# Determination of the Structures of the Ions Produced in the Single and Double McLafferty Rearrangements by Ion Cyclotron Resonance Spectroscopy[1,2]

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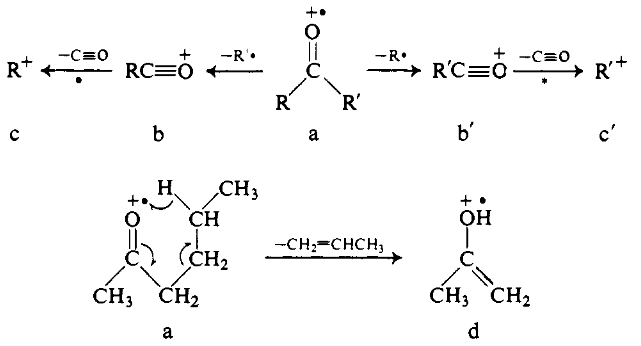
**Abstract:** Two possible structural isomers of the $C_3H_6O\cdot^+$ ion produced by electron impact induced fragmentations are the keto ion k and the enol ion d. The electron impact induced "double McLafferty" rearrangement can also produce a $C_3H_6O\cdot^+$ ion which could conceivably exist in either the enol (d) or symmetrical oxonium ion structure h. Ion cyclotron resonance and pulsed double resonance spectroscopy are used to study the ion–molecule reactions of the keto (k) species, generated from acetone (I); the enol (d and m) species, generated from 2-hexanone (II) (*via* a McLafferty rearrangement) and from 1-methylcyclobutanol (III); and the double McLafferty species, generated from 5-nonanone. Seven ion–molecule reactions (see Scheme IV) are found which distinguish between the keto (k) and enol (d and m) ions, thus substantiating the proposed differences in structure. In all cases studied, the enol ion d, from 2-hexanone, and the enol ion m, from 1-methylcyclobutanol, behave identically indicating their structures to be equivalent. The same ion–molecule reactions (Scheme IV) which distinguish between the keto and enol isomers can be utilized to distinguish between the keto and double McLafferty species. The enol and double McLafferty species react identically in all systems studied thus suggesting identical structures and raising serious doubts about the earlier proposed existence of a symmetrical double McLafferty oxonium ion h. Deuterium labeling (Ib, IIb, IIIb) is employed to distinguish between isomeric ions of identical mass.

In the last 10 years, the mass spectral behavior of aliphatic ketones has been exhaustively studied and thoroughly documented.[4] Such experimental techniques as deuterium and substituent labeling,[4] appearance potential measurements,[4] metastable correlations,[5] molecular orbital calculations,[6] and ion cyclotron resonance experiments[7] have been employed in substantiating the fragmentation patterns and ion chemistry associated with ketones. Three prominent fragment ions uniformly dominate these mass spectra of aliphatic ketones (Scheme I). Cleavage adjacent to the carbonyl function of the molecular ion (a) yields the oxonium ion products (b and b′) which can subsequently eliminate carbon monoxide, as supported by metastable evidence, producing simple hydrocarbon fragments (c and c′).[8] The third primary fragment results from the ubiquitous McLafferty rearrangement[9] (see for instance a → d) involving transfer of a γ-hydrogen atom to the carbonyl group with subsequent[7b] elimination of an olefin.

**Scheme I**



The McLafferty rearrangement is probably the most widely studied mass spectral fragmentation process.[9] A great deal of information is available concerning the details of its occurrence not only in simple ketones, but in esters, carboxylic acids, aldehydes, amides, and many other species. The site specificity of this abundant ($\Sigma_{40} = 21.5\%$ in the case of 2-hexanone, Figure 1) process has been proven by labeling the γ-carbon with deuterium atoms; this specificity may be attributed to the highly directional character of the radical orbital of oxygen, requiring at least a six-membered transition state.[9] Further evidence was obtained by blocking the γ position with methyl groups,[10] and by substitution of an olefinic bond in the γ[11] and β[12] positions, thus preventing the rearrangement in all three cases. It has also been shown[13] that transfer of a tertiary hydrogen atom[14]

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(1) Part CLXIX in the series "Mass Spectrometry in Structural and Stereochemical Problems." For the preceding paper (CLXVIII) see W. Carpenter, A. M. Duffield, and C. Djerassi, *Org. Mass Spectry.*, in press.

(2) Financial assistance from the National Institutes of Health (Grant No. AM-04257), the National Science Foundation under Grant GP-4724-X, the National Aeronautics & Space Administration under Grant NGL 05-020-250, and the Center for Materials Research, Stanford University, is gratefully acknowledged.

(3) National Science Foundation Predoctoral Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–1968.

(4) For a detailed and recent summary see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapter 3.

(5) F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, **89**, 5953 (1967).

(6) F. P. Boer, T. W. Shannon, and F. W. McLafferty, Sixteenth Conference on Mass Spectrometry of the American Society for Testing Materials, Pittsburgh, Pa., 1968; *J. Am. Chem. Soc.*, **90**, 7239 (1968); R. C. Dougherty, *ibid*, **90**, 5788 (1968).

(7) (a) J. L. Beauchamp, to be submitted for publication; (b) J. L. Beauchamp, to be submitted for publication; (c) F. Kaplan, to be submitted for publication; (d) F. Kaplan, J. L. Beauchamp, J. Diekman, and C. Djerassi, to be submitted for publication.

(8) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 6167 (1967).

(9) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959). For a recent review see ref 4, pp 155–162.

(10) R. R. Arndt and C. Djerassi, *Chem. Commun.*, 578 (1965).

(11) L. Ahlquist, R. Ryhage, E. Stenhagen, and E. von Sydow, *Arkiv Kemi*, **14**, 211 (1959).

(12) N. C. Yang and D. Thap, *Tetrahedron Letters*, 3671 (1966).

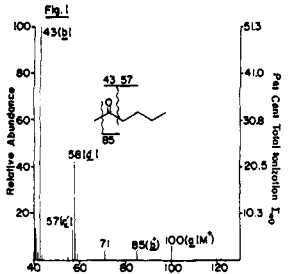


Figure 1. Mass spectrum (Atlas CH-4) of 2-hexanone, 70 eV.

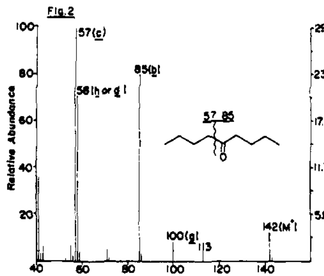
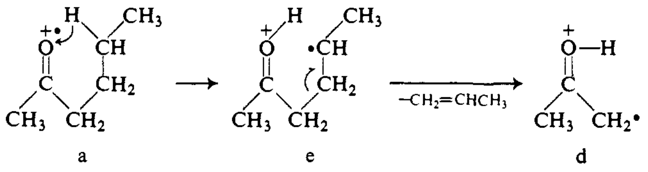


Figure 2. Mass spectrum (Atlas CH-4) of 5-nonanone, 70 eV.

occurs more readily than shift of a secondary hydrogen atom, which in turn is preferred to migration of a primary hydrogen atom. Until recently, one of the few aspects of the McLafferty rearrangement yet to be substantiated by concrete experimental evidence involved the question of whether this fragmentation occurred in a stepwise or concerted manner. Beauchamp's[7b] recent ion cyclotron resonance studies offer elegant evidence for the existence of the parent ion in the configuration e, thus suggesting a stepwise procedure (a → e → d).



The one aspect of the McLafferty rearrangement which perhaps still needs more definitive experimental substantiation concerns the actual structure of the product ion. In the case of 2-hexanone (a, $R = CH_3$; $R' = C_4H_9$) it is assumed that elimination of propene from the intermediate species (e)[7b] yields an *enolic* odd-electron ion of mass 58. Correlations[18] based on estimated ionization potential measurements of the enol tautomers of a series of carbonyl compounds provide good support in favor of an *enol* as opposed to a *keto* structure for this ion, an excess of energy of approximately 1 eV being necessary to induce ketonization. Occolowitz[19] has reached similar conclusions in the case of some ω-phenyl carbonyl compounds, as have Murad and Inghram[20] in their photoionization studies of aliphatic ketones. Experimental evidence obtained from more complex systems[21] (including α-alkylated cyclohexanones,[22] β-diketones,[23] β-keto esters,[24] malonates,[22,25] and substituted barbiturates[26]) also indicates that the enolic McLafferty rearrangement product does not ketonize prior to further fragmentation.

Particularly relevant to a discussion of the structure of the McLafferty rearrangement product is the nature of the ion resulting from the "double McLafferty" rearrangement,[27] a fragmentation scheme prevalent in the mass spectra of aliphatic ketones in which both side chains possess γ-hydrogen atoms. The enolic product (g, *m/e* 100, $\Sigma_{40} = 2.3$) of the initial McLafferty rearrangement of 5-nonanone (Figure 2) can further fragment with transfer of a hydrogen atom through a six-membered transition state or intermediate[7b] yielding an ion of mass 58 (h or d, $\Sigma_{40} = 20.7$); deuterium-labeling studies[13b] have substantiated the site specificity of this process. MacLeod, *et al.*,[22] have shown that the initial McLafferty rearrangement product (g) does *not* ketonize and subsequently rearrange (g → g′ → d). It has been previously assumed[28] that rearrangement of the γ-hydrogen to the enolic double bond occurs (g → d); but equally plausible is rearrangement to the enolic oxygen (g → h), especially in light of McLafferty's recent investigations[5] (see below). Therefore another possible structure, different from the keto (k) and enol (d) form, of the *m/e* 58 ion is the symmetrical stabilized oxonium ion (h).

After initiation of the research described in this report, McLafferty and Pike[5] presented their conclusions, based upon metastable ion characteristics, regarding the structures of the $C_3H_6O\cdot^+$ ions (*m/e* 58) derived (1) from expulsion of an electron from acetone (k); (2) from the McLafferty rearrangement of 2-alkanones (d); and (3) from the "double McLafferty" rearrangement of 4- and 5-alkanones (h). All three of these $C_3H_6O\cdot^+$ ions suffer two further decompositions as demonstrated by metastable peaks at $m^*$ 3.88 and $m^*$ 31.9. A plot of log [metastable ion abundance] *vs.*

$$C_3H_6O\cdot^+ \rightarrow CH_3^+ + C_2H_3O\cdot \qquad (m^*\ 3.88)$$

$$C_3H_6O\cdot^+ \rightarrow CH_3\cdot + C_2H_3O^+ \qquad (m^*\ 31.9)$$

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(13) (a) H. Fritz, H. Budzikiewicz, and C. Djerassi, *Chem. Ber.*, **99**, 35 (1966); (b) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, **22**, 1391 (1966).

(14) Although there is considerable debate[6,15–17] as to whether the migrating moiety should be represented as a proton, hydrogen radical, or hydride ion, recent ion cyclotron resonance studies[7b] by Beauchamp make transfer of a hydrogen radical more plausible.

(15) W. Carpenter, A. M. Duffield, and C. Djerassi, *Org. Mass Spectry.*, in press.

(16) F. W. McLafferty and T. Wachs, *J. Am. Chem. Soc.*, **89**, 5043 (1967).

(17) G. Spiteller, "Massenspektrometrische Strukturanalyse Organischer Verbinduggen," Verlag Chemie, Weinheim, 1966, p 73; G. Spiteller and M. Spiteller-Friedmann, *Monatsh. Chem.*, **95**, 257 (1964); M. Kraft and G. Spiteller, *Chem. Commun.*, 943 (1967).

(18) S. Meyerson and J. D. McCollum in "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilley, Ed., Interscience Publishers, New York, N. Y., 1963, pp 187–198.

(19) J. L. Occolowitz, *Australian J. Chem.*, **20**, 2387 (1967).

(20) E. Murad and M. G. Inghram, *J. Chem. Phys.*, **40**, 3263 (1964).

(21) See ref 4, pp 158–160.

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

(23) J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, **21**, 1384 (1966); N. Schamp and M. Vandewalle, *Bull. Soc. Chim. Belges*, **75**, 539 (1966).

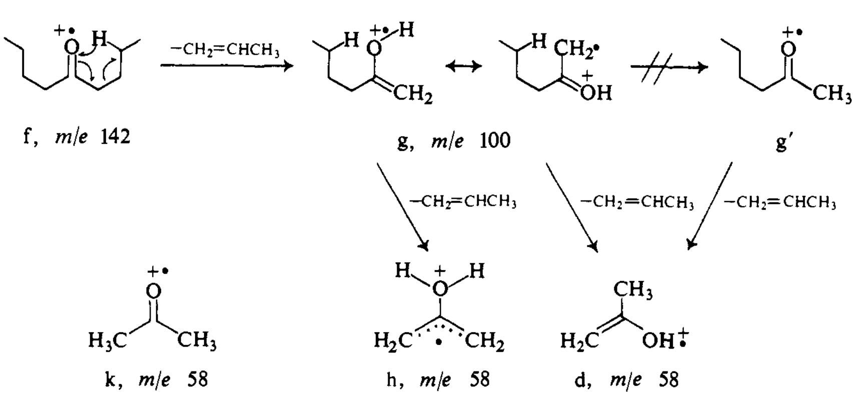
(24) J. H. Bowie, S.-O. Lawesson, G. Schroll, and D. H. Williams, *J. Am. Chem. Soc.*, **87**, 5742 (1965).

(25) J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, **31**, 1792 (1966).

(26) F. Grutzmacher and W. Arnold, *Tetrahedron Letters*, 1365 (1966).

(27) See ref 4, p 160.

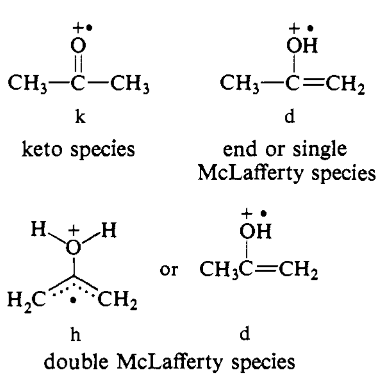
(28) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 7.



the inverse of the degrees of freedom of the molecular ion for each metastable transition resulted[5] in different slopes for the three $C_3H_6O\cdot^+$ species in each case ($m^*$ 3.88 and $m^*$ 31.9). Based on reasoning presented in an earlier communication,[29] they concluded that at least a substantial part of the product of the "double McLafferty" rearrangement is the symmetrical species (h), which is significantly different in structure from the isomeric ketonic (k) and enolic (d) species.

Although some insight has already been gained into the possible structures of the $C_3H_6O\cdot^+$ ions produced by (1) ionization of acetone, (2) the single McLafferty rearrangement, and (3) the double McLafferty rearrangement (see Scheme II), it was deemed highly desirable to provide additional concrete experimental evidence regarding their structures. The ion chemistry of isomeric species is often correlated with specific structural features,[30] and it has been recently demonstrated[31] that isomeric ion structures can be differentiated by their chemical reactivity. If the $C_3H_6O\cdot^+$ ion structures are indeed different, as has been previously reported,[5] an excellent experimental method of substantiating this conclusion is by observing the ion–molecule reactions of these species. Since ion reactivity is to be used to differentiate these isomeric structures, ion cyclotron resonance and double resonance[30] appear to be uniquely suitable means of obtaining such evidence.

**Scheme II**



The principles, theory, instrumentation, applications, and other techniques concerned with ion cyclotron resonance have been previously described in considerable detail.[30-32] There are two qualitative characteristics of the ion cyclotron resonance spectrometer which make it particularly attractive for this study. First, mass spectra may be recorded at high enough pressures ($10^{-7}$ to $10^{-5}$ torr) to observe gas phase ion reactions of the charged $C_3H_6O\cdot^+$ species with the neutral molecules in the cell. Second, the extremely useful pulsed double resonance technique[30-32] (analogous to double resonance experiments in nmr spectroscopy) makes possible verification of ion reaction sequences, thus providing a method for distinguishing between the reactions of the $C_3H_6O\cdot^+$ ions and those of all the other ions.

In order to study the ion reactions of the $C_3H_6O\cdot^+$ ions, they must be generated in a facile manner; the methods of generating these species are depicted in Scheme III. As has been previously mentioned, electron bombardment of acetone (Ia) yields its keto molecular ion (k), and the site-specific transfer of a γ-hydrogen atom with expulsion of propene from the molecular ion (a) of 2-hexanone (IIa) provides the enol McLafferty ion d. A report by Ausloos and Rebbert[33] suggests a second facile mode of generating this enolic ion (d). They report that in the mass spectrum of 1-methylcyclobutanol (IIIa), the base peak occurs at *m/e* 58, and they postulate its structure to be the enolic $C_3H_6O\cdot^+$ ion ($1 \rightarrow m$). Finally, the "double McLafferty" ion can be generated from 5-nonanone ($IV \rightarrow a \rightarrow h$ or d).

Having generated the three $C_3H_6O\cdot^+$ isomer ions in a facile and unambiguous manner, a comparison of their reactivities by ion cyclotron techniques should (1) provide additional definitive experimental evidence regarding the structural differences of the keto (k) and enol (d and m) ions, and (2) offer further comment upon the third proposed[5] structural $C_3H_6O\cdot^+$ isomer, the symmetrical double McLafferty ion (h). Comparison of reactivities is accomplished by "mixing" the various $C_3H_6O\cdot^+$ ions in all combinations and observing their respective reactions with the neutral species present in each "mixture." This necessitates utilizing deuterium-labeled analogs in order to distinguish between ions of identical mass. For this purpose the keto species (k)

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(29) F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, **89**, 5951 (1967).

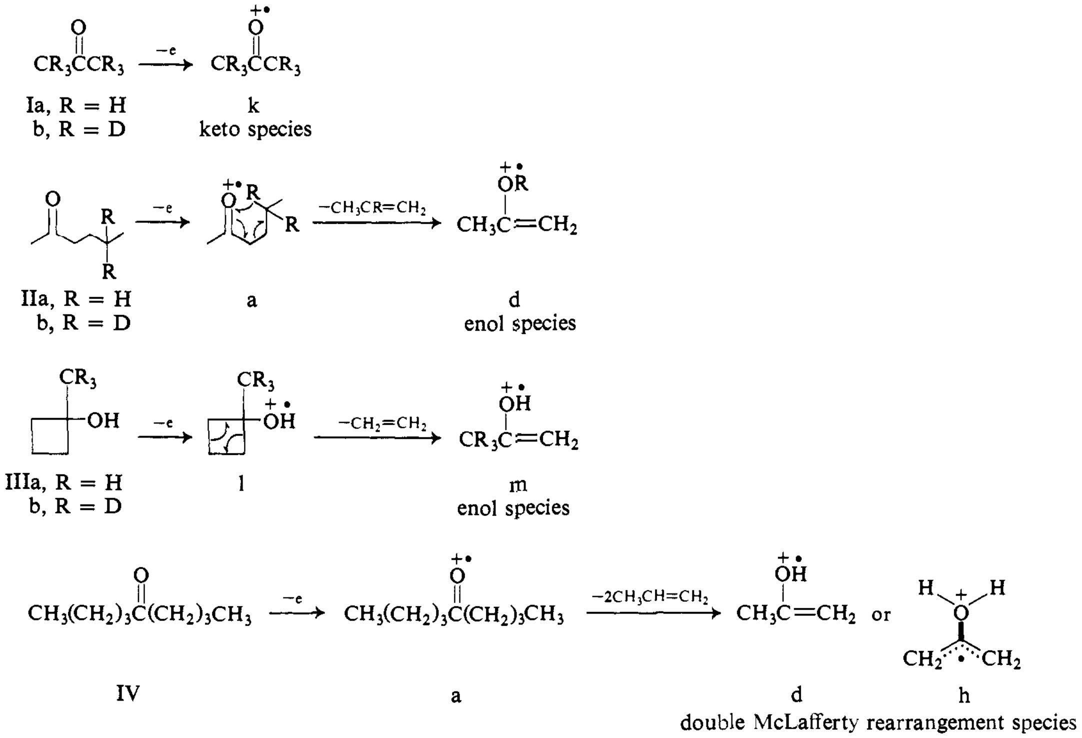
(30) (a) J. L. Beauchamp, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967; (b) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(31) (a) L. W. Sieck and J. H. Futrell, *J. Chem. Phys.*, **45**, 560 (1966); (b) M. S. B. Munson, *J. Am. Chem. Soc.*, **89**, 1772 (1967).

(32) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966); J. L. Beauchamp, *ibid.*, **46**, 1231 (1967); J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967); J. M. S. Henis, *ibid.*, 90, 844 (1968); G. A. Gray, *ibid.*, **90**, 2177 (1968).

(33) P. Ausloos and R. E. Rebbert, *ibid.*, **83**, 4897 (1961).

**Scheme III.** Generation of $C_3H_6O\cdot^+$ Ions



is always generated from hexadeuterioacetone (Ib) and has a mass of 64.

## Results and Discussion

**Generation of the $C_3H_6O\cdot^+$ Ions. Keto Species.** The ion cyclotron mass spectrum of hexadeuterioacetone[34] (Figure 3)[35] exhibits a strong *m/e* 64 peak corresponding to the keto isomer (k′) formed from hexadeuterioacetone (Ib) either by electron impact or through a charge transfer reaction.[7a,b] This spectrum (Figure 3) will be discussed in detail in the succeeding papers;[7c,d] therefore, only brief mention will be made concerning the ion structures of the prominent peaks (*m/e* 46, *m/e* 66, *m/e* 110, and *m/e* 130). The acylium ion (n) of mass 46 is the only species which results from the unimolecular or collision-induced[36] decomposition of hexadeuterioacetone. Ion–molecule reactions[7a-c] produce the deuterated molecular ion (*m/e* 66, o) and the loosely bound deuterated dimer (*m/e* 130, p). The only remaining peak in Figure 3 falls at *m/e* 110 and is of particular importance to this study. The proposed[7c] mechanism for the genesis of this ion involves condensation of ionized acetone (k′, *m/e* 64) and a molecule of neutral acetone (eq 1) with expulsion of a methyl radical ($CD_3\cdot$) to yield the oxonium ion product (q).[37]

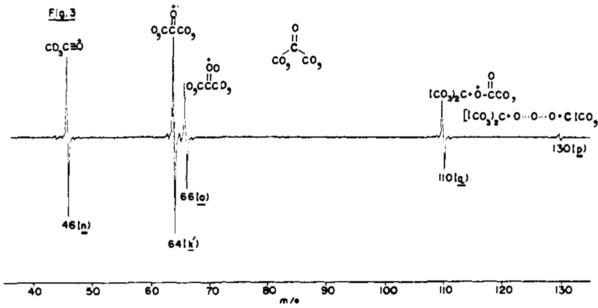
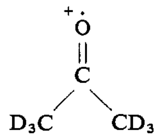


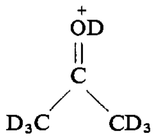
Figure 3. Ion cyclotron resonance spectrum of hexadeuterioacetone, $\omega_1/2\pi$ = 153.5 kcps, $2 \times 10^{-5}$ torr, 15 eV.



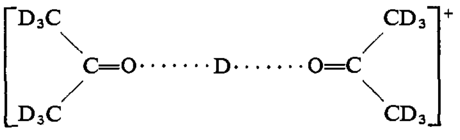
k′, *m/e* 64

$CD_3C\equiv\overset{+}{O}$

n, *m/e* 46



o, *m/e* 66



p, *m/e* 130

$$64\cdot^+ + 64 \rightarrow 110^+ + 18\cdot(CD_3) \qquad (1)$$

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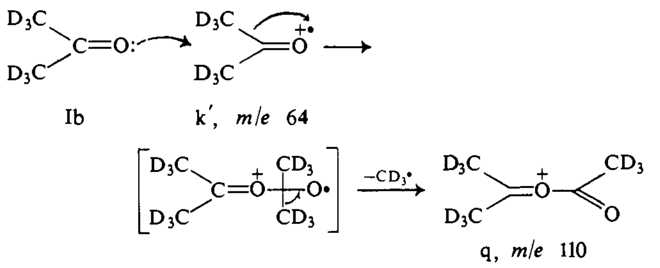
[34] Kinetic information derived from such ion cyclotron resonance experiments with acetone will be discussed in ref 7c.

[35] This and all other single and double resonance spectra reported in this paper were recorded using field modulation (20-G field modulation amplitude) which gives the derivative line shape. No single resonance spectra were recorded below *m/e* 40. The cyclotron resonance frequency ($\omega_1/2\pi$), ionizing energy, and pressure are reported with each individual spectrum.

[36] F. Kaplan, *J. Am. Chem. Soc.*, **90**, 4483 (1968).

[37] Pulsed double-resonance experiments[7c] verify this sequence and also indicate that the expelled methyl group originates from the neutral and charged reactants in approximately a 1:3 ratio, respectively; this implies that some of the initial condensation involves a one-electron process[7c] instead of the depicted two-electron process.



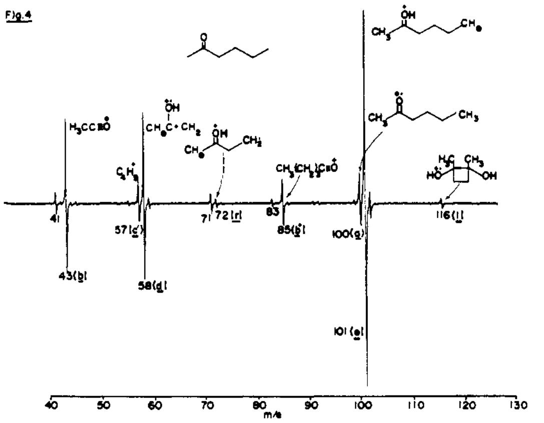
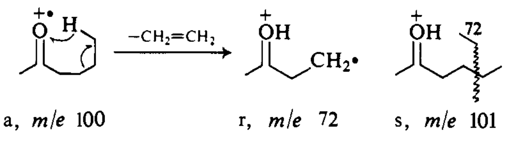


Figure 4. Ion cyclotron resonance spectrum of 2-hexanone, $\omega_1/2\pi$ = 153.5 kcps, 7 × $10^{-6}$ torr, 20 eV.

**Enol Species. a. From 2-Hexanone.** The intense *m/e* 58 peak in the ion cyclotron resonance spectrum (Figure 4) of 2-hexanone (IIa) corresponds to the enol ion d formed by the McLafferty rearrangement. Scheme I summarizes most of the peaks resulting from the normal unimolecular decomposition[38] of 2-hexanone (see Figure 1); species a corresponds to *m/e* 100, b to *m/e* 43, b' to *m/e* 85, c' to *m/e* 57, and d to *m/e* 58. The small *m/e* 41 peak corresponds to the $C_3H_5^+$ hydrocarbon ion, and *m/e* 71 is most probably due to cleavage of the terminal ethyl radical, although a reciprocal hydrogen-transfer process of the type reported by Carpenter, *et al.*,[39] may also contribute to this peak. The small *m/e* 72 peak appears only at low ionizing energy (less than 22 eV) and is most likely an example of a "McLafferty + 14" peak[39] (a → r). It might also result from expulsion of an ethyl radical from the protonated molecular ion (*m/e* 101, s). The intense protonated molecular ion (s, *m/e* 101) dominates the spectrum and it is conceivable that loss of water from this species could yield the small *m/e* 83 peak.[40] Since the latter is noticeable only at higher pressures (greater than 6 × $10^{-6}$ torr) it is likely that it arises from an ion-molecule reaction.



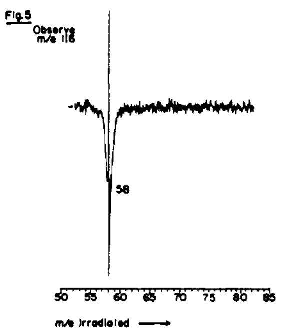
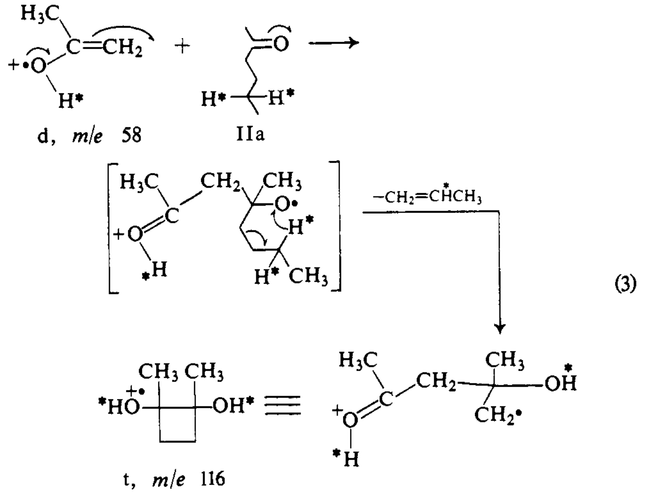


Figure 5. Pulsed double resonance spectrum of the *m/e* 116 species with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 4 was recorded.

The pulsed double resonance spectrum[41] (Figure 5) of the small *m/e* 116 peak exhibits a contribution from *m/e* 58 indicating an ion reaction involving the enol ion d (eq 2). In light of other reported ion condensations,[7d] one possible mechanistic rationalization of eq 2 is a sequence of condensation, γ-hydrogen rearrangement, and elimination of propene to yield an ion product perhaps possessing a cyclic structure such as t (eq 3). In the ion cyclotron resonance spectrum of 5,5-$d_2$-2-hexanone (IIb), the *m/e* 116 peak is shifted to *m/e* 118 in accord with this representation; in this system the hydrogen bonded to the enolic oxygen, the transferred γ-hydrogen, and one of the hydrogens in the eliminated propene molecule are all replaced by deuterium atoms (see asterisks). It must be emphasized that other plausible structural representatives can also be employed to accommodate these data.

$$58^{\cdot+} + 100 \rightarrow 116^{\cdot+} + 42 \qquad (2)$$

**Enol Species. b. From 1-Methylcyclobutanol.** Generation of the enol species (d) by some means other than



(3)

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(38) See ref 4, pp 134-135.

(39) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Am. Chem. Soc.*, 90, 160 (1968).

(40) Pulsed double resonance experiments were not attempted on these suggested reactions (*m/e* 101 → *m/e* 72 and *m/e* 101 → *m/e* 83); however, Dr. J. L. Beauchamp has informed us that he has observed pulsed double resonance evidence for the loss of water from the protonated molecular ions of numerous aldehydes.

(41) The contribution from *m/e* 58 in the pulsed double-resonance spectrum (Figure 5) of *m/e* 116 is indicated by a peak which points down; this signifies a reaction whose rate constant decreases with increasing ion energy. This direction of the pulsed double-resonance signal occurs in all double-resonance spectra reported in this study with the exception of the charge-transfer reaction whose double-resonance spectrum is shown in Figure 11a. In this case the signal points up and indicates an increasing reaction rate with increasing ion energy. Beauchamp and Buttrill[42] have presented a detailed discussion of this sign convention. The sharp spike observed at exactly the same frequency (307 kcps) as the *m/e* 58 signal is due to the irradiating oscillator exciting the first overtone of the marginal oscillator; this spike is visible in many of the reported pulsed double-resonance spectra.

(42) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

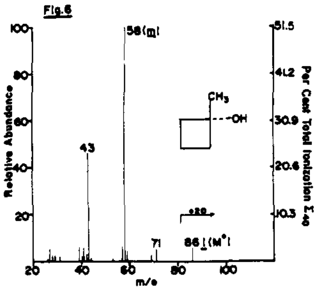


Figure 6. Mass spectrum (AEI MS-9) of 1-methylcyclobutanol, 70 eV.

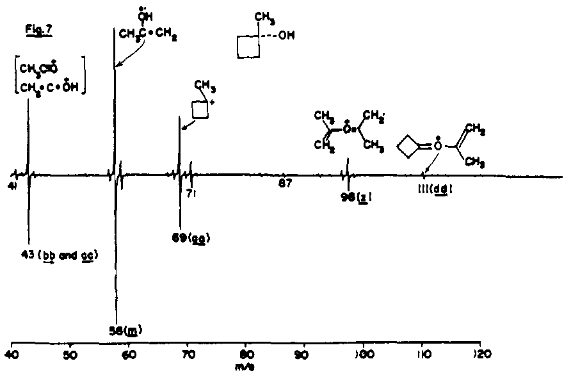
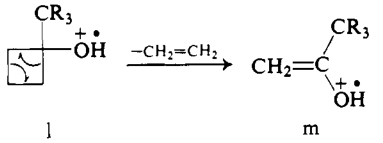


Figure 7. Ion cyclotron resonance spectrum of 1-methylcyclobutanol, $\omega_1/2\pi = 153.5$ kcps, $2 \times 10^{-6}$ torr, 20 eV.

the McLafferty rearrangement of 2-hexanone (II → d) was undertaken in order to compare the reactivity of this enol species with the keto (k′) and double McLafferty (h or d) ions as well as to assess the comparative reactivities of the differently generated enol (*m/e* 58) species. The 70-eV mass spectrum (Figure 6) of 1-methylcyclobutanol (IIIa) exhibits a base peak at *m/e* 58 ($\Sigma_{40} = 56$); even more important is the fact that this ion contributes 79% of the total ion current at 15 eV. Ausloos and Rebbert's suggestion[33] that this *m/e* 58 ion was enolic in structure and formed by elimination of ethylene from the molecular ion (l → m, R = H, eq 4) was verified by high-resolution mass measurements and deuterium labeling. Exact mass



(4)

measurements indicated a composition of $C_3H_6O$, and labeling the methyl group with deuterium atoms (R = D) shifted the *m/e* 58 peak to *m/e* 61.

The ion cyclotron resonance spectrum (Figure 7) of 1-methylcyclobutanol (IIIa) exhibits the expected *m/e* 58 peak, thus providing a second means (IIIa → m, Scheme III) of generating the enol $C_3H_6O\cdot^+$ ion. Cleavage of a methyl group from the molecular ion (*m/e* 86, l) which is of such weak intensity that it does not appear in Figure 7 produces the *m/e* 71 peak, and loss of a methyl group from the ion (m) of mass 58 yields the mass 43 species.[43] There are three peaks (*m/e* 69, *m/e* 98, and *m/e* 111) in the spectrum of 1-methylcyclobutanol corresponding to ion–molecule reaction products, and these species are discussed below in the context of differentiating between the various $C_6H_3O\cdot^+$ ions.

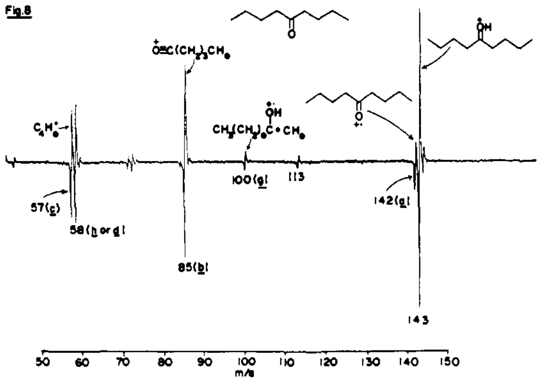


Figure 8. Ion cyclotron resonance spectrum of 5-nonanone, $\omega_1/2\pi = 115.1$ kcps, $5 \times 10^{-6}$ torr, 20 eV.

**Double McLafferty Species.** 5-Nonanone is utilized for the generation of the controversial "double McLafferty" species of mass 58 (see Scheme III, IV → h or d). The *m/e* 58 peak is one of the strongest peaks in the ion cyclotron resonance spectrum (Figure 8) of 5-nonanone, and, aside from the intense protonated molecular ion peak (*m/e* 143), this spectrum closely resembles the ordinary mass spectrum (Figure 2) of this compound with the M − 29 (*m/e* 113), the single McLafferty (*m/e* 100), the α-cleavage (*m/e* 85), and the $C_4H_9$ (*m/e* 57) peaks all in evidence.

## Differentiation of the Isomeric $C_3H_6O\cdot^+$ Ions

**Differentiation of the Keto (k′) and Enol (d) Species.** An approximately equimolar mixture of hexadeuterioacetone (Ib) and 2-hexanone (IIa) not only provides a system for simultaneously generating both the keto (k′) and enol (d) species, but offers a means of distinguishing between them due to the mass difference of the deuterium-labeled keto ion (*m/e* 64) and the unlabeled enol ion (*m/e* 58). One crucial region of the ion cyclotron resonance spectrum (Figure 9) of this mixture is between *m/e* 103 and *m/e* 109 where there are no significant peaks. This indicates that the condensation observed in the spectrum (Figure 3) of hexadeuterioacetone (eq 1) which produced the *m/e* 110[44] peak is unique for the keto (k′) form of the $C_3H_6O\cdot^+$ species. Either an *m/e* 107 or *m/e* 104 peak would be observed in the spectrum of the mixture of hexadeuterioacetone and 2-hexanone (Figure 9), *if* the enol species (d, *m/e* 58) condensed with hexadeuterioacetone (k′, eq 5 and 6) in a manner analogous to the condensation of ionized acetone with itself (eq 1). Cleavage of a methyl radical from an

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[43] This fragmentation scheme is supported by labeling, high-resolution mass measurements, and metastable evidence. Less than 4% of *m/e* 43 is due to the $C_3H_7^+$ ion.

[44] The *m/e* 110 peak is of very low intensity in this spectrum (Figure 9) because it was recorded at relatively low ($1 \times 10^{-6}$ torr) pressure which diminishes the intensity of reaction product ions. The spectrum (Figure 10) of a mixture of hexadeuterioacetone (Ib) and 5,5-$d_2$-2-hexanone (IIb) was recorded at $5 \times 10^{-6}$ torr and reveals a more intense *m/e* 110 peak. Here also there are no significant peaks in the *m/e* 103 and *m/e* 109 region, thus substantiating the above evidence. The intensity of the *m/e* 110 peak in these mixtures (Figures 9 and 10) is diminished with respect to its intensity in the spectrum (Figure 3) of hexadeuterioacetone alone because the keto ion (k′, *m/e* 64), in the mixtures, participates not only in the condensation reaction (eq 1) but in charge transfer processes with neutral 2-hexanone (IIb, see below). Thus, fewer keto ions are available for formation of the *m/e* 110 species (q).

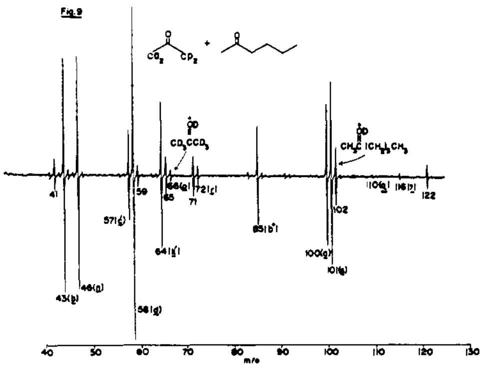


Figure 9. Ion cyclotron resonance spectrum of a mixture of hexadeuterioacetone and 2-hexanone, $\omega_1/2\pi = 153.5$ kcps, $1 \times 10^{-6}$ torr, 20 eV.

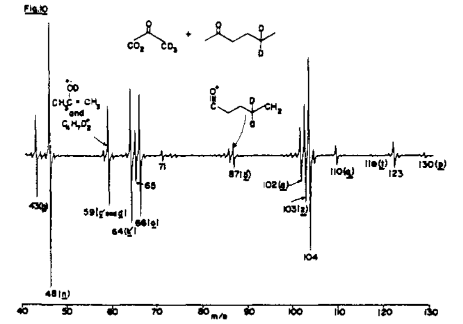


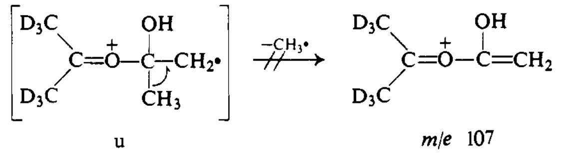
Figure 10. Ion cyclotron resonance spectrum of a mixture of hexadeuterioacetone and 5,5-$d_2$-2-hexanone, $\omega_1/2\pi = 153.5$ kcps, $5 \times 10^{-6}$ torr, 20 eV.

intermediate condensation product (depicted here as u

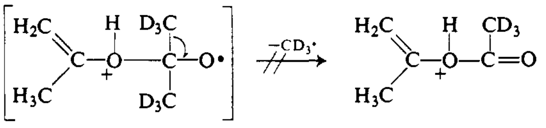
$$58\cdot^{+} + 64 \rightarrow 107^{+} + 15\cdot(CH_3\cdot) \quad (5)$$

$$58\cdot^{+} + 64 \rightarrow 104^{+} + 18\cdot(CD_3\cdot) \quad (6)$$

for descriptive purposes) would yield species of mass 107 (eq 5), whereas loss of a deuterated methyl radical from the isomeric form v would give an *m/e* 104 peak (eq 6). *The absence of either an m/e 104 or m/e 107 peak in Figure 9 thus provides the first example of an ion reaction capable of distinguishing between the enol (d) and keto (k) isomers of the m/e 58 ion (see reaction A of Scheme IV); this also substantiates the previous conclusions*[9] *regarding the inability of the McLafferty rearrangement product (d) to ketonize prior to subsequent decomposition.*

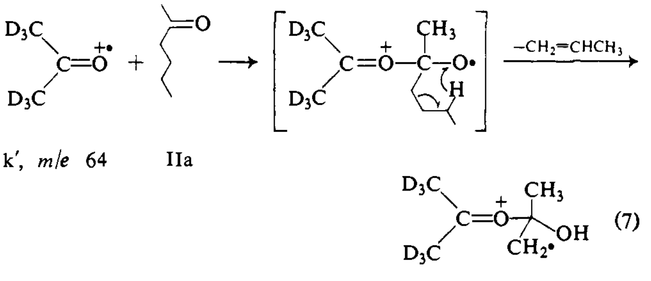


u *m/e* 107



v *m/e* 104

The potentiality of the condensation of the enolic species of mass 58 with 2-hexanone followed by propene elimination (d → t, eq 2 and 3) as yet another "enol–keto" distinguishing reaction is precluded by the existence of a significantly intense *m/e* 122 peak in the spectrum (Figure 9) of hexadeuterioacetone and 2-hexanone. This peak, which is discussed in a succeeding publication,[7d] results from the condensation of the keto ion (k') with 2-hexanone (IIa) in an ion reaction (k' → w, eq 7) analogous to eq 3.



k', *m/e* 64 IIa

w, *m/e* 122

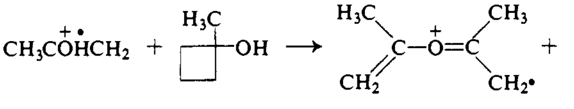
The ion "cross-products" evident in the mixture of hexadeuterioacetone and 2-hexanone (Figure 9) which are discussed elsewhere in this series[7] include the protonated molecular ion of hexadeuterioacetone[7c] (*m/e* 65), the deuterated molecular ion of 2-hexanone[7d] (*m/e* 102), the condensation–displacement ion[7a,d] x (*m/e* 146),[45] and the deuterated loosely bound cross-dimer, y (*m/e* 166).[45]

**Scheme IV.** Ion–Molecule Reactions Which Distinguish between the Enol (d and m) and Keto (k) Isomers of the $C_3H_6O\cdot^{+}$ Ion

$$\underset{k}{CH_3\overset{+\cdot}{C}OCH_3} + \underset{Ia}{CH_3COCH_3} \rightarrow \underset{q}{(CH_3)_2C{=}\overset{+}{O}COCH_3} + CH_3\cdot \quad (A)$$

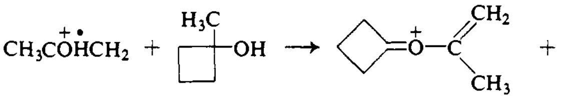
$$\underset{k}{CH_3\overset{+\cdot}{C}OCH_3} + \underset{IIa}{CH_3CO(CH_2)_3CH_3} \rightarrow \underset{a}{CH_3\overset{+\cdot}{C}O(CH_2)_3CH_3} + CH_3COCH_3 \quad (B)$$

$$\underset{d}{CH_3\overset{+\cdot}{C}(OH)CH_2} + \underset{IIa}{CH_3CO(CH_2)_3CH_3} \rightarrow \underset{s}{CH_3\overset{+}{C}(OH)(CH_2)_3CH_3} + CH_3COCH_2\cdot \quad (C)$$



d and m IIIa z

$H_2O + CH_2{=}CH_2$ (D)



d and m IIIa dd

$H_2O + CH_3\cdot$ (E)

$$\underset{k}{CH_3\overset{+\cdot}{C}OCH_3} + \underset{IV}{CH_3(CH_2)_3CO(CH_2)_3CH_3} \rightarrow \underset{gg}{(CH_3)_2C{=}\overset{+}{O}\underset{CH_2\cdot}{\overset{OH}{C}}CH_3} + 2C_3H_6 \quad (F)$$

$$\underset{d\ and\ m}{CH_3\overset{+\cdot}{C}OHCH_2} + \underset{IV}{CH_3(CH_2)_3CO(CH_2)_3CH_3} \rightarrow CH_3(CH_2)_3\overset{+}{C}(OH)(CH_2)_3CH_3 + CH_3COCH_2\cdot \quad (G)$$

---

[45] The *m/e* 146 and *m/e* 166 peaks are not visible in Figure 9 because the spectrum was recorded with $\omega_1/2\pi = 153.5$ kcps; this limits the mass range from *m/e* 1 to *m/e* 143.

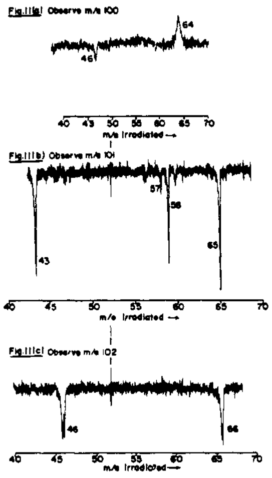
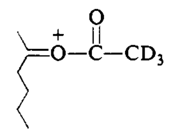
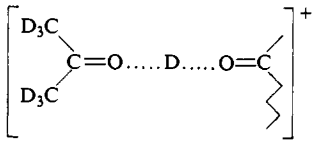


Figure 11. (a) Pulsed double resonance spectrum of the *m/e* 100 species with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 9 was recorded. (b) Pulsed double resonance spectrum of the *m/e* 101 species with the irradiating voltage = 0.06 V and other conditions identical with those under which Figure 9 was recorded. (c) Pulsed double resonance spectrum of the *m/e* 102 species with the irradiating voltage = 0.08 V and other conditions identical with those under which Figure 9 was recorded.



x, *m/e* 146



y, *m/e* 166

There are two other aspects of the ion–molecule chemistry of the mixture of hexadeuterioacetone and 2-hexanone which must be investigated with respect to potential "enol-keto" differentiating reactions. Pulsed double resonance experiments greatly facilitate the study of charge transfer and proton transfer reactions; such measurements (Figure 11a)[41] on the molecular ion (*m/e* 100) of 2-hexanone in the mixture of hexadeuterioacetone and 2-hexanone indicate charge transfer from the molecular ion of hexadeuterioacetone (k′, *m/e* 64) to the neutral 2-hexanone (IIa) moiety (eq 8), but not from the McLafferty enol ion (d, *m/e* 58). This is consistent with the observation that the reported[46] ionization potential of 2-hexanone (9.34 eV) lies between the reported[46] ionization potential of acetone (9.69 eV) and the enol form of the $C_3H_6O$ species (8.2 eV).[20] *This charge transfer reaction (eq 8) is thus the second ion–molecule reaction capable of distinguishing between the enol and keto isomers of the m/e 58 ion*[47] *(see reaction B of Scheme IV).*

$$64\cdot^{+} + 100 \rightarrow 64 + 100\cdot^{+} \tag{8}$$

Although the enol *m/e* 58 species (d) does not transfer its charge to 2-hexanone, it does transfer a proton to this species. The pulsed double resonance spectrum (Figure 11b) of protonated 2-hexanone (s, *m/e* 101) indicates that not only the *m/e* 58 enol ion, but the acylium ion (b, *m/e* 43), the protonated molecular ion of hexadeuterioacetone (*m/e* 65), and to a lesser extent the hydrocarbon species (c′) of mass 57 all transfer a proton to 2-hexanone. Charge transfer from the keto ion (k′) of mass 64 to 2-hexanone dominates the reaction of this species (k′) to the extent of obscuring any deuterium transfer to 2-hexanone as is indicated by the pulsed double resonance spectrum (Figure 11c) of the deuterated molecular ion of 2-hexanone (*m/e* 102). The acylium ion (n, *m/e* 46) and the deuterated molecular ion (o, *m/e* 66) of hexadeuterioacetone, but *not* the molecular ion of hexadeuterioacetone (k′, *m/e* 64), contribute to the formation of the *m/e* 102 species. *This then is the third ion–molecule reaction (eq 9) capable of distinguishing the $C_3H_6O\cdot^{+}$ ion isomers (see reaction C, Scheme IV).*

$$58\cdot^{+} + 100 \rightarrow 101^{+} + 57\cdot \tag{9}$$

**Identity of the Enol Ions (d) and (m).** Prior to reporting the reactions differentiating between the ion radical of acetone (k′) and the isomeric enol ion (m), derived (see Scheme III) from 1-methylcyclobutanol (IIIa), comment must be made not only on some of the characteristic reactions of this enol ion (m), but on its identity with the enol ion (d), derived from 2-hexanone (IIa).

It has been noted that the ion cyclotron resonance spectrum (Figure 7) of 1-methylcyclobutanol, from which the enol m (*m/e* 58) is generated, contains three peaks (*m/e* 69, 98, and 111) resulting from ion–molecule reactions. Pulsed double resonance experiments demonstrate that the ion of mass 98 arises by the following reaction sequence (eq 10). In the spectrum (Figure 12)

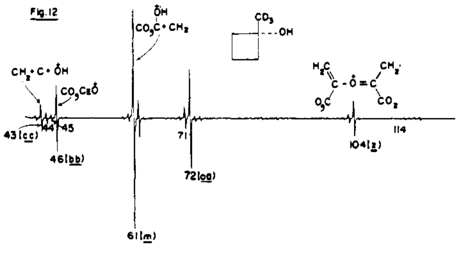


Figure 12. Ion cyclotron resonance spectrum of 1′,1′,1′-$d_3$-1-methylcyclobutanol, $\omega_1/2\pi$ = 153.5 kcps, 3 × $10^{-6}$ torr, 18 eV.

$$58\cdot^{+} + 86 \rightarrow 98\cdot^{+} + 46 \tag{10}$$

of the labeled analog (IIIb), this *m/e* 98 peak is shifted to *m/e* 104 and pulsed double-resonance data (Figure 13a) indicate the following sequence (eq 11). A mechanistic

$$61\cdot^{+} + 89 \rightarrow 104\cdot^{+} + 46 \tag{11}$$

representation of this ion reaction must involve elimination of the elements of water (including either the enol or alcohol hydroxyl group) and also elimination of the elements of ethylene from the 1-methylcyclobutanol (IIIa) species in order to accommodate the labeling results. One possible formulation (eq 12) might be proton transfer of the oxygen-bonded enolic hydrogen to the alcohol oxygen atom followed by displacement

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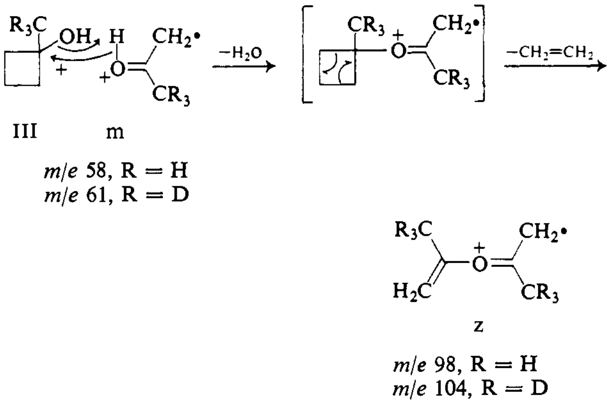
(46) R. K. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, Appendix IV.

(47) Dr. J. L. Beauchamp, California Institute of Technology, has also observed this charge transfer reaction, as well as the small contribution from the deuterated acylium ion (*m/e* 46), and has substantiated this observation on the basis of energetic calculations. His work was reported at the Symposium on Ion-Molecule Reactions and Photoionization, Hakone, Japan, Sept 1968.

of water by the carbonyl oxygen.[48] Concomitant or subsequent elimination of ethylene from the cyclobutyl ring would yield the conjugated product ion z (*m/e* 98, R = H; *m/e* 104, R = D).



III m

*m/e* 58, R = H
*m/e* 61, R = D

(12)

z

*m/e* 98, R = H
*m/e* 104, R = D

The prominent ion of mass 69 (M − 17) in Figure 7 could conceivably be generated by unimolecular elimination of a tertiary hydroxyl group from the molecular ion of 1-methylcyclobutanol (l) yielding the $C_5H_9{}^+$ hydrocarbon fragment (aa). However, the absence of this peak in the ordinary mass spectrum (Figure 6) and its enormous increase in intensity at higher pressures, suggest its genesis *via* an ion-molecule reaction. Pulsed double resonance experiments reveal the following reaction (eq 13). Labeling the methyl group (R = D)

$$43^+ + 86 \rightarrow 69^+ + 60 \qquad (13)$$

shifts the *m/e* 69 peak to *m/e* 72 and also distributes the *m/e* 43 peak between *m/e* 43, 44, 45, and 46 (see Figure 12); the pulsed double resonance spectrum (Figure 13b) indicates that all four of these ions (*m/e* 43–46) contribute to the formation of the methylcyclobutyl cation (aa, *m/e* 72, R = D). The major contributor (*m/e* 46) probably extracts a hydroxyl group from 1-methylcyclobutanol forming neutral acetic acid (m → bb → aa).[49] A similar scheme (eq 15) involving *m/e* 43 can be visualized as proceeding *via* protonated ketone (cc): m → cc → aa.

Although of very weak intensity (Figure 7), the *m/e* 111 ion product proved to be a potentially important peak because of its genesis from the enol ion (m) of mass 58 as is indicated by its pulsed double resonance spectrum (Figure 13c). This reaction can be depicted in a manner similar to the reaction (eq 12) m → z, namely proton transfer, followed by displacement of water and cleavage of a methyl radical (m → dd, eq 16) to yield the oxonium product ion (*m/e* 111). As the pressure is increased (greater than $4 \times 10^{-6}$ torr), the *m/e* 69 species (aa) increases substantially in intensity, and pulsed double resonance (see Figure 13d) indicates that it becomes the major reactant in the formation (aa → dd, eq 17) of the ion of mass 111.

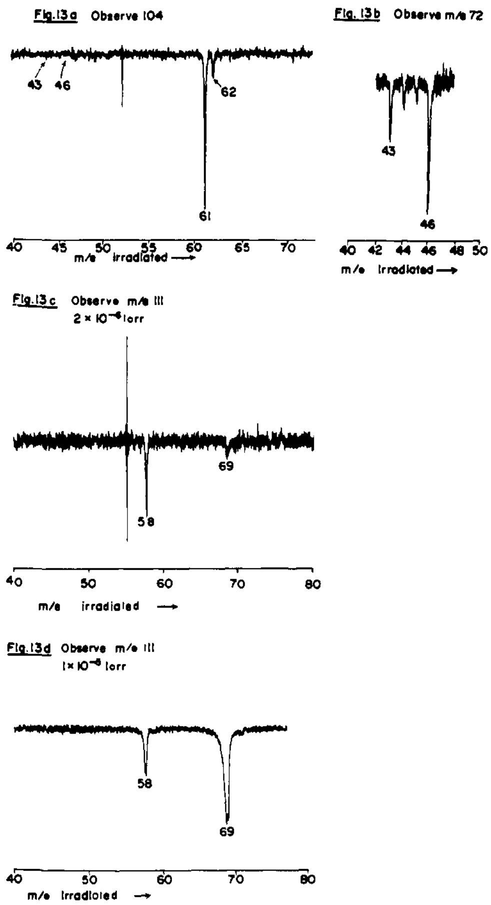


Figure 13. (a) Pulsed double resonance spectrum of the *m/e* 104 species in the spectrum of 1′,1′,1′-$d_3$-1-methylcyclobutanol with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 12 was recorded. (b) Pulsed double resonance spectrum of the *m/e* 72 species in the spectrum of 1′,1′,1′-$d_3$-1-methylcyclobutanol with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 12 was recorded. (c) Pulsed double resonance spectrum with the *m/e* 111 species in the spectrum of 1-methylcyclobutanol with the irradiating voltage = 0.06 V, the pressure = $2 \times 10^{-6}$ torr, and other conditions identical with those under which Figure 7 was recorded. (d) Pulsed double resonance spectrum of the *m/e* 111 species in the spectrum of 1-methylcyclobutanol with the irradiating voltage = 0.06 V, the pressure = $1 \times 10^{-5}$ torr, and other conditions identical with those under which Figure 7 was recorded.

The ion cyclotron resonance spectrum (Figures 7 and 12) of 1-methylcyclobutanol exhibits an intense peak at *m/e* 98, corresponding to an ion-molecule reaction product (z, eq 12) which can be utilized to assess the comparative behavior of the two enol ions (d and m) generated from structurally different species (II and III). An equimolar mixture of 1-methylcyclobutanol (IIIa) and 5,5-$d_2$-2-hexanone (IIb) generates the enol species m of mass 58 from the former and the enol species d of mass 59 from the latter (resulting from transfer of a deuterium atom to the enol oxygen in a McLafferty rearrangement of II). Not only does this system (Figure 14) illustrate the identical behavior of these two species (d and m) but it also points out the particular value of the pulsed double resonance technique as a unique analytical tool. Although there is apparently no mass shift of the *m/e* 98 peak (z) in this spectrum (Figure 14), the pulsed double resonance spectrum (Figure 15a) indicates clearly that

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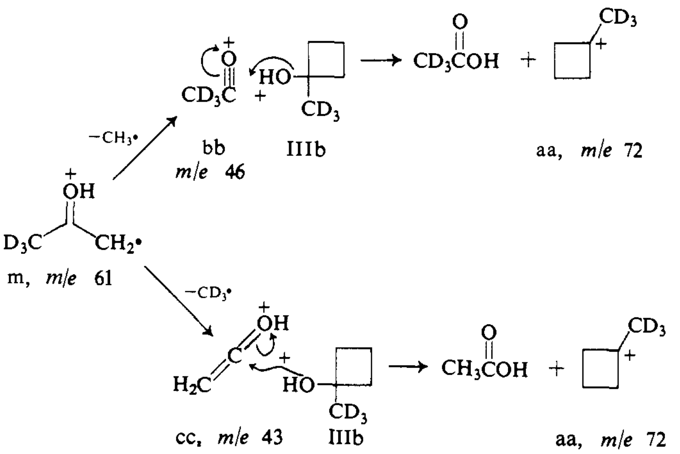
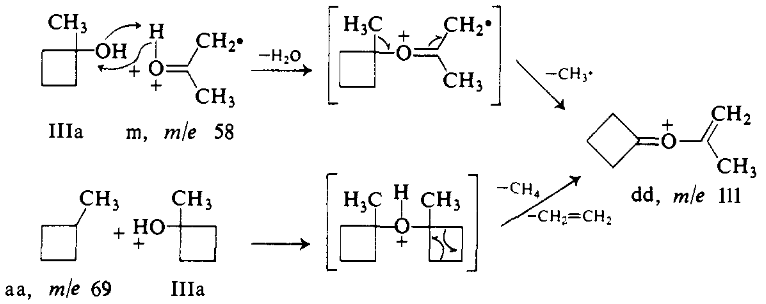
(48) A frequently observed ion-molecule reaction in the case of carbonyl-alcohol mixtures is hydrogen transfer from the protonated carbonyl function followed by displacement of water from the intermediate to yield a similar product ion. We thank Dr. J. L. Beauchamp for informing us of these results prior to publication.

(49) Generation of the ions of mass 46 (R = D) and 43 (R = H) from the labeled and unlabeled enol precursors, respectively, is supported by large metastable peaks in the ordinary mass spectra.



(14)

(15)



(16)

(17)

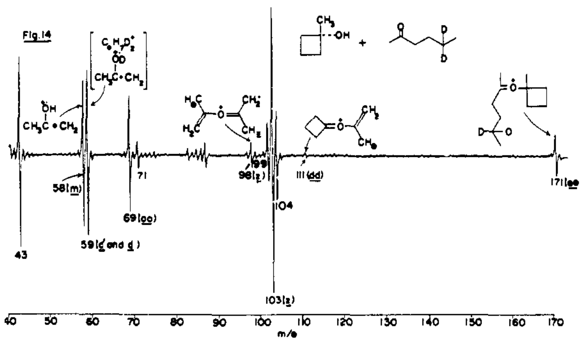


Figure 14. Ion cyclotron resonance spectrum of a mixture of 1-methylcyclobutanol and 5,5-$d_2$-2-hexanone, $\omega_1/2\pi$ = 115.0 kcps, 6 × $10^{-6}$ torr, 20 eV.

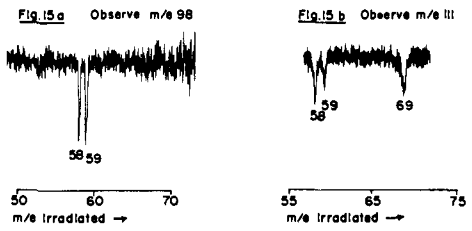


Figure 15. (a) Pulsed double resonance spectrum of the m/e 98 species with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 14 was recorded. (b) Pulsed double resonance spectrum of the m/e 111 species with the irradiating voltage = 0.08 V and other conditions identical with those under which Figure 14 was recorded.

both enol ions (m and d) are producing this ion product. Pulsed double resonance was also performed on the small m/e 99 peak[50] and indicated no reaction involving the m/e 59 species (d). This labeling result is in accord with the previously suggested reaction path ( m→ z, eq 12) in that the enol oxygen-bonded hydrogen atom is not present in the charge-retaining ion product, but is a component of the expelled water molecule.

The identical behavior of the enol ions (d and m) is also exhibited by pulsed double resonance (Figure 15b) on the small m/e 111 peak. This experiment shows that the unlabeled (m/e 58, m) and labeled (m/e 59, d) enol ions, as well as the methylcyclobutyl cation (m/e 69, aa), participate in the formation of this ion; these results are also in accord with the previously suggested reaction schemes, m → dd (eq 16) and aa → dd (eq 17).

The fairly intense m/e 171 ion product is generated in a reaction found in all 1-methylcyclobutanol–ketone mixtures observed in this study (see below). The protonated molecular ion (s) of labeled 2-hexanone combines with neutral 1-methylcyclobutanol and eliminates water (s → ee, eq 18) in a manner similar to the reaction m → z (eq 12) yielding a charged oxonium ion product (ee).

The ion cyclotron resonance spectrum (Figure 16) of an equimolar mixture of hexadeuterioacetone (Ib) and 1-methylcyclobutanol (IIIa) constitutes another example

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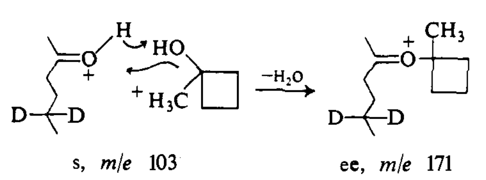
(50) The appearance of peaks of weak intensity in the m/e 71–76, m/e 83–87, and m/e 95–99 region is typical of spectra of 1-methylcyclobutanol recorded at pressures of 5 × $10^{-6}$ torr or higher.



(18)

of the identical behavior of the two differently generated enol ions (d and m), in that m like d (see Figure 9) fails to condense with hexadeuterioacetone producing neither an *m/e* 104 nor *m/e* 107 peak (eq 5 and 6) in a manner analogous to the genesis of the species (q, eq 1) of mass 110. There are numerous other examples of the identical behavior of these two enol ions (d and m) which will not be reported in detail. Suffice it to say that in all subsequent reactions, the behavior of one of these species always was found to hold true for the other.

**Differentiation of the Keto (k′) and Enol (m) Ions.** The ion cyclotron resonance spectrum (Figure 16) of an equimolar mixture of hexadeuterioacetone and 1-methylcyclobutanol substantiates the existence of two more enol–keto distinguishing reactions (see reactions D and E, Scheme IV). If the molecular ion of hexadeuterioacetone (k′) had reacted with neutral 1-methylcyclobutanol, eliminating water and ethylene, in a manner analogous to the enol reaction (m → z, eq 12) a peak would exist in the *m/e* 101 → 104 region. The absence of such a peak verifies that *only an enolic species can participate in the ion reaction scheme (m → z, eq 12) and constitutes the fourth differentiating reaction (see reaction D, Scheme IV).* The pulsed double resonance spectrum (Figure 17a) of *m/e* 98 makes certain that this peak owes its genesis only to the enol ion of mass 58. Likewise, the absence of a significant peak in the *m/e* 112–117 region indicates the existence of the fifth enol–keto distinguishing reaction m → dd (eq 16, see reaction E of Scheme IV). The pulsed double resonance spectrum (Figure 17b) verifies the conclusion that the ketonic species of mass 64 does not contribute to the genesis of the *m/e* 111 peak (dd).

Pulsed double resonance experiments indicate that in an ion reaction similar to that which produced the *m/e* 171 peak in the previously discussed system (s → ee, Figure 14, eq 18), the protonated (*m/e* 65) or deuterated (*m/e* 66) molecular ion of hexadeuterioacetone reacts with 1-methylcyclobutanol (IIIa) to produce the intense *m/e* 133 peak (o → ff, eq 19) in this spectrum (Figure 16).

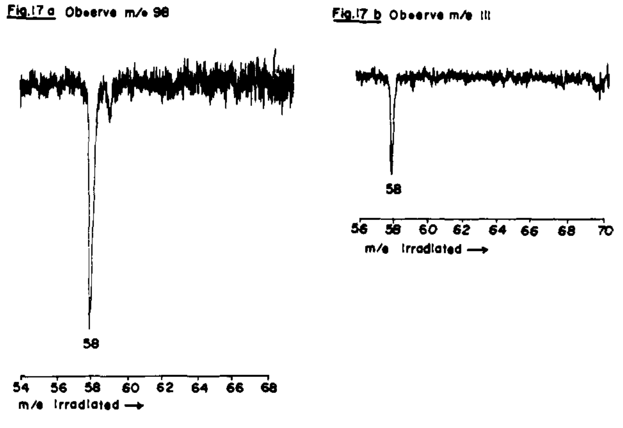
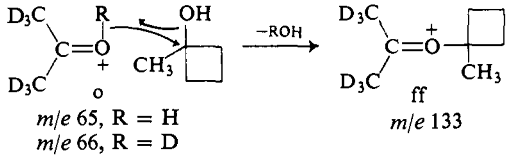


Figure 17. (a) Pulsed double resonance spectrum of the *m/e* 98 species with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 16 was recorded. (b) Pulsed double resonance spectrum of the *m/e* 111 species with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 16 was recorded.



(19)

Although the ion cyclotron resonance spectrum (Figure 18) of an approximately equimolar mixture of hexadeuterioacetone (Ib) and 5-nonanone (IV) is recorded primarily for the purpose of observing the reactions of the double McLafferty ion (h or d), the easily detectable *m/e* 122 peak in this spectrum is particularly relevant to the discussion of the differentiation of the keto and enol ions. The ion-molecule reaction which produces this *m/e* 122 ion is discussed in detail in a succeeding publication,[7d] and is believed to involve condensation of the molecular ion (k′) of hexadeuterioacetone with neutral 5-nonanone and subsequent elimination of two

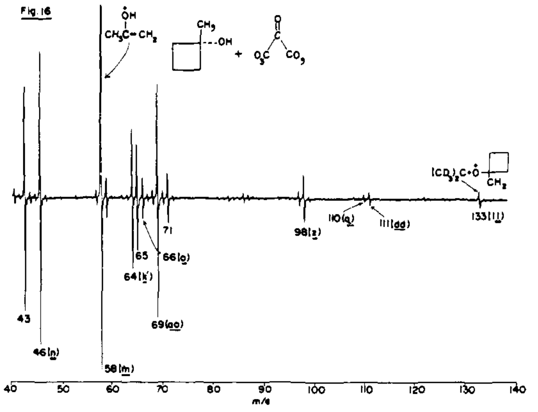


Figure 16. Ion cyclotron resonance spectrum of a mixture of 1-methylcyclobutanol and hexadeuterioacetone, $\omega_1/2\pi = 153.5$ kcps, $1 \times 10^{-6}$ torr, 20 eV.

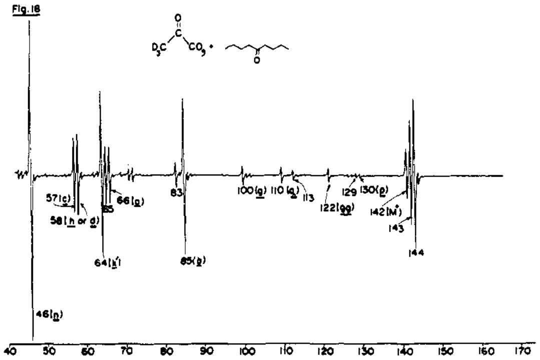


Figure 18. Ion cyclotron resonance spectrum of a mixture of hexadeuterioacetone and 5-nonanone, $\omega_1/2\pi = 109.0$ kcps, $5 \times 10^{-6}$ torr, 20 eV.

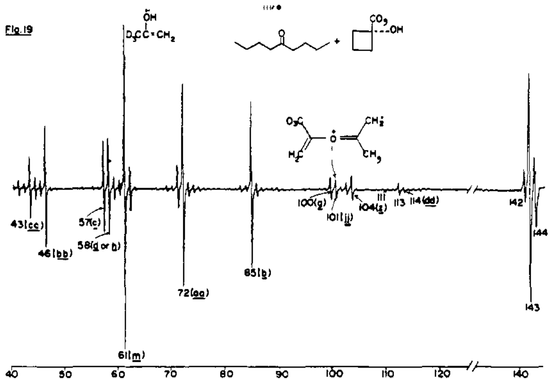


Figure 19. Ion cyclotron resonance spectrum of a mixture of 1′,1′,1′-$d_3$-1-methylcyclobutanol and 5-nonanone, $\omega_1/2\pi = 153.5$ kcps, $3 \times 10^{-6}$ torr, 20 eV.

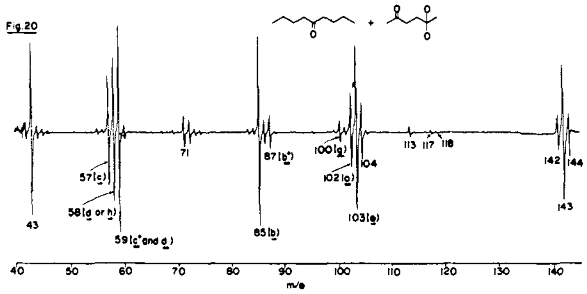
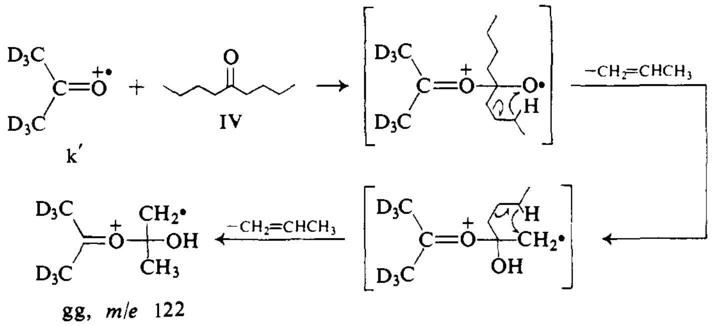


Figure 20. Ion cyclotron resonance spectrum of a mixture of 5,5-$d_2$-2-hexanone and 5-nonanone, $\omega_1/2\pi = 153.5$ kcps, $5 \times 10^{-6}$ torr, 20 eV.

molecules of propene (k′ → gg, eq 20). The ion cyclotron resonance spectrum (Figure 19) is of an approximately equimolar mixture of 5-nonanone and 1′,1′,1′-$d_3$-1-methylcyclobutanol (IIIb) reveals that the enol ion (m, *m/e* 61) fails to react with 5-nonanone and eliminate 2 molecules of propene in a manner analogous to the behavior of the keto (k′) species (eq 20). If the enol species did undergo such a reaction, an *m/e* 119 peak would be evident in Figure 19. *Thus, the m/e 122 species (gg) in the previous spectrum (Figure 18) represents the sixth means (see reaction F, Scheme IV) of distinguishing the enol and keto m/e 58 species.*

As in the case of the previous two spectra (Figures 18 and 19), the ion cyclotron resonance spectrum (Figure 20) of a mixture of 5,5-$d_2$-2-hexanone (IIb) and 5-nonanone (IV) was recorded primarily in order to observe the behavior of the double McLafferty species. This mixture, however, provides the seventh and final method of distinguishing the enol and keto species (see reaction G, Scheme IV). Pulsed double resonance of the protonated (*m/e* 143, Figure 21a) and deuterated (*m/e* 144, Figure 21b) molecular ions of 5-nonanone affords spectra which are practically identical with those of the protonated and deuterated molecular ions of 5,5-$d_2$-2-hexanone (Figures 13b and 13c, respectively). Again, the acylium ion (*m/e* 43), the hydrocarbon ion (c, *m/e* 57), the double McLafferty ion (*m/e* 58, h or d), and to a very small extent the deuterated hydrocarbon ion (*m/e* 59, $C_4H_7D_2^+$) transfer a proton to generate the *m/e* 143 species. Similarly the pulsed double resonance spectrum of *m/e* 144 shows a deuteron transfer only from the *m/e* 59 single McLafferty species (d). Pulsed double resonance (Figure 21c) of the deuterated molecular ion of 5-nonanone (*m/e* 144) in the mixture of hexadeuterioacetone and 5-nonanone (Figure 18) indicates, however, that the keto molecular ion of hexadeuterioacetone (k′, *m/e* 64) does *not* transfer a proton to this species. In this mixture, only the deuterated acylium ion (*m/e* 46, n) contributes to this reaction product, thus providing the final "enol-keto" distinguishing reaction (reaction G of Scheme IV). The *m/e* 143 peak in this spectrum (Figure 18) results from proton transfer from the hydrocarbon species of mass 57, the double McLafferty ion (*m/e* 58), and the protonated molecular ion of hexadeuterioacetone (Figure 21d). Pulsed double resonance (Figure 21e) of this same ion (*m/e* 143) in the mixture of 1′,1′,1′-$d_3$-1-methylcyclobutanol and 5-nonanone (Figure 19) offers further supporting evidence for this differentiating reaction with proton transfer from the enol *m/e* 61 ion (m, R = D), as well as the $C_4H_9^+$ hydrocarbon ion (*m/e* 57, c), the double McLafferty ion (*m/e* 58), the labeled methylcyclobutyl ion (*m/e* 72), and the α-cleavage ion (b, *m/e* 85).

**Differentiation of the Keto (k′) and Double McLafferty (d or h) Ions.** The ion cyclotron resonance spectrum (Figure 18) of the mixture of hexadeuterioacetone and 5-nonanone, from which the double McLafferty peak (d or h, *m/e* 58, see Figure 8) is generated, offers two ion-molecule reactions capable of distinguishing between the keto ion (k′, *m/e* 64) and the double McLafferty species. First, it has been previously noted (eq 1) that the molecular ion of hexadeuterioacetone condenses with neutral hexadeuterioacetone and eliminates a labeled methyl radical to yield the *m/e* 110 species (q). In this spectrum (Figure 18) *no* peak is observed in the *m/e* 103–109 region indicating that, like the single McLafferty enolic ion (d, *m/e* 58), the double McLafferty ion fails



(20)

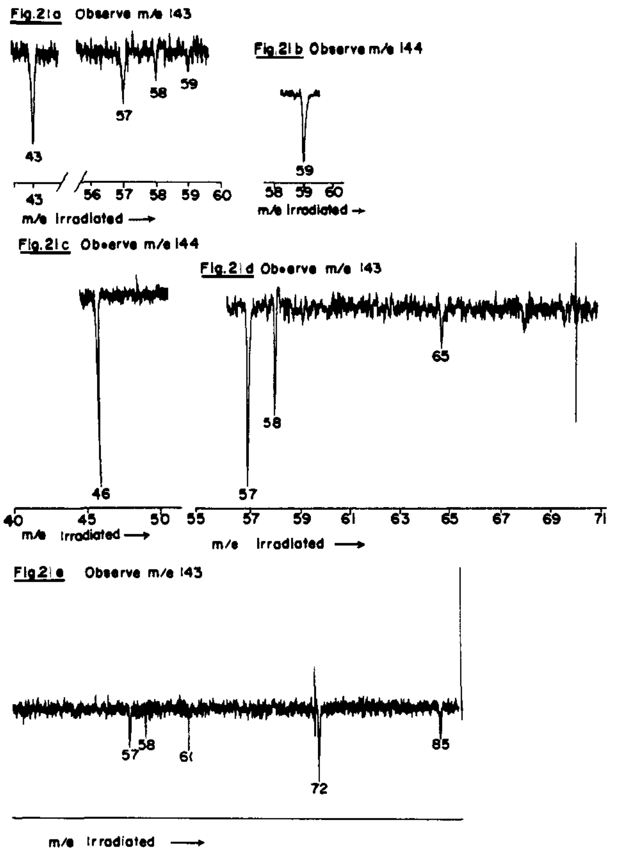


Fig.21a Observe m/e 143

Fig.21b Observe m/e 144

Fig.21c Observe m/e 144

Fig.21d Observe m/e 143

Fig.21e Observe m/e 143

Figure 21. (a) Pulsed double resonance spectrum of the *m*/*e* 143 species in the mixture of 5,5-$d_2$-2-hexanone and 5-nonanone with the irradiating voltage = 0.08 V and other conditions identical with those under which Figure 20 was recorded. (b) Pulsed double resonance spectrum of the *m*/*e* 144 species in the mixture of 5,5-$d_2$-2-hexanone and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 20 was recorded. (c) Pulsed double resonance spectrum of the *m*/*e* 144 species in the mixture of hexadeuterioacetone and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 18 was recorded. (d) Pulsed double resonance spectrum of the *m*/*e* 143 species in the mixture of hexadeuterioacetone and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 18 was recorded. (e) Pulsed double resonance spectrum of the *m*/*e* 143 species in the mixture of 1′,1′,1′-$d_3$-1-methylcyclobutanol and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 19 was recorded.

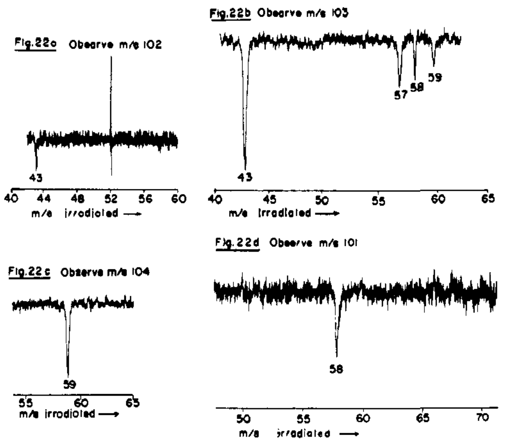


Fig.22a Observe m/e 102

Fig.22b Observe m/e 103

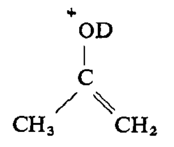
Fig.22c Observe m/e 104

Fig.22d Observe m/e 101

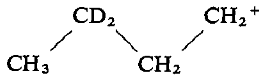
Figure 22. (a) Pulsed double resonance spectrum of the *m*/*e* 102 species in the mixture of 5,5-$d_2$-2-hexanone and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 20 was recorded. (b) Pulsed double resonance spectrum of the *m*/*e* 103 species in the mixture of 5,5-$d_2$-2-hexanone and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 20 was recorded. (c) Pulsed double resonance spectrum of the *m*/*e* 104 species in the mixture of 5,5-$d_2$-2-hexanone and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 20 was recorded. (d) Pulsed double resonance spectrum of the *m*/*e* 101 species in the mixture of 1′,1′,1′-$d_3$-1-methylcyclobutanol and 5-nonanone with the irradiating voltage = 0.1 V and other conditions identical with those under which Figure 19 was recorded.

to condense with hexadeuterioacetone in a manner analogous to the reaction of the keto *m*/*e* 64 (k′) species (k′ $\rightarrow$ q, eq 1; see reaction A, Scheme IV). Second, it has also been noted that the keto ion (k′) condenses with 5-nonanone eliminating 2 molecules of propene to yield the species of mass 122 (gg, eq 20). Here too (Figure 18) the double McLafferty ion of mass 58 does *not* participate in an analogous reaction since otherwise a relatively intense peak would exist at *m*/*e* 116. The spectrum (Figure 19) of the mixture of 5-nonanone and 1′,1′,1′-$d_3$-1-methylcyclobutanol, as has been noted, confirms the failure of the double McLafferty rearrangement product to participate in this reaction to any significant extent, a *m*/*e* 119 peak being nonexistent. In fact, such a conclusion can be derived from the spectrum of 5-nonanone itself (Figure 8) because there is no *m*/*e* 116 peak in this spectrum corresponding to the participation of the double McLafferty ion in such a reaction.

Pulsed double resonance spectra of the mixture of 5,5-$d_2$-2-hexanone (IIb) and 5-nonanone (IV) (Figure 20) also serve to distinguish between the double McLafferty and keto ions. It has been previously pointed out (Figure 11a and eq 8) that the keto species (k′) transfers its charge to neutral 2-hexanone (see reaction B, Scheme IV). Pulsed double resonance (Figure 22a) on the molecular ion of 5,5-$d_2$-2-hexanone (in its mixture with 5-nonanone) indicates that the double McLafferty ion (*m*/*e* 58), unlike the keto ion, does not transfer its charge to neutral 5,5-$d_2$-2-hexanone (IIb); only the acylium ion (*m*/*e* 43, n) does so. Pulsed double resonance (Figure 22b) on the protonated molecular ion (*m*/*e* 103) of 5,5-$d_2$-2-hexanone (IIb) in this mixture (Figure 20) shows that the double McLafferty ion (*m*/*e* 58), as well as the acylium ion (*m*/*e* 43, see Figure 11b), the $C_4H_9$ hydrocarbon ion generated from 5-nonanone (*m*/*e* 57, c), and an *m*/*e* 59 species all transfer a proton to the labeled 2-hexanone species. It is doubtful that in this case the *m*/*e* 59 species is the single McLafferty ion (d) because transfer of an oxygen-bonded *deuteron* from hh to labeled 2-hexanone and not a *proton* would be expected. Thus, this species of mass 59 is probably the deuterated hydrocarbon ion $C_4H_7D_2$ (ii) which has been previously shown to transfer a proton to a small extent (Figure 11b). This prediction is substantiated by pulsed double resonance experiments (recorded under identical conditions) (Figure 22c) on the deuterated 5,5-$d_2$-2-hexanone ion (*m*/*e* 104). Here, the contribution from *m*/*e* 59 is substantially more intense suggesting transfer of the oxygen-bonded deuteron from the single McLafferty peak.



hh, *m/e* 59



ii, *m/e* 59

At this stage it will have become evident that the reactions reported thus far, which are capable of differentiating between the keto (k′) and double McLafferty ions (h or d), are exactly the same reactions which have been utilized for distinguishing between the keto (k′) and enol (m and d) ions. In other words, the criteria for differentiation covered in this section are exactly analogous to reactions A, B, C, and F of Scheme IV, which serve to identify keto and *single* McLafferty enol ions. As will be shown in the subsequent section, reactions D and G (Scheme IV) can also be utilized to distinguish the keto ion from the double McLafferty ion as well as the single McLafferty enol species.

**Presumed Identity of the Enol Ions (d and m) and the Double McLafferty Ion (d or h).** In all ion cyclotron resonance spectra (Figures 18–20) representing ion-molecule mixtures containing 5-nonanone (IV), and hence the double McLafferty species (d or h), it is impossible to differentiate between the single McLafferty enol ion (d), the enol ion (m), and the double McLafferty species by ion reactivity. It has already been shown (see previous section) that in the enol–keto distinguishing reactions of Scheme IV, the double McLafferty ion behaves identically with the enol ions in reactions A, B, C, and F. Pulsed double resonance of the protonated (*m/e* 143, Figure 21a) and deuterated (*m/e* 144, Figure 21b) molecular ions of 5-nonanone in the mixture of 5-nonanone and 5,5-$d_2$-2-hexanone (Figure 20) illustrates that the double McLafferty species (*m/e* 58, Figure 21a), like the single McLafferty species (*m/e* 59, Figure 21b), transfers a proton to 5-nonanone forming the protonated *m/e* 143 species (see reaction G, Scheme IV). Pulsed double resonance of the protonated species of mass 143 (Figure 21e) in the mixture of 1′,1′,1′-$d_3$-1-methylcyclobutanol (IIIb) and 5-nonanone (IV) (Figure 19) likewise shows that both the enol ion (m, *m/e* 61) and the double McLafferty species (*m/e* 58) transfer a proton in the generation of this reaction product.

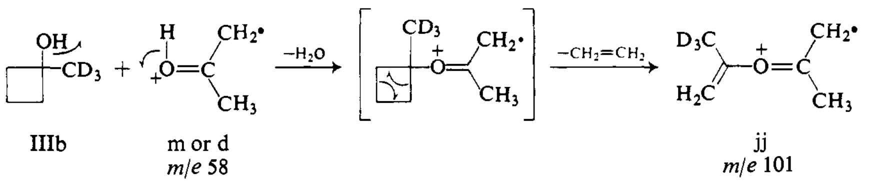
The presence of both an *m/e* 101 and an *m/e* 104 peak in this spectrum (Figure 19) further substantiates the identical behavior of the enol and double McLafferty ions. It has been shown (see reaction D, Scheme IV) that the *m/e* 104 species is generated by an enol–keto distinguishing reaction (m → z, eq 12, R = D). Pulsed double resonance experiments (Figure 22d) show the production of the *m/e* 101 peak from the *m/e* 58 double McLafferty precursor. It thus appears that the double McLafferty species (*m/e* 58) exists, in fact, in the enol form (d or m) and generates the *m/e* 101 peak (jj, eq 21) in a manner analogous to the formation of the *m/e* 104 peak (eq 12). It is still possible, however, that the symmetrical form (h) of the double McLafferty ion can react to form an *m/e* 101 species.

Because the enol and double McLafferty ions appear to be reacting identically in all systems investigated, the ion cyclotron resonance spectrum (Figure 19) of the mixture of 1′,1′,1′-$d_3$-1-methylcyclobutanol and 5-nonanone should exhibit an *m/e* 111 peak, formed in a manner identical with the genesis of the *m/e* 114 species (m → dd, eq 16) (see reaction E, Scheme IV). Unfortunately, the *m/e* 111 peak (Figure 19) is too small to perform pulsed double resonance experiments. Its weak intensity (as compared to the *m/e* 114 peak) may be attributed to a higher concentration of ions of mass 61 (m) as compared to the double McLafferty ions of mass 58 in the cell of the spectrometer. At this relatively low ionizing energy (20 eV), it is rather difficult to generate by electron bombardment a significant concentration of double McLafferty ions (*via* a two-step process, *m/e* 142 → *m/e* 100 → *m/e* 58), whereas the one-step elimination of ethylene from the molecular ion of 1-methylcyclobutanol still leads to a large amount of the enol species (m, *m/e* 61).

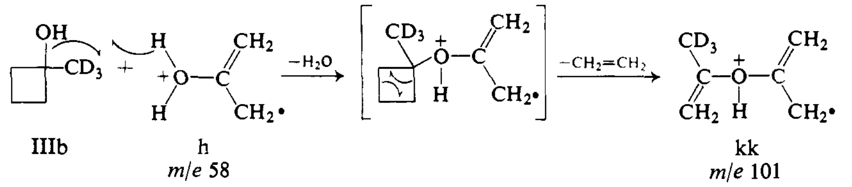
The spectrum (Figure 20) of a mixture of 5-nonanone and 5,5-$d_2$-2-hexanone contains one final incidence of the identical reactivity of the enol and double McLafferty ions. As has been previously noted, condensation of the labeled (*m/e* 59) single McLafferty ion (d) with 5,5-$d_2$-2-hexanone and subsequent expulsion of 2-$d_1$-1-propene yields the product ion of mass 118 (d → t, eq 3). Similarly, condensation of the unlabeled double McLafferty ion with loss of the same neutral molecule produces the ion of mass 117. The latter could conceivably result from reaction of the labeled McLafferty ion (*m/e* 59) with 5-nonanone and subsequent expulsion of two molecules of propene in a manner similar to reaction F of Scheme IV. If this were the case, however, an *m/e* 119 peak would appear in Figure 19 and this is absent.

## Conclusion

It was stated in the introductory section that the intention of this research was to provide concrete experimental evidence regarding the proposed[5] differences in the structures of the keto (k), enol (d), and symmetrical "double McLafferty" (h) isomers of the $C_3H_6O\cdot^+$ ion. It was noted that structural differences in these isomeric ions could be detected by observing the differences in



(21)



(22)

the reactivity of these species, and it was suggested that ion cyclotron resonance and double resonance would be particularly suitable means of obtaining such evidence.

The results of this work offer an excellent example of the applicability of ion cyclotron resonance and double resonance for observing the similarities and differences in the chemical reactivity of isomeric ions. These results thus illustrate the importance of ion cyclotron resonance as an analytic tool for studying the structures of ions formed by electron impact.

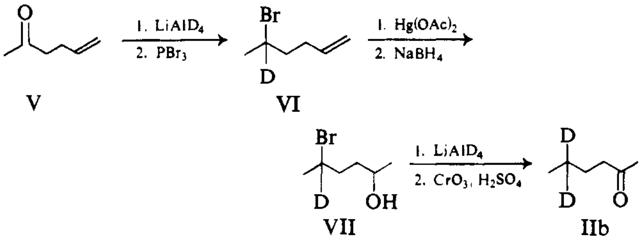
The ion cyclotron resonance experiments presented in this report provide substantial evidence with regard to the proposed[5,18-26] structural differences of the keto (k) and enol (d and m) $C_3H_6O\cdot^+$ ions. Seven ion–molecule reactions (see Scheme IV) have been found which are capable of distinguishing between these isomeric ions, and these "distinguishing reactions" may be attributed to the structural differences of these ions. The enol ions d and m have been generated by two different unimolecular decompositions (see Scheme III); in all cases observed herein, these species (d and m) react identically, thus substantiating that their structures are identical.

The reactivity and thus structural differences in the keto (k) and double McLafferty isomers of the $C_3H_6O\cdot^+$ ion have likewise been demonstrated. In fact, six of the "enol–keto" distinguishing reactions (Scheme IV, excluding reaction E) can be utilized to differentiate between the double McLafferty and keto ions by replacing the enol species with the double McLafferty species in each reaction.

McLafferty has recently developed a method utilizing metastable ion characteristics for determining structures of ions produced by electron impact.[5,29,51] On the basis of this technique, he has proposed that the enol (d) and double McLafferty (h) isomers of the $C_3H_6O\cdot^+$ ion have different structures. The results of the ion cyclotron resonance and double resonance studies present an anomaly because in all systems investigated in this case, the enol and double McLafferty isomers behave identically. This observation leads to the following conclusion: (1) the enol and double McLafferty ions have identical structures (d); or (2) that this is the first instance of ions of different structure exhibiting identical reactivity; or (3) that the lifetimes of ions in the cell of the ion cyclotron resonance spectrometer are significantly longer than the lifetimes of ions in a conventional mass spectrometer (which is utilized in the determination of metastable ion characteristics) and that increased lifetimes permit the symmetrical double McLafferty ion h to isomerize to the enol species d prior to undergoing ion–molecule reactions; or (4) increased lifetimes may also result in complete decomposition of the symmetrical $C_3H_6O\cdot^+$ species h (if it is formed at all) prior to reacting with neutral molecules.

## Synthesis of Labeled Compounds

It was necessary to synthesize only two deuterium-labeled analogs in this study: 1′,1′,1′-$d_3$-1-methylcyclobutanol (IVb) and 5,5-$d_2$-2-hexanone (IIb).[52] The former was synthesized by reacting methyl-$d_3$-magnesium iodide with cyclobutanone utilizing the conditions of Semenow, *et al.*[53] Synthesis of the latter involved reduction of commercially available 1-hexen-5-one (V) with lithium aluminum deuteride, followed by treatment with phosphorus tribromide to yield 5-$d_1$-5-bromohex-1-ene (VI). Hydration of VI by Brown's[54] oxymercuration–demercuration reaction gave the slightly unstable 5-$d_1$-5-bromohexan-2-ol (VII) which was again reduced with lithium aluminum deuteride; a subsequent Jones oxidation produced the desired analog, 5,5-$d_2$-2-hexanone (IIb) in high isotopic purity.



## Experimental Section[55]

**1′,1′,1′-$d_3$-1-Methylcyclobutanol (IVb).** Under extremely anhydrous conditions and utilizing a system ordinarily used for $^{13}C$ labeling,[56] 4.4 g of trideuteriomethyl iodide[57] was treated with 760 mg of purified magnesium in 12 ml of anhydrous ether, forming trideuteriomethylmagnesium iodide; 1.7 ml of cyclobutanone[58] was added dropwise to the Griginard reagent. After heating the reaction mixture under reflux for 1.5 hr, water was cautiously added and the ethereal layer separated. The aqueous layer was extracted twice with ether, and the combined ethereal layers were washed with saturated sodium thiosulfate and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, 960 mg of 1′,1′,1′-$d_3$-1-methylcyclobutanol (IVb) was isolated by preparative gas–liquid partition chromatography on a 10 ft × 0.25 in. stainless steel column packed with 15% Carbowax on Chromosorb W with a He flow rate of 40 cc/min at 110°. The infrared spectrum exhibited a hydroxyl absorption band at $\lambda_{max}$ 2.9 μ, and the mass spectrum showed the isotopic composition to be greater than 98% $d_3$.

**5,5-$d_2$-2-Hexanone (IIb).** Utilizing conditions reported in previous deuterium-labeling syntheses,[59] 3.9 g of 1-hexen-5-one (V)[58] was reduced with 1.1 g of lithium aluminum deuteride.[57] Preparative gas–liquid partition chromatography on a 10 ft × 0.25 in. aluminum column packed with DC-200 on Chromosorb W with a He flow rate of 50 cc/min at 105° yielded 3.6 g of 5-$d_1$-1-hexen-5-ol which exhibited characteristic infrared absorptions at $\lambda_{max}$ 2.9 and 6.1 μ. Employing the procedure of Wood,[60] 5-$d_1$-1-hexen-5-ol was converted to 5-$d_1$-5-bromohex-1-ene (VI) with 3.3 g of phosphorus tribromide. Distillation at 140–142° yielded 3.0 g of product whose infrared spectrum did not exhibit any hydroxyl band. Hydration of 1.6 g of 5-$d_1$-5-bromohex-1-ene (VI) according to the conditions Brown[54] used for 1-hexene yielded 1.5 g of

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(51) See also F. W. McLafferty, T. Wachs, and W. T. Pike in "Advances in Mass Spectrometry," Vol. 4, E. Kendrick, Ed., Institute of Petroleum, London, 1968; W. F. Haddon and F. W. McLafferty, *J. Am. Chem. Soc.*, 90, 4746 (1968).

(52) Hexadeuterioacetone was purchased from Mallinckrodt Chemical Works, St. Louis, Mo.

(53) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 3221 (1956).

(54) H. C. Brown and P. Geoghegan, *ibid.*, **89**, 1522 (1967).

(55) The basic spectrometer used in this study is the Varian V-5900 spectrometer. The spectrometer, the method, and the applications of single and double resonance have been recently described.[30] Mass spectra were recorded on an Atlas CH-4 mass spectrometer with an ion-source temperature of 190° by Mr. Nelson Garcia. High-resolution measurements and some low-resolution measurements were carried out by Mr. R. G. Ross using an A.E.I. MS-9 instrument equipped with a 200° heated inlet system. Infrared absorption spectra were measured with a Perkin-Elmer Model 137 infracord spectrophotometer.

(56) J. Trudell and C. Djerassi, to be published.

(57) Trideuteriomethyl iodide and lithium aluminum deuteride were purchased from Stohler Isotope Chemicals, Azusa, Calif.

(58) Cyclobutanone and 1-hexen-5-one were purchased from Aldrich Chemicals, Milwaukee, Wis.

(59) J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **33**, 2271 (1968).

(60) H. B. Wood and E. C. Horning, *J. Am. Chem. Soc.*, **75**, 5511 (1953).

an unstable compound which could not be purified by distillation or gas–liquid partition chromatography. The crude reaction product was reduced with 1.5 g of lithium aluminum deuteride[57] according to previously reported conditions[59] (except that the reaction mixture was heated under reflux for 4 days) to yield 750 mg of a crude product which was purified by gas–liquid partition chromatography on a 10 ft × 0.25 in. stainless steel column packed with 5% SE-30 on Chromosorb W with a He flow rate of 75 cc/min at 100°. The infrared spectrum was identical with unlabeled hexanol and the mass spectrum showed that the product, 5,5-$d_2$-2-hexanol, had an isotopic composition of 99% $d_2$ and 1% $d_1$. Oxidation of this labeled alcohol according to the conditions of Djerassi, *et al.*,[61] and purification of the product by gas–liquid partition chromatography (conditions identical with those used for the isolation of 5,5-$d_2$-2-hexanol) yielded 600 mg of 5,5-$d_2$-2-hexanone (IIb).

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[61] C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

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# Relative Rates of Cleavage by Alkoxide Ions of Diphenylcyclopropenone and of Diphenylthiirene 1,1-Dioxide

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*Contribution from the Chemistry Department, Northwestern University, Evanston, Illinois 60201.*
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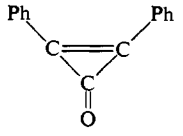
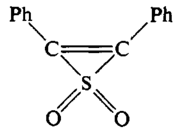
**Abstract:** The rates of reaction of diphenylcyclopropenone (**1**) with sodium methoxide in methanol, sodium ethoxide in ethanol, and sodium isopropoxide in isopropyl alcohol have been determined at several temperatures. A comparable study has been made with diphenylthiirene 1,1-dioxide (**2**). In each instance the relative rates were in the order, NaOMe:NaOEt:NaO-*i*-Pr ≅ 1:2:6. The ratio of rates for **2** to **1** was *ca.* 5000 to 1. This striking reversal of the usual much more facile attack of base on the carbonyl group than on the sulfonyl group is attributed to a marked conjugative stabilization of **1** as contrasted to a slight conjugative stabilization of **2**.

The extensive investigations of Breslow and his coworkers on cyclopropenone,[2a] its mono- and dialkyl derivatives, and its diphenyl derivative (**1**)[2b] have clearly established that the cyclopropenone system has considerable conjugative stabilization. The much greater thermal stability of diphenylthiirene 1,1-dioxide (**2**)[3,4] as compared to its saturated analogs, *cis*- and *trans*-2,3-diphenylthiirane 1,1-dioxides,[4] suggested that this might be true also for thiirene 1,1-dioxides, although much less information concerning this series is available.[5] It appeared to be of interest to compare the rates of cleavage of **1** and **2** with alkoxide ions. Ordinarily attack at the carbonyl group by hydroxide or alkoxide ions is much more facile than attack at the sulfonyl group. We wanted to see whether this would be true also for systems **1** and **2**.



**1**



**2**

## Results

Diphenylcyclopropenone (**1**) is known to hydrolyze rapidly in aqueous sodium hydroxide to give a high yield of *cis*-2,3-diphenylpropenoic acid.[2b] In 95% ethanol at 24° the half-life of this reaction with 0.1 *N* base was found to be about 5 min.[2b] In the present study **1** was observed to give high yields (95%) of the methyl, ethyl, and isopropyl esters of *cis*-2,3-diphenylpropenoic acid when treated with the appropriate sodium alkoxide in the corresponding alcohol. Rate constants for these reactions were determined spectrophotometrically by following the rate of disappearance of the band at 296 m$\mu$, characteristic of diphenylcyclopropenone, in the presence of excess standard base. The results are summarized in Table I.

The reaction of sodium methoxide in methanol with diphenylthiirene 1,1-dioxide (**2**) at 0° has been found to give methyl *cis*-2,3-diphenylethenesulfonate (75%) and diphenylacetylene (16%); similar results were obtained

**Table I.** Kinetic Data for the Reactions of Diphenylcyclopropenone (**1**) with Sodium Alkoxides in Alcohol Solvents

| Alkoxide (concn, *M*) | *T*,°C | $k$, $M^{-1}$ sec$^{-1}$ [a] | $E_a$, kcal/mol | $\Delta S^*$, eu |
|---|---|---|---|---|
| NaOMe (0.03116) | 10 | $9.59 \times 10^{-3}$ | | |
| NaOMe (0.03116) | 25 | $3.46 \times 10^{-2}$ | | |
| NaOMe (0.08628) | 25 | $(3.72 \times 10^{-2})$[b] | 14 | −21 |
| NaOMe (0.03116) | 40 | $1.07 \times 10^{-1}$ | | |
| NaOEt (0.01390) | 10 | $1.55 \times 10^{-2}$ | | |
| NaOEt (0.01390) | 25 | $6.83 \times 10^{-2}$ | 17 | −9 |
| NaOEt (0.01422) | 40 | $2.74 \times 10^{-1}$ | | |
| NaO-*i*-Pr (0.02495) | 10 | $6.90 \times 10^{-2}$ | | |
| NaO-*i*-Pr (0.02495) | 25 | $2.70 \times 10^{-1}$ | 14 | −16 |
| NaO-*i*-Pr (0.02495) | 40 | $7.88 \times 10^{-1}$ | | |

[a] Average of three or more runs; individual runs on the same day were reproducible to within ±5%, but the over-all reproducibility was closer to ±10%. [b] When corrected for a small positive salt effect (determined in separate runs with added salt) the order of the reaction in base is calculated to be 1.04.

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[1] National Science Foundation Undergraduate Research Participant, Summer, 1966.

[2] (a) R. Breslow and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 3072 (1967), and references cited therein; (b) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

[3] L. A. Carpino and L. V. McAdams, III, *ibid.*, **87**, 5804 (1965).

[4] F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *ibid.*, **90**, 429 (1968).

[5] Only one additional compound in this series appears to have been prepared to date, see L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966).