−0.9 kcal/mol (cyclohexene) and −2.1 kcal/mol (cyclopentene).

From the synthetic point of view the present observations have two consequences. Firstly, there is noted here the minor effect previously observed in the addition of maleic ester to cyclohexene,[2] that a change in temperature may lead to a change in isomer composition in a particular photoannelation. Secondly, as reported here for the case of cyclopentene and cyclohexene, the preference for an addition to one of two substrates may be modified with a change in temperature. This may lead, in future studies to possible selectivity in addition to polyfunctional substrates.

(8) Holder of a National Research Council Studentship, 1966–present.

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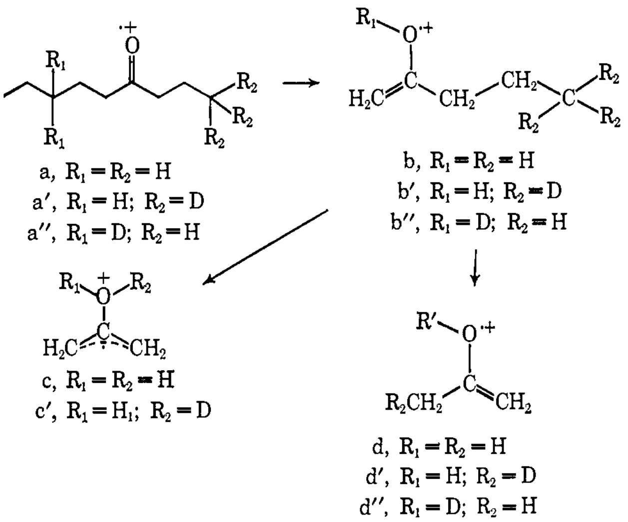
Application of Ion Cyclotron Resonance to the Structure Elucidation of the $C_3H_6O\cdot^+$ Ion Formed in the Double McLafferty Rearrangement[1,2]

Sir:

The mass spectrum of a dialkyl ketone containing one or more γ-hydrogen atoms in each alkyl group usually exhibits an intense peak corresponding to the consecutive rearrangement of two γ-hydrogen atoms accompanied by β cleavage, a process generally known as the "double McLafferty rearrangement."[3] The second step of the decomposition can be envisaged as occurring in two ways: hydrogen transfer could proceed either to the enolic oxygen (b → c), or to the enolic double bond (b → d).[4] A number of methods have been utilized in an effort to determine the structure of the double McLafferty ion. On the basis of metastable ion characteristics,[6] McLafferty and Pike have concluded that "a substantial part of the $C_3H_6O\cdot^+$ ions from 4- and 5-alkanones must not correspond to" structure d.[6a] Furthermore, MO calculations have been presented which suggest that the transition state for transfer to the enolic oxygen is of lower energy than the transition state for the alternative process.[7] On the other hand, ion cyclotron resonance (icr) experiments[5] have tended to support the alternative structure d.



The theory, instrumentation, and applications of icr spectroscopy have already been described in considerable detail.[8] Icr single-resonance spectra are similar to ordinary mass spectra, except that ion–molecule reactions are readily observed. Consider the reaction $AH^+ + B \rightarrow A + BH^+$. By using pulsed double-resonance and phase-sensitive detection, the signal from BH^+ can be monitored while an irradiating radiofrequency field is swept through a range of frequencies. When the irradiating frequency equals the natural cyclotron frequency of AH^+, the translational energy of AH^+ increases. Because reaction rate constants are generally energy dependent, the population of BH^+ changes, and this change produces a peak in the double-resonance spectrum. Thus, if the irradiating frequency is swept through the cyclotron frequencies of all ions, it is possible to determine the genesis of the product ion.

In a previous paper,[7] seven ion–molecule reactions capable of distinguishing between the keto and enol forms of the McLafferty ion were described; in every case, the double McLafferty ion and the independently generated enol ion (d) reacted identically. Since there is no precedent for ions of different structure exhibiting identical reactivity, it was concluded tentatively that the correct structure is d rather than c. Therefore, further investigation of the double McLafferty ion was undertaken, and icr was again the technique chosen for use.

It has been established that secondary hydrogens participate in the single McLafferty rearrangement ten to twenty times as readily as primary ones.[9] It has also been demonstrated that only hydrogens directly bonded to oxygen are transferred from the single and double McLafferty ions to neutral ketones.[7] Thus, the possibility of generating and detecting a specifically labeled double McLafferty ion exists. For example, 4-nonanone-1,1,1-d_3 (I) could produce either c′ or d′. The latter has only protium bonded to oxygen, and thus can donate only protium to neutral 4-nonanone. On the other hand, ion c′ has both protium and deuterium bonded to oxygen and would be expected to transfer both to 4-nonanone. Observation of the mass 147 (M + 2) ion with irradiation through the appropriate mass range (Figure 1a) indicates almost no contribution

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(1) Paper CLXXVII in the series "Mass Spectrometry in Structural and Stereochemical Problems." For preceding paper see L. Tökés and C. Djerassi, *J. Am. Chem. Soc.*, in press.

(2) Financial assistance by the National Institutes of Health (Grants AM-12758 and AM-04257) is gratefully acknowledged. We are indebted to Professor J. D. Baldeschwieler for generously providing access to his ion cyclotron resonance spectrometer, which was purchased on funds supplied by the National Science Foundation (GP 4924-X), NASA (NGL 05-020-S1), and the Center for Materials Research, Stanford University.

(3) For a summary see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1967, pp 155–162.

(4) Mechanisms requiring ketonization of the intermediate enol ion b are unlikely in light of recent evidence that ketonization does not occur under ordinary electron impact (J. K. MacLeod, J. B. Thomson, and C. Djerassi, *Tetrahedron*, **23**, 2095 (1967)) or icr[5] experimental conditions.

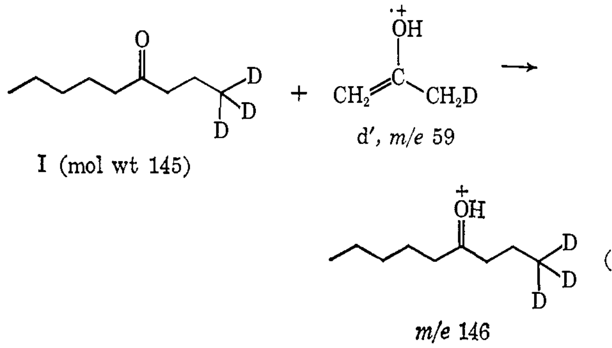
(5) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **91**, 2069 (1969).

(6) (a) F. W. MacLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967); (b) F. W. McLafferty, T. Wachs, and W. T. Pike, *Advan. Mass. Spectrom.*, 4, 153 (1968); (c) W. F. Haddon and F. W. McLafferty, *J. Am. Chem. Soc.*, 90, 4745 (1968).

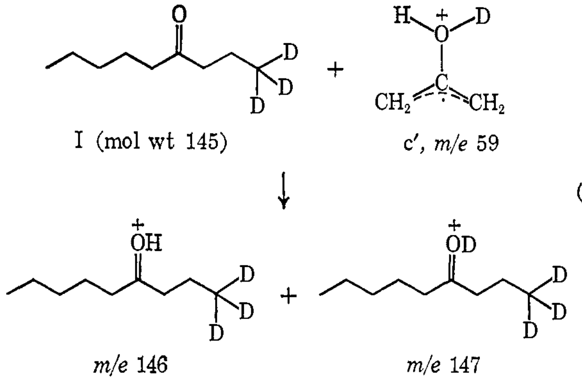
(7) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Am. Chem. Soc.*, 90, 7239 (1968).

(8) (a) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); (b) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967.

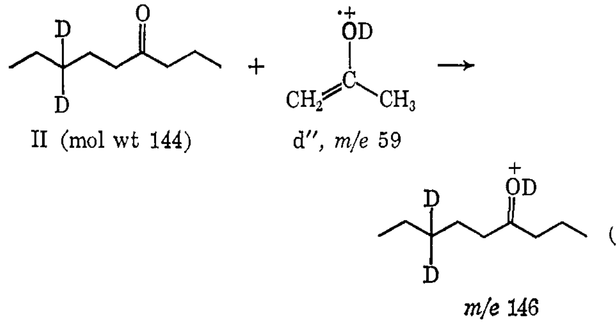
(9) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).



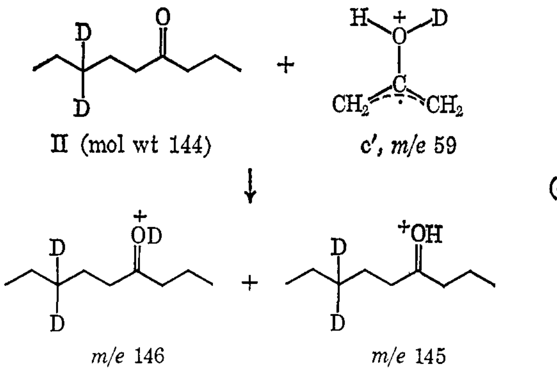
(1)



(2)



(3)



(4)

from mass 59, demonstrating the virtual absence of deuterium transfer (eq 2). In contrast, the pulsed double-resonance spectrum of the mass 146 (M + 1) ion shows an appreciable contribution from mass 59, indicating that protium transfer, corresponding to eq 1, does occur (see Figure 1b).[10] That this result is not due to a large isotope effect discriminating against deuterium transfer is demonstrated by the pulsed double-resonance spectrum of the M + 1 and M + 2 ions of 4-nonanone-7,7-d_2 (II); here, observation of the mass 146 (M + 2) ion with irradiation through the low mass region indicates appreciable contribution from mass 59, while the double-resonance spectrum of the mass 145 (M + 1) ion shows almost no contribution from mass 59, demonstrating that deuterium transfer (eq 3) is highly favored over protium transfer (eq 4). Thus, at least a substantial portion of the double McLafferty ion must, in fact, correspond to structure d. Results completely consistent with this conclusion were obtained using several different neutral ketones as proton acceptors and with ionizing voltages varying between 70 and 15 eV.

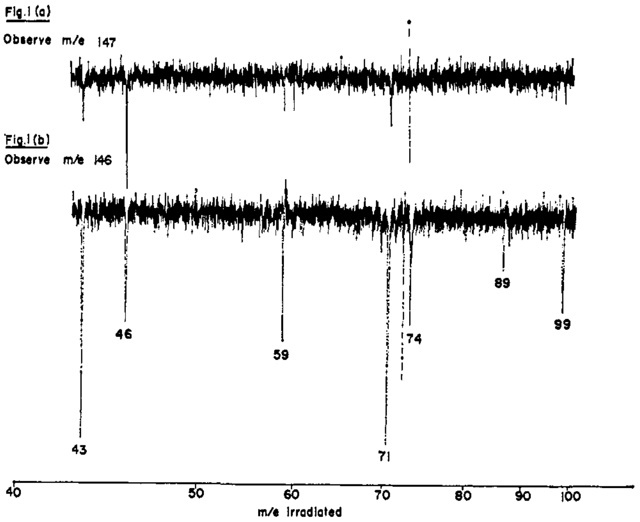
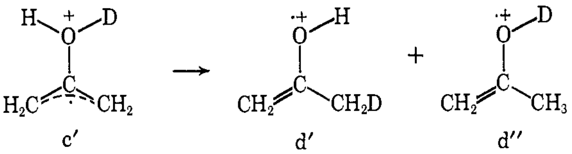


Figure 1. The pulsed double-resonance spectra of the M + 2 and M + 1 ions of 4-nonanone-1,1,1-d_3 (I). The species of mass 147 (146) is observed with $w_1/2\pi$ = 145 kcps, while frequency w_2 is swept through the mass range 40 to 100. The change in intensity of the mass 147 (146) signal is plotted as a function of the mass corresponding to w_2. Both spectra were recorded on a Varian V-5900 spectrometer at 2×10^{-6} torr, 0.1-V irradiating voltage, and 20-eV ionizing voltage.

Since MO calculations suggesting that ion c is the initial product of the double McLafferty rearrangement have been presented,[6] the possibility that ion d is produced from the isomerization of c must be considered. If the symmetrical ion c′ isomerizes, it must produce nearly equal amounts of d′ and d″ (eq 5); such a mixture must donate protium and deuterium to neutral ketone to a nearly equal extent. The results described earlier do not correspond to such behavior. Thus ion d must



(5)

be a direct product of the double McLafferty rearrangement and is not produced in significant amounts by the isomerization of c.

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[10] The origins of the other double resonance signals present in Figure 1a and 1b will be discussed in a future publication.

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