-6} sec, and thus are energetically distinct from the population of ions observed using either metastable or icr techniques. In light of recent examples of variations in mechanism, ion structure, and relative rates with ion lifetime and energy,[2,3] and the increasing use of metastable and icr techniques to elucidate ion structure,[4] it is particularly important that the mechanisms and structures determined through these techniques be confirmed for the ions observed in the conventional mass spectrum. An earlier investigation has demonstrated that the double McLafferty rearrangement does not proceed *via* ketonization of the intermediate enol ion (eq 2) among these high energy–short lifetime ions.[5] The results of an attempt to differentiate between the two remaining possibilities are described below.



(1)



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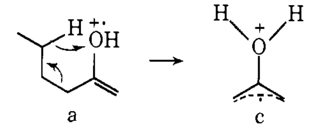

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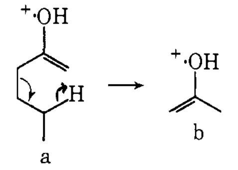
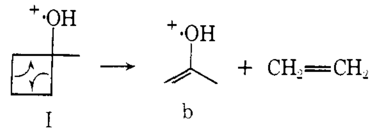


(4)

It has been observed that the mass spectrum of 1-methylcyclobutanol (I) exhibits a very intense peak at *m/e* 58, corresponding to the elimination of ethylene (eq 5).[6] Deuterium labeling experiments, metastable studies, and icr studies have demonstrated that the *m/e* 58 ion has the enol structure b.[1,2,6] A logical extension of this observation requires the preparation of 1-butylcyclobutanol (II);[7-9] electron impact induced elimination of ethylene produces ion a, which possesses a set of γ hydrogens suitably disposed to participate in the double McLafferty rearrangement (eq 6). In fact, intense peaks are observed at *m/e* 100 and 58, shifting to *m/e* 102 and 59 in the $3',3'$-d_2 compound III (eq 7).[8,10]



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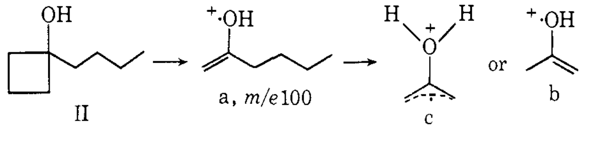

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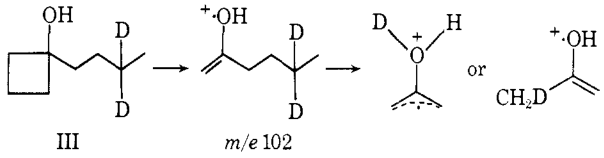
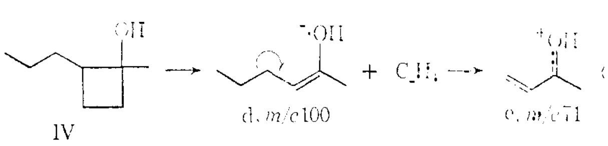


(7)

Conversely, the M − 28 ion d of 1-methyl-2-propylcyclobutanol (IV)[8,11] cannot undergo the double McLafferty rearrangement; deuterium labeling experiments indicate, in fact, that no such rearrangement occurs. Instead, an interesting γ-cleavage reaction generates the *m/e* 71 ion e (eq 8).[12] The prediction that an identical process should be observed in the mass spectrum of 3-propyl-2-hexanone (V)[13] was readily confirmed (eq 9). These observations, then, demonstrate that the two isomeric *m/e* 100 ions a and d undergo distinctly different fragmentations, and that these frag-



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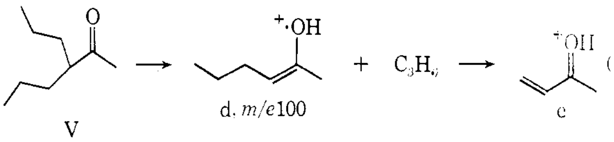

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(1) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969); G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91**, 3986 (1969); G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **92**, 6205 (1970).

(2) D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *ibid.*, **92**, 6343 (1970); F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfield, *ibid.*, **93**, 3720 (1971); D. J. McAdoo, F. W. McLafferty, and T. E. Parks, *ibid.*, **94**, 1601 (1972).

(3) J. R. Hass, M. M. Bursey, D. G. I. Kingston, and H. P. Tannenbaum, *ibid.*, **94**, 5095 (1972); A. N. H. Yeo and D. H. Williams, *ibid.*, **93**, 395 (1971); I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

(4) I. Howe in "Specialist Periodical Reports—Mass Spectrometry," Vol. 1, D. H. Williams, Ed., The Chemical Society, Burlington House, London, 1971, pp 31–89.

(5) J. K. MacLeod, J. B. Thompson, and C. Djerassi, *Tetrahedron*, 23, 2095 (1967).

(6) P. Ausloos and R. E. Rebbert, *J. Amer. Chem. Soc.*, 83, 4897 (1961).

(7) Obtained by reaction of the Grignard reagent prepared from 1-bromobutane and magnesium with cyclobutanone.

(8) All cyclobutanols mentioned in this paper exhibited appropriate nmr, ir, and mass spectra. Exact mass measurements on the molecular ions of the trimethylsilyl derivatives were, in every case, consistent with the proposed structures.

(9) Y. Leroux and H. Normant, *C. R. Acad. Sci. Paris, Ser. C*, 265, 1472 (1967).

(10) Obtained by reaction of the Grignard reagent prepared from 1-bromobutane-$3,3$-d_2 and magnesium with cyclobutanone.

(11) Obtained by photolysis of 2-octanone in pentane using 2537-Å light (*cf.* N. C. Yang and D. H. Yang, *J. Amer. Chem. Soc.*, 80, 2913 (1958)).

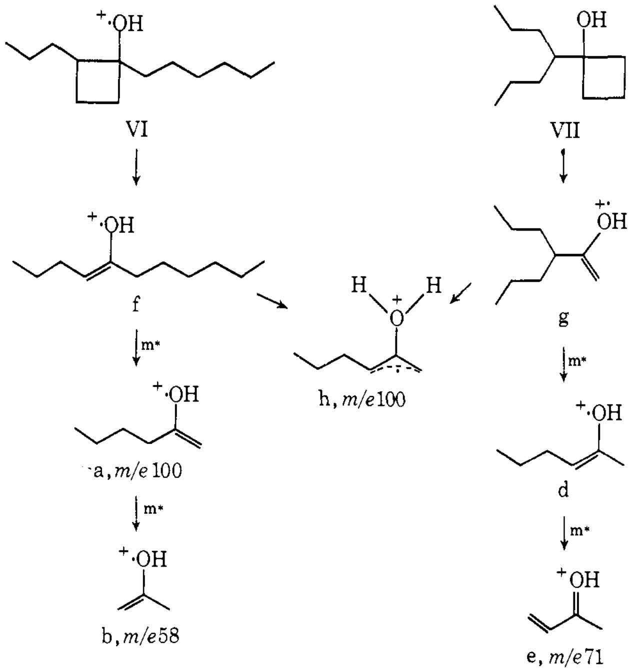
(12) An analogous situation has been observed in the mass spectra of α-branched esters (J. K. MacLeod, J. B. Thompson, and C. Djerassi, *Tetrahedron*, 23, 2095 (1967)).

(13) D. Bardan, *Bull. Soc. Chim. Fr.*, **49**, 1875 (1931).

mentations occur more rapidly than interconversion of the two ions. It should therefore be possible to utilize these reactions to differentiate between the two possible mechanisms of the double McLafferty rearrangement (*cf.* Scheme I).

Elimination of ethylene from 1-hexyl-2-propylcyclobutanol (VI)[8,14] forms the enol ion f. Elimination of ethylene from 1-(4′-heptyl)cyclobutanol (VII)[8,15] generates the enol ion g. If the second step of the double McLafferty rearrangement proceeds with hydrogen transfer to the enolic oxygen, fragmentation of ions f and g generates an identical ion h, *m/e* 100. To the extent that the double McLafferty rearrangement occurs *via* this pathway, the *m/e* 100 ions should fragment identically. The alternative mechanism, hydrogen transfer to the carbon–carbon double bond, generates two isomeric *m/e* 100 ions, a and d. As has already been demonstrated, a fragments to give *m/e* 58 (eq 6), and d fragments to give *m/e* 71 (eq 8). In fact, it is the latter fragmentations which are observed. An intense peak is observed at *m/e* 71 (C_4H_7O by high resolution) in the mass spectrum of 1-(4′-heptyl)cyclobutanol, while the *m/e* 58 peak is of negligible intensity (71/58 = 8.5). Conversely, the *m/e* 58 peak predominates in the mass spectrum of 1-hexyl-2-propylcyclobutanol (71/58 = 0.7).[16] It can therefore be concluded that the predominant mechanism of the double McLafferty rearrangement among the high energy–short lived ions observed in the conventional mass spectrum involves transfer of hydrogen to the carbon–carbon double bond. The apparent invariance of mechanism among these ions, those observed in the icr spectrometer, and those fragmenting in the metastable regions lends credence to the validity of these latter techniques as probes into the behavior of ions fragmenting in the source region of the mass spectrometer. In addition, these observations demonstrate that cyclobutanols have wide utility in the study of mechanistic and structural problems relating to enolic ions.

Scheme I



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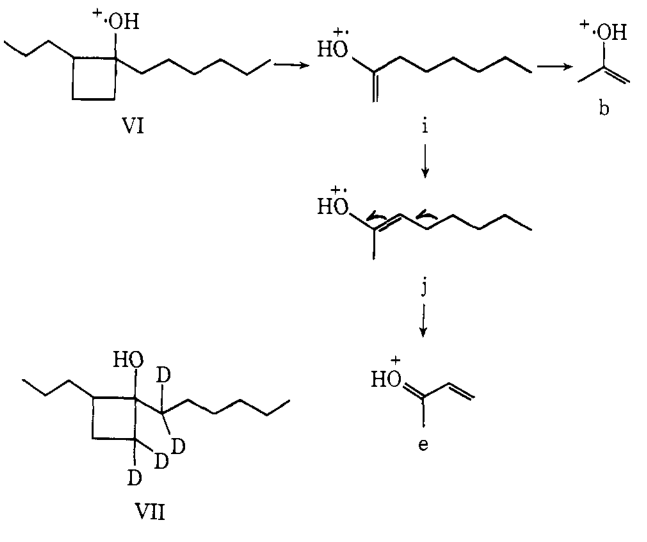
(14) Obtained by photolysis of 7-tridecanone in pentane using 2537-Å light. Two stereoisomers with nearly identical mass spectral behavior were isolated.

(15) Obtained by reaction of the Grignard reagent prepared from 4-bromoheptane and magnesium with cyclobutanone.

(16) A competing reaction sequence also produces peaks at *m/e* 58 (VI → i → b) and 71 (probably VI → i → j → e). Since it was desired



to exclude these processes from consideration, the labeled alcohol VII was prepared; the number quoted here represents the ratio of the sum o the intensities of *m/e* 71, 72, and 73 to the intensity of *m/e* 60 in the mass spectrum of this compound.

Experimental Evidence for Statistical Randomization of Hydrogen Atoms in the Ethyl Cation[1]

Sir:

Recently there has been considerable interest in the problem of hydrogen migration in the ethyl cation.[2] Theoretical calculations have led to the conclusion that the bridged structure represents the transition state (activated complex) involved in the 1,2 hydride shift.[2c,d] Although several calculations have shown the bridged structure to be nearly 10 kcal/mol less stable than the classical ion,[2c,e] some recent improved theoretical treatments[2f,g] suggest that the energy of the bridged configuration is slightly less than that of the classical ion. Assuming the latter, the energy barrier for H atom migration in $CH_3CH_2^+$ may be quite low and one would expect complete statistical

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(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) (a) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968); (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); (c) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); (d) G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970); (e) W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971); (f) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972); (g) J. J. Dannenberg and T. D. Berke, *Theor. Chim. Acta*, **24**, 99 (1972); (h) H. H. Jaffe and S. Billets, *J. Amer. Chem. Soc.*, **94**, 674 (1972); (i) L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972); (j) M. Saunders, E. C. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968); (k) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).