spectrum is in clear contrast to those of tridehydro[26]annulene,[7] tridehydro[30]annulene,[3] and pentadehydro[30]annulene,[3] in which all the protons appear as a very broad band at $\sim\tau$ 2.0–4.5.

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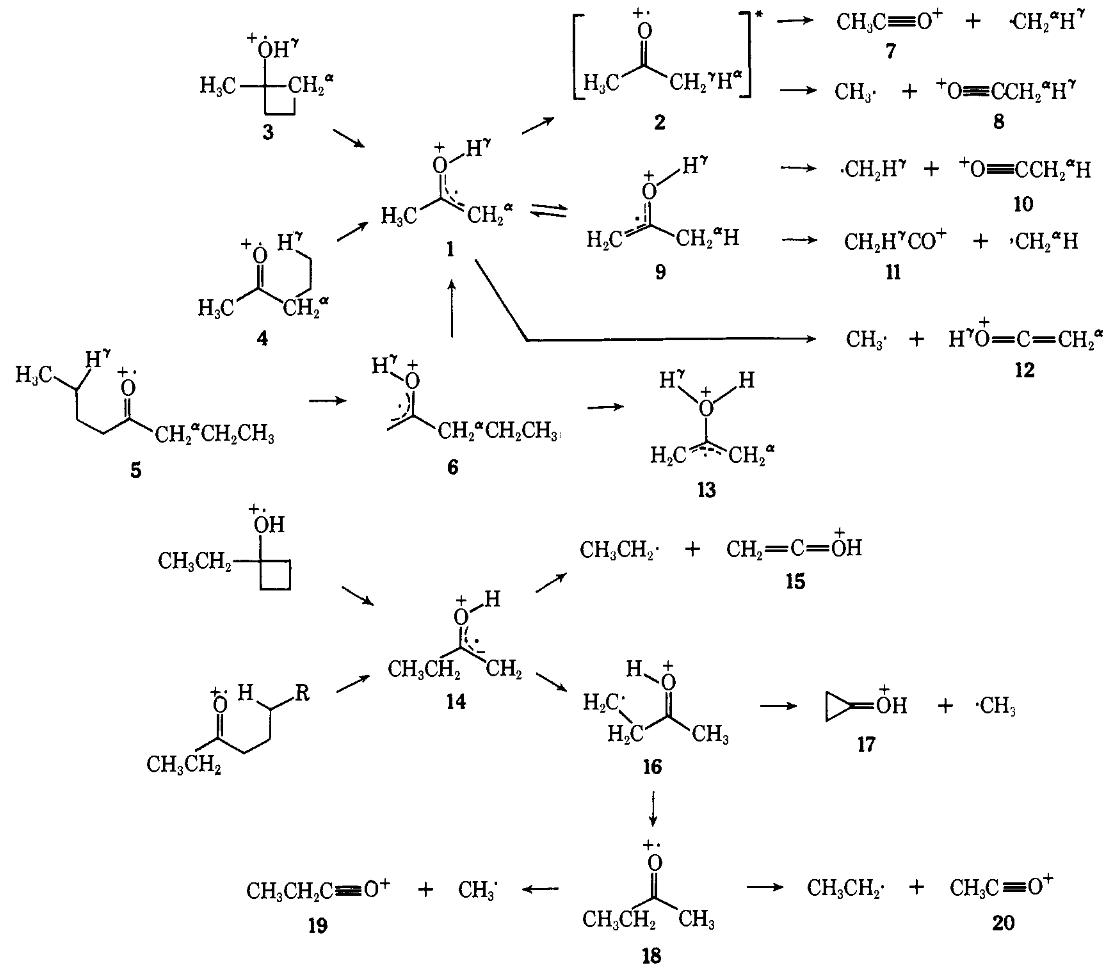
Ketonization of Gaseous Enol Ions[1]

Sir:

In the mass spectra of aliphatic ketones abundant ions can be formed in both the keto and enol forms, but interconversion between such tautomers has not been reported.[2-4] Considerable evidence[3] has been presented to show that the keto tautomer is of higher energy, and that the enol ion does not ketonize prior to fragmentation.[5] We report evidence from the metastable ion abundances of labeled compounds that the major decomposition pathways of three simple enol ions appear to involve initial ketonization.

In ion cyclotron resonance studies[3,4] of $C_3H_6O^+$ ions no appreciable tautomerism between the keto and enol forms was observed despite the relatively long (millisecond) ion lifetimes involved. However, we find that the predominant product, $C_2H_3O^+$, arising from decomposition of the enolic $C_3H_6O^+$ (**1**) in the mass spectrometer appears to be formed through rearrangement to an unstable keto intermediate, **2**, not through the simple cleavage **1** → **12** (Table I).[7] Direct losses of CH_2^α and H^γ from **1** to form CH_3CO^+ (**7**), especially in greater abundance than $C_2H_2^\alpha H^\gamma O^+$ (**8** or **12**), as observed, appear improbable. However, formation of **7** and **8** through the common intermediate **2** is consistent with the identity (±0.2 eV) found for the appearance potentials of **7** and **8**. Also **1** → **12** is a simple cleavage reaction, and so should be favored over the rearrangement **1** → **2** in decomposition of the higher energy normal ions;[8] the data of Table I are



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(1) (a) Metastable Ion Characteristics. XVI. Paper XV: I. Howe and F. W. McLafferty, *J. Amer. Chem. Soc.*, **92**, 3797 (1970); (b) reported in part at the International Mass Spectroscopy Conference, Kyoto, Japan, Sept 1969, Preprints, p 217.

(2) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 18.

(3) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969), and references therein.

(4) G. Eadon, J. Diekman, and C. Djerassi, *ibid.*, **91**, 3986 (1969); submitted for publication. We are indebted to Professor Djerassi for preprints of these manuscripts.

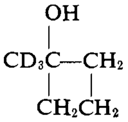
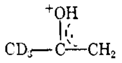
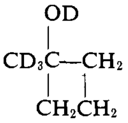
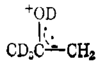
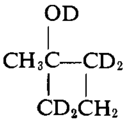
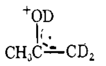
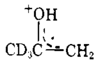
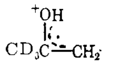
(5) For example, the reactions **6** → **1**[1b,3,4] and **14** → **15** + **17**.[6]

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

(7) The full papers will include data on nine different labeling patterns of enolic $C_3(H,D)_6O^+$ ions and six of $C_4(H,D)_8O^+$ ions. Except where noted, the normal spectra indicated that the isotopic enolic ions were formed in good purity.

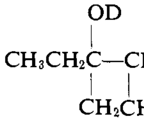
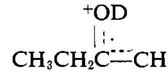
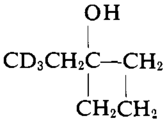
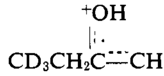
(8) F. W. McLafferty and R. B. Fairweather, *J. Amer. Chem. Soc.*, **90**, 5915 (1968).

Table I. Decomposition of $C_3(H,D)_6O^+$ Ions

Precursor molecule	Ion	Relative metastable[a] (normal)[b] ion abundances			
		$C_2H_3O^+$	$C_2H_2DO^+$	$C_2HD_2O^+$	$C_2D_3O^+$
 $\overset{\mathrm{OH}}{\underset{\mathrm{CH_2CH_2}}{\mathrm{CD_3C{-}CH_2}}}$	 $\overset{+\mathrm{OH}}{\mathrm{CD_3{-}C{\cdots}CH_2}}$	54 ± 4[c] (32)	8 ± 3 (21)	7 ± 3 (20)	100 (100)
 $\overset{\mathrm{OD}}{\underset{\mathrm{CH_2CH_2}}{\mathrm{CD_3C{-}CH_2}}}$	 $\overset{+\mathrm{OD}}{\mathrm{CD_3C{\cdots}CH_2}}$		60 ± 3 (47)	9 ± 2 (21)	100 (100)
 $\overset{\mathrm{OD}}{\underset{\mathrm{CD_2CH_2}}{\mathrm{CH_3C{-}CD_2}}}$	 $\overset{+\mathrm{OD}}{\mathrm{CH_3C{\cdots}CD_2}}$	99 ± 4 (100)	54 ± 4 (67)	62 ± 6 (50)	100 (75)
$CD_3C(=O)C_4H_9$[d]	 $\overset{+\mathrm{OH}}{\mathrm{CD_3C{\cdots}CH_2}}$	54 ± 4	22 ± 3	20 ± 3	100
$CD_3CH_2CH_2C(=O)CD_2C_3H_7$[e]	 $\overset{+\mathrm{OH}}{\mathrm{CD_3C{\cdots}CH_2}}$	54 ± 4	19 ± 3	18 ± 5	100

[a] Determined by the Barber–Elliot–Major defocusing technique. [b] Hydrocarbon species eliminated by high resolution. [c] Error limits indicate the reproducibility of the results. [d] Contained 10–15% $CD_2HC(=O)CHDC_3H_7$ due to α–α' exchange on storage. [e] Contained 10–15% $CD_3CH_2CHDCOCHDC_3H_7$ due to α–α' exchange on storage.

Table II. Decomposition of $C_4(H,D)_8O\cdot^+$ Ions

Precursor molecule	Ion	Relative metastable (normal) ion abundances[a]						
		$C_3H_5O^+$	$C_3H_4DO^+$	$C_3H_3D_2O^+$	$C_3H_2D_3O^+$	$C_2H_3O^+$	$C_2H_2DO^+$	$C_2H_3D_2O^+$
 $\overset{\mathrm{OD}}{\underset{\mathrm{CH_2CH_2}}{\mathrm{CH_3CH_2C{-}CH_2}}}$	 $\overset{+\mathrm{OD}}{\mathrm{CH_3CH_2C{\cdots}CH_2}}$	0.6 ± 0.2 (14)	67 ± 5 (97)			100 (100)	2.1 ± 0.2 (25)	
 $\overset{\mathrm{OH}}{\underset{\mathrm{CH_2CH_2}}{\mathrm{CD_3CH_2C{-}CH_2}}}$	 $\overset{+\mathrm{OH}}{\mathrm{CD_3CH_2C{\cdots}CH_2}}$	0.4 ± 0.2 (<4)	0.8 ± 0.2 (<4)	70 ± 4 (70)	1.0 ± 0.2 (51)	1.2 ± 0.2 (60)	100 (100)	0.8 ± 0.2 (2)

[a] See Table I.

not consistent with this. Furthermore, while a substantial primary isotope effect is observed[9] when H^γ is changed from hydrogen to deuterium, as would be predicted for reaction **1** → **2**, abundances of **7** and **8** *relative to each other* are nearly the same from $CD_3C(OH)CH_2\cdot^+$ and $CD_3C(OD)CH_2\cdot^+$;[10] this is consistent with the existence of identical primary isotope effects for the formation of **7** and **8**, which would be expected if they arise from a common intermediate, but not if a substantial proportion of one is due to **12**.

The data of Table I are not consistent with the intermediacy of **2** in an important way, however; **7** and **8** are *not formed in equal amounts*, after correcting for secondary isotope effects. We propose that this is due to incomplete randomization of internal energy in **2** before decomposition. Immediately after the rearrangement of H^γ to $CH_2{}^\alpha$ in **1** → **2** the $CH_2{}^\alpha H^\gamma$ group should be vibrationally excited; decomposition of **2** is apparently more rapid than the redistribution of this energy. A basic assumption of the quasiequilibrium theory is that the relative rates of competing decompositions of an ion are independent of the method of ion preparation; apparently this is the first exception to this rule which has been reported.[11]

In contrast to our earlier postulation,[12] Djerassi and coworkers[4] find that at least a substantial part of the ions produced by the double hydrogen rearrangement of higher alkanones (**5**) have the enol structure **1**, not that of the oxonium ion **13**. The data of Table I give strong independent confirmation of this;[1b] the identity of the metastable abundances for the $CD_3C(OH)CH_2\cdot^+$ ions produced from **4** and **5** show that no significant amount of the *decomposing* ions have structure **13**.

The postulated decomposition of **1** only through ketonization is in contrast to the published[6] conclusion that the next higher enolic homolog can decompose

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[9] ([7] + [8] + [10] + [11])/[1] = 0.67 ± 0.03 and 0.42 ± 0.02 for H^γ = H and D, respectively; for the corresponding metastables [m*(1 → 7, 8, 10, and 11)]/[1] = 6.7 ± 0.3 × 10^{-3} and 5.2 ± 0.6 × 10^{-3} for H^γ = H and D, respectively.

[10] Note that $C_2H_2DO^+$ from $C_3H_2D_4O\cdot^+$ is composed of both **8** and **10**, and $C_2D_3O^+$ of **7** and **11**.

[11] H. M. Rosenstock, *Advan. Mass Spectrom.*, **4**, 523 (1968); see p 542.

[12] F. W. McLafferty and W. T. Pike, *J. Amer. Chem. Soc.*, **89**, 5953 (1967).

without ketonization through **14** → **15** and **14** → **17**. This prompted us to reexamine the decompositions of deuterated analogs of **14** (Table II).[7] These data indicate that the direct cleavage, **14** → **15**, is not important, but that the loss of the ethyl radical occurs only after rearrangement[13] *and ketonization*, **14** → **16** → **18**. The decompositions of **18** are similar to those of ionized 2-butanone.

It is well established that normal (higher energy) ions of the next higher enolic homolog **6** rearrange specifically to **1** with the transfer of a γ-H atom.[2–4] Metastable ion evidence, such as the formation of $C_4H_7O^+$, $C_3H_6O^+$, and $C_2H_3O^+$ from $CH_3CH_2CH_2C(OD){=}CH_2\cdot^+$, again indicates that ketonization can occur prior to decomposition of these low energy ions; six-membered ring rearrangements are favored over the five- and four-membered analogs. It appears that much of the "scrambling" of H and D atoms observed in the low-energy spectra of ketones[6,14] can be accounted for through similar H transfers to specific active sites.[7,15]

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(13) Note when five-membered ring rearrangements are possible (**14** → **16**, **16** → **18**) that the four-membered analogs (**1** → **2**, **1** → **9**) are almost completely eliminated in the metastable transitions; the latter rearrangements actually become more competitive in the higher energy normal ions in contrast to previous observations that scrambling decreases with increasing ion internal energy.[6,14]

(14) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).

(15) Helpful discussions with S. H. Bauer, R. Kornfeld, I. Howe, and H. D. R. Schuddemage, and the financial support of the Army Research Office, Durham, are gratefully acknowledged.

(16) NIH Predoctoral Fellow, 1969–1970.

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1,6-Sigmatropic Hydrogen Shifts in Pentadienyl Anions. Relative Stabilities of Pentadienyl Anions

Sir:

We wish to report high-yield equilibrations of pentadienyl anions in several systems, and that these reactions are intramolecular, thermal antarafacial, and photochemical suprafacial 1,6-sigmatropic rearrangements in accordance with the Woodward–Hoffmann rules.[1]

In the course of preparing 1,1-dimethylpentadienyllithium (I) from 5-methyl-1,4-pentadiene[2] with *n*-butyllithium in THF–hexane,[3] a partial rearrangement of I to II at 40° was detected by nmr.[4] To confirm the identity of II and to show that equilibrium had been reached, II was synthesized at 20° from 2-methyl-1,4-hexadiene,[5] and on warming to 40° gave a I–II mixture of the same composition. Other equilibrated systems included III–IV–V (approached from III,[6] IV,[7] and V[8]), VI–VII (approached from VI[2] only), and VIII–IX (approached from VIII[2] only). This last case presumably involves three sigmatropic rearrangements to 1-propylheptatrienyl anion, which rapidly electrocyclizes to IX.[9]

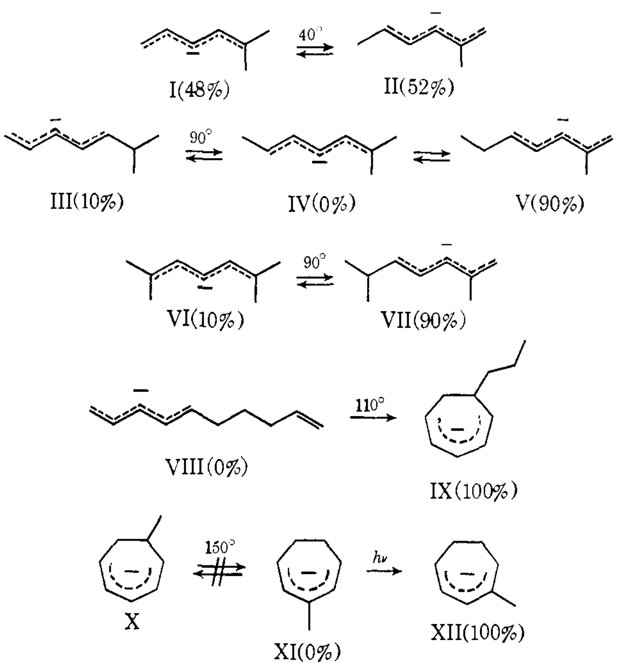

Figure 1. Isomerized pentadienyl anions with equilibrium concentrations in parentheses.

To determine whether these isomerizations are intramolecular, 6-methyl-5-hepten-2-one was pentadeuterated by four exchanges in basic D_2O, converted[7] to 2-methyl-5,7,7,7-tetradeuterio-2,5-heptadiene, and thence to tetradeuterated IV. After heating to 90° for 30 min, the equilibrated anions were protonated. The absence of deuterium scrambling, shown by mass spectrometry, indicated the intramolecularity of the isomerizations. A second test, consisting of heating a 1 : 1 mixture of undeuterated and tetradeuterated IV, also showed no scrambling of deuterium.

If these thermal isomerizations involve concerted 1,6-hydrogen shifts, the Woodward–Hoffmann rules predict that they will occur *antarafacially via* a helical all-cisoid transition state (Figure 2).[1a,b] This cannot be conveniently tested with cyclohexadienyl anions due to their tendency to aromatize,[3] so we employed the cyclo-

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(1) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965). (b) J. Klein, S. Glily, and D. Kost (*J. Org. Chem.*, **35**, 1281 (1970)) have noted migration of the pentadienyl anion system in long aliphatic chains. They suggest without isotopic labeling experiments that the isomerizations are intramolecular, and (incorrectly) that a minimum of 14 carbons in a chain is necessary for reaction. (c) Taken in part from the Ph.D. Theses of D. E. Potter (1969) and W. H. Deines (1970). For a preliminary report, see Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN 144.

(2) Purchased from the Chemical Samples Co.

(3) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(4) For nmr parameters of pentadienyllithiums, see R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *ibid.*, 205 (1967). For anions like II with one alkyl group at the end of the pentadienyl system, the two species differing in the configuration of this alkyl group were generally visible in the nmr; the percentages in Figure 1 include both stereoisomers. The relative amounts of these stereoisomers and the rotation barriers in these pentadienyllithiums will be discussed in a later publication.

(5) Prepared in 20% yield from 5-methyl-5-hexen-3-ol[2] by acetylation, pyrolysis, and preparative glpc, and characterized by nmr and mass spectral analysis. This synthesis gives the cis/trans isomers in a 29/71 ratio; the mixture was used in the preparation of II.

(6) *trans*-6-Methyl-1,4-heptadiene was obtained as the major byproduct in the synthesis of 6,6-dimethyl-1,4-cyclohexadiene[3] from 1,3-cyclohexanedione by the sequence methylation, lithium aluminum hydride reduction, acetylation, acetate pyrolysis, and preparative glpc.

(7) 2-Methyl-2,5-heptadiene was prepared from 6-methyl-5-hepten-2-one by lithium aluminum hydride reduction, acetylation, acetate pyrolysis, and preparative glpc.

(8) IV rearranges quantitatively to V in 4 hr at 35°; on heating further to 90° for 1 hr, the equilibrium mixture of III and V is observed.

(9) (a) R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969); (b) K. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1984 (1969).