ness of the nmr technique to be used as a tool from which to decide such questions,[2] is further illustrated by the opposite conclusions drawn regarding the nature of the barrier to rotation, twofold[8] *vs.* threefold[9,10] about the analogous bond of vinylcyclopropane.

From the similarity between the vicinal coupling constants of cyclopropanecarboxaldehyde and glycidaldehyde, and on the basis of the microwave and electron diffraction results just mentioned, it may be concluded that glycidaldehyde also exhibits a twofold barrier to rotation.

Experimental Section

Phenoxyacetaldehyde,[11] methylmercaptoacetaldehyde,[12] and cyclopropanecarboxaldehyde[13] were prepared according to published procedures. Methoxyacetaldehyde (Jefferson Chemical Co.) and glycidaldehyde (Aldrich Chemical Co.) were commercially available. All compounds were purified either by fractional distillation or by gas chromatography prior to use.

All nmr spectra were determined at 60 Mc on a Model A-60 spectrometer (Varian Associates, Palo Alto, Calif.) equipped with a variable-temperature probe and a V-6040 variable-temperature controller.

Acknowledgment. We thank the National Science Foundation for generous financial support.

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[9] H. Günther and D. Wendisch, *ibid.*, **5**, 251 (1966).

[10] G. R. DeMare and J. S. Martin, *J. Am. Chem. Soc.*, **88**, 5033 (1966).

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Internal Hydrogen Rearrangement as a Function of Ion Lifetime in the Mass Spectra of Aliphatic Ketones

Adrian N. H. Yeo and Dudley H. Williams

Contribution from the University Chemical Laboratory, Cambridge, England.
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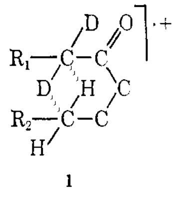
Abstract: From a study of various specifically deuterated aliphatic ketones, it has been shown that internal hydrogen rearrangement (H/D scrambling) occurs at a rate which is slow on the time scale of the mass spectrometer. Single-bond cleavage processes show little evidence of H/D scrambling at 70 eV because the rate of fragmentation is much faster than that of the scrambling processes. On the other hand, fragmentation processes accompanied by rearrangement show signs of H/D scrambling prior to the formation of the fragment ions at 70 eV because such processes occur with *k vs. E* curves that are comparable to those of the scrambling processes. Ions of relatively long lifetimes, such as those decomposing in the first and second field-free regions of the MS-9 double focussing mass spectrometer show extensive H/D scrambling prior to all the various decompositions. The relationship between lifetime and the extent of H/D scrambling requires that great care must be exercised in the interpretation of deuterium-labeling data, particularly when rearrangement processes are implicated.

A recent study[1] of the low electron voltage spectra of deuterated octan-3-one showed that H/D scrambling occurs in the alkyl chain prior to loss of an ethyl radical by α cleavage. The observation that such scrambling is evident only at low electron voltages indicates that the scrambling processes (or process) must be slow relative to the fragmentation processes at 70 eV, but proceed at a comparable (or faster) rate at about 10 eV. This suggests that the scrambling processes have relatively low activation energies (E_0) and low-frequency factors (ν).[2] Any mechanism proposed for such scrambling processes must therefore be consistent with these two factors. Relatively low activation energies are frequently associated with processes in which cyclic transition states, with concerted making and breaking of bonds, are operative. Low-frequency factors are also often associated with rearrangement processes, with transition states in which certain spatial orientations must be attained. These reactions usually have a low probability which is reflected by the low-frequency factor. A transition state of the type **1** might satisfy both the conditions (low E_0, low ν) for the scrambling processes; obviously, various ring sizes for the transition states may be visualized.



1

From consideration of the quasi-equilibrium theory of mass spectra in its original and simplest from,[3] the rate constant, k, of any process occurring in an ion with internal energy E is given to a first approximation, by the equation

$$k = \nu\left(\frac{E - E_0}{E}\right)^{s-1} \qquad (1)$$

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

[2] R. G. Cooks and D. H. Williams, *Chem. Commun.*, 663 (1968); see also S. Meyerson, *Appl. Spectry.*, 22, 30 (1968); B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, 3, 1 (1964).

[3] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **38**, 667 (1952). For a recent review, see H. M. Rosenstock in "Advances in Mass Spectrometry," Vol. 4, E. Kendrick, Ed., the Institute of Petroleum, London, 1968, p 523.

where ν is the frequency factor of the process, E_0 is the activation energy, and s is the effective number of oscillators in the ion. For the scrambling processes, with both ν and E_0 relatively small, the equation would give a log k *vs.* E curve in which there is a relatively slow rise of k with E (such as k_s in Figure 1). On the other hand, a single-bond cleavage process, with ν and E_0 relatively large, would in general (but not necessarily always) have a fast rise of k with E as in k_f (Figure 1), so that the curves k_s and k_f would intersect for some value of E. A fragmentation process accompanied by rearrangement, if it also had a relatively low-frequency factor and a low activation energy, would give rise to a curve k_r similar in shape to that of the scrambling process k_s. Whether an intersection occurs between k_s and k_r will depend on the relative values of $(E_0)_s$ and $(E_0)_r$, and ν_s and ν_r.

As the internal energy, E, tends to infinity, k tends to the frequency factor. The relatively low-frequency factor of the scrambling process imposes an upper limit to the rate at which the scrambling process can go regardless of the internal energy of the ion. On the other hand, the single-bond cleavage process has a relatively high-frequency factor so that for ions with high internal energies, the fragmentation process goes much faster than the scrambling process as indicated in Figure 1. No scrambling is therefore observed in ions formed from single-bond cleavages at high electron voltage. However, for fragmentation processes involving extensive rearrangement such as is necessary in the "McLafferty + 1"[1,4] and the "γ-cleavage + 1" rearrangements, it may be possible, even at 70 eV, to observe scrambling (although to only a slight extent) in the daughter ions, depending on the relative values of ν_r and ν_s. At low electron voltage, where ions have low internal energies and hence longer lifetimes, scrambling may be observed even in ions formed by single-bond cleavage processes, provided that E_0 is higher for this cleavage than for the internal scrambling process. Near the threshold, the rate of any process is highly dependent on the activation energy E_0.

Results

On the basis of the above plausible generalizations it was felt that extensive H/D scrambling might be evident in the mass spectra of specifically deuterated aliphatic ketones, particularly in the ions decomposing in the first and second field-free regions, and hence giving rise to "metastable peaks" (such ions have relatively low internal energies). The labeled ketones 2–7 were therefore synthesized by base-catalyzed exchanges of the ketones with deuterium oxide. The detailed analyses of their mass spectra are summarized in Tables II–XVI. In Table I, the appearance potentials of some fragment ions of interest are given for three representative ketones.

Discussion

The object of the investigation was to determine the extent of H/D scrambling both in ions of relatively long lifetimes (>10^{-6} sec) as well as ions of relatively short lifetimes (<10^{-6} sec), and therefore processes which give "metastable peaks" in the second field-free region of the AEI MS-9 mass spectrometer have been selected. Such processes can be examined when occurring after about 10–15 μsec.[5] Ions with lifetimes in the order of 5–10 μsec, decomposing in the first field-free region of the mass spectrometer, were studied

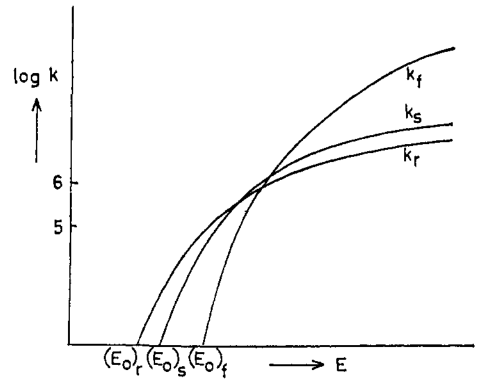
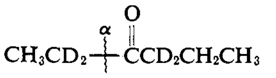


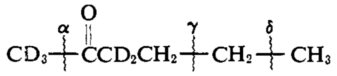
Figure 1. Schematic curves showing the rise of log k with E for hypothetical fragmentation (k_f), fragmentation accompanied by rearrangement (k_r), and H/D scrambling processes (k_s).

Table I. The Appearance Potentials of Fragment Ions of Some Aliphatic Ketones

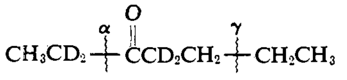
Ketone	Process	*m/e*	AP, eV
Hexan-3-one	$M^+ \rightarrow M^+ - C_2H_5$	71	10.6
	McLafferty rearrangement	72	10.2
Heptan-3-one	$M^+ \rightarrow M^+ - C_2H_5$	85	10.8
	McLafferty rearrangement	72	10.3
Octan-3-one	$M^+ \rightarrow M^+ - C_2H_5$	99	10.2
	McLafferty rearrangement	72	10.5
	"McLafferty + 1" rearrangement	73	9.8
	$M^+ \rightarrow (M^+ - C_2H_5) - CO$	71	11.5
	"γ cleavage"	85	10.9
	"γ cleavage + 1" rearrangement	86	10.4
	$M^+ \rightarrow M^+ - C_5H_{11}$	57	12.0


$CH_3CD_2\overset{\alpha}{|}\overset{O}{\overset{\|}{C}}CD_2CH_2CH_3$

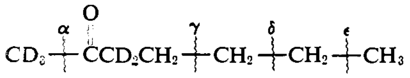
2


$CD_3\overset{\alpha}{|}\overset{O}{\overset{\|}{C}}CD_2CH_2\overset{\gamma}{|}CH_2\overset{\delta}{|}CH_3$

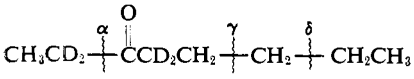
5


$CH_3CD_2\overset{\alpha}{|}\overset{O}{\overset{\|}{C}}CD_2CH_2\overset{\gamma}{|}CH_2CH_3$

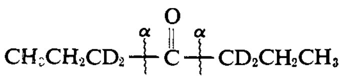
3


$CD_3\overset{\alpha}{|}\overset{O}{\overset{\|}{C}}CD_2CH_2\overset{\gamma}{|}CH_2\overset{\delta}{|}CH_2\overset{\epsilon}{|}CH_3$

6


$CH_3CD_2\overset{\alpha}{|}\overset{O}{\overset{\|}{C}}CD_2CH_2\overset{\gamma}{|}CH_2\overset{\delta}{|}CH_2CH_3$

4


$CH_3CH_2CD_2\overset{\alpha}{|}\overset{O}{\overset{\|}{C}}\overset{\alpha}{|}CD_2CH_2CH_3$

7

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(4) G. Spiteller, "Massenspektrometrische Strukturanalyse Organischer Verbindungen," Verlag Chemie, Weinheim, 1966, p 129.

(5) I. Howe and D. H. Williams, *Chem. Commun.*, 220 (1968).

with the aid of a "metastable defocusser."[6] It may be seen from the data in Tables II–XVI that the generalizations made in the introductory section appear to hold. The detail discussions are classified as given.

Table II.[a] Peak Distributions Showing the Loss of Ethyl and Ethylene from d_0- and d_4-Hexan-3-one

	Transition								
	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$	$M^+ - 27$	$M^+ - 32$	$M^+ - 31$	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$
	m/e								
	70	71	72	73	72	73	74	75	76
	Hexan-3-one (*MW* = 100)				2,2,4,4-d_4-Hexan-3-one (*MW* = 104)				
70 eV	0	95	5	0	0	95	0	0	5
10 eV	0	88	12	0	0	71	6	10	13
^{1}m* (70 eV)	0	33	67	0	0	18	23	43	16
^{2}m* (70 eV)	0	23	77	0	0	16	24	44	16

[a] The total intensity of all the peaks in the group is normalized to 100 in Tables II–XVI. Intensities of less than 2% are not given. Correction for ^{13}C isotopes as well as d_3 contributions has been made. The 10 eV is nominal only. Spectra of undeuterated ketones are given for direct comparison.

Table III. Peak Distributions Showing the Loss of Ethyl from d_0- and d_4-Heptan-3-one

	Transition						
	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$	$M^+ - 32$	$M^+ - 31$	$M^+ - 30$	$M^+ - 29$
	m/e						
	84	85	86	86	87	88	89
	Heptan-3-one (*MW* = 114)			2,2,4,4-d_4-Heptan-3-one (*MW* = 118)			
70 eV	0	100	0	0	100	0	0
10 eV	0	100	0	0	76	24	0
^{1}m* (70 eV)	0	100	0	0	26	55	19
^{2}m* (70 eV)	0	100	0	0	16	52	32

Table IV. Peak Distributions Showing the Loss of Propylene from d_0- and d_4-Heptan-3-one by the McLafferty Rearrangement

	Transition								
	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$	$M^+ - 46$	$M^+ - 45$	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$
	m/e								
	71	72	73	72	73	74	75	76	77
	Heptan-3-one (*MW* = 114)			2,2,4,4-d_4-Heptan-3-one (*MW* = 118)					
70 eV	0	100	0	0	0	0	11	89	0
10 eV	0	100	0	0	0	7	44	49	0
^{1}m* (70 eV)	0	100	0	0	3	9	50	38	0
^{2}m* (70 eV)	0	100	0	2	18	26	34	20	0

Table V. Peak Distributions Showing the Loss of Ethyl from d_0- and d_4-Octan-3-one

	Transition						
	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$	$M^+ - 32$	$M^+ - 31$	$M^+ - 30$	$M^+ - 29$
	m/e						
	98	99	100	100	101	102	103
	Octan-3-one (*MW* = 128)			2,2,4,4-d_4-Octan-3-one (*MW* = 132)			
70 eV	0	100	0	0	94	6	0
10 eV	0	100	0	0	40	40	20
^{1}m* (70 eV)	0	100	0	0	24	53	23
^{2}m* (70 eV)	0	100	0	0	20	53	27

Table VI. Peak Distributions Showing the Loss of C_4H_8 and C_4H_7 from d_0- and d_4-Octan-3-one by the McLafferty and "McLafferty + 1" Rearrangements

	Transition									
	$M^+ - 57$	$M^+ - 56$	$M^+ - 55$	$M^+ - 54$	$M^+ - 59$	$M^+ - 58$	$M^+ - 57$	$M^+ - 56$	$M^+ - 55$	$M^+ - 54$
	m/e									
	71	72	73	74	73	74	75	76	77	78
	Octan-3-one (*MW* = 128)				2,2,4,4-d_4-Octan-3-one (*MW* = 132)					
70 eV	0[a]	94	6	0	0[b]	0	7	87	6	0
10 eV	0	81	19	0	0	8	37	52	3	0
^{1}m* (70 eV)	0	57	43	0	10	26	32	24	8	0
^{2}m* (70 eV)	0	42	58	0	*c*	*c*	*c*	*c*	*c*	*c*

[a] A peak due to $[(M - CH_3CH_2) - CO]$ is not included. [b] A peak due to $[(M - CH_3CD_2) - CO]$ is not included. [c] Intensity too low to permit accurate measurement.

Table VII. Peak Distributions Showing the Loss of Propyl and Propylene from d_0- and d_4-Octan-3-one by γ-Cleavage and "γ-Cleavage + 1" Processes

	Transition									
	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$	$M^+ - 46$	$M^+ - 45$	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$
	m/e									
	84	85	86	87	86	87	88	89	90	91
	Octan-3-one (*MW* = 128)				2,2,4,4-d_4-Octan-3-one (*MW* = 132)					
70 eV	0	82	18	0	0	23	47	28	2	0
10 eV	0	8	92	0	0	24	46	22	8	0
^{1}m* (70 eV)	0	0	100	0	0	46	39	13	2	0
^{2}m* (70 eV)	0	0	100	0	0	31	52	17[a]	0	0

[a] Estimated value; ^{2}m* under *m/e* 60.0.

Table VIII. Peak Distribution Showing the Loss of Methyl from d_0- and d_4-Hexan-2-one

	Transition						
	$M^+ - 16$	$M^+ - 15$	$M^+ - 14$	$M^+ - 18$	$M^+ - 17$	$M^+ - 16$	$M^+ - 15$
	m/e						
	84	85	86	87	88	89	100
	Hexan-2-one (*MW* = 100)			1,1,1,3,3-d_5-Hexan-2-one (*MW* = 105)			
70 eV	0	100	0	72	0	4	24
10 eV	0	100	0	12	5	12	71
^{1}m* (70 eV)	0	100	0	0	7	22	71
^{2}m* (70 eV)	0	100	0	0	9	27	64

A. α Cleavage. The 70-eV mass spectrum of hexan-3-one shows a large peak at *m/e* 71 for the loss of an ethyl radical by α cleavage and a relatively small peak at *m/e* 72 (5% of *m/e* 71) for the loss of ethylene by the McLafferty rearrangement (Table II). The single-bond cleavage process (α cleavage) has a higher acti-

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(6) (a) M. Barber and R. M. Elliot, ASTM E-14 Conference on Mass Spectrometry, Montreal, June 1964; (b) J. H. Futrell, K. R. Ryan, and L. W. Sieck, *J. Chem. Phys.*, **43**, 1832 (1965); (c) K. R. Jennings, *ibid.*, 43, 4176 (1965); (d) K. R. Jennings in "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davies, Ed., United Trade Press, London, 1967, p 105; (e) T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).

Table IX. Peak Distributions Showing the Loss of C_3H_6 and C_3H_5 from d_0- and d_4-Hexan-2-one by the McLafferty and "McLafferty + 1" Rearrangements

	Transition									
	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$	$M^+ - 47$	$M^+ - 46$	$M^+ - 45$	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$
	m/e									
	57	58	59	58	59	60	61	62	63	64
	Hexan-2-one ($MW = 100$)			1,1,1,3,3-d_5-Hexan-2-one ($MW = 105$)						
70 eV	0[a]	100	0	0	0[b]	0	0	8	92	0
10 eV	0	94	6	0	0	0	0	12	88	0
$^1m^*$ (70 eV)	0	82	18	0	5	15	26	27	22	5
$^2m^*$ (70 eV)	0	65	35	*c*	*c*	*c*	*c*	*c*	*c*	*c*

[a] A peak due to [(M − CH_3) − CO] is not included. [b] A peak due to [(M − CD_3) − CO] is not included. [c] Intensity too low to permit accurate measurement.

Table X. Peak Distributions Showing the Loss of Ethyl and Ethylene from d_0- and d_4-Hexan-2-one by the γ-Cleavage and the "γ-Cleavage + 1" Processes

	Transition								
	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$	$M^+ - 27$	$M^+ - 32$	$M^+ - 31$	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$
	m/e								
	70	71	72	73	73	74	75	76	77
	Hexan-2-one ($MW = 100$)				1,1,1,3,3-Hexan-2-one ($MW = 105$)				
70 eV	0	88	12	0	0	5	21	74	0
10 eV	0	50	50	0	0	19	45	30	6
$^1m^*$ (70 eV)	0	30	70	0	2	23	43	27	5
$^2m^*$ (70 eV)	0	25	75	0	2	25	43	19[a]	11

[a] Estimated value; $^2m^*$ under *m/e* 55.0.

Table XI. Peak Distributions Showing the Loss of Methyl from d_0- and d_4-Heptan-2-one

	Transition							
	$M^+ - 16$	$M^+ - 15$	$M^+ - 14$	$M^+ - 19$	$M^+ - 18$	$M^+ - 17$	$M^+ - 16$	$M^+ - 15$
	m/e							
	98	99	100	100	101	102	103	104
	Heptan-2-one ($MW = 114$)			1,1,1,3,3-d_5-Heptan-2-one ($MW = 119$)				
70 eV	0	100	0	0	94	6	0	0
10 eV	0	100	0	0	83	17	0	0
$^1m^*$ (70 eV)	0	100	0	0	52	37	11	0
$^2m^*$ (70 eV)	0	100[a]	0	0	34	42	24	0[b]

[a] $^2m^*$ under *m/e* 86.0. [b] Small $^2m^*$ peak at *m/e* 90.9 difficult to estimate.

Table XII. Peak Distributions Showing the Loss of C_4H_8 and C_4H_7 from d_0- and d_4-Heptan-2-one by the McLafferty and "McLafferty + 1" Rearrangements

	Transition										
	$M^+ - 57$	$M^+ - 56$	$M^+ - 55$	$M^+ - 54$	$M^+ - 60$	$M^+ - 59$	$M^+ - 58$	$M^+ - 57$	$M^+ - 56$	$M^+ - 55$	$M^+ - 54$
	m/e										
	57	58	59	60	59	60	61	62	63	64	65
	Heptan-2-one ($MW = 114$)				1,1,1,3,3-d_5-Heptan-2-one ($MW = 119$)						
70 eV	0	87	13	0	0	0	0	0	92	8	0
10 eV	0	61	39	0	0	0	0	4	65	31	0
$^1m^*$ (70 eV)	0	29	71	0	0[a]	11	24	36	23	6	0
$^2m^*$ (70 eV)	0	23	77	0	*b*	*b*	*b*	*b*	*b*	*b*	*b*

[a] Not measurable on our metastable defocusser because parent/daughter ratio >2. [b] $^2m^*$ present in the same mass region as intense $^2m^*$ for other processes such as 63 → 45 and 63 → 46.

Table XIII. Peak Distributions Showing the Loss of Propyl and Propylene from d_0- and d_4-Heptan-2-one by the γ-Cleavage and "γ-Cleavage + 1" Processes

	Transition								
	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$	$M^+ - 41$	$M^+ - 46$	$M^+ - 45$	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$
	m/e								
	70	71	72	73	73	74	75	76	77
	Heptan-2-one ($MW = 114$)				1,1,1,3,3-d_5-Heptan-2-one ($MW = 119$)				
70 eV	0	91	9	0	28[a]	9	36	27	0
10 eV	0	50	50	0	13[a]	16	55	16	0
$^1m^*$ (70 eV)	0	0	100	0	0	15	43	33	19
$^2m^*$ (70 eV)	0	0	100	0	*b*	*b*	*b*	*b*	*b*

[a] Contribution from [(M − CD_3) − CO] is included. [b] Intensity too low to permit accurate measurement.

Table XIV. Peak Distributions Showing the Loss of Ethyl and Ethylene from d_0- and d_4-Heptan-2-one by the δ-Cleavage and "δ-Cleavage + 1" Processes

	Transition							
	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$	$M^+ - 32$	$M^+ - 31$	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$
	m/e							
	84	85	86	87	88	89	90	91
	Heptan-2-one ($MW = 114$)			1,1,1,3,3-d_5-Heptan-2-one ($MW = 119$)				
70 eV	0	89	11	0	21	22	54	3
10 eV	0	85	15	0	18	23	55	4
$^1m^*$ (70 eV)	0	83	17	0	23	34	39	4
$^2m^*$ (70 eV)	0	100	*a*	0	28	38	34	0

[a] $^2m^*$ under *m/e* 65.0 difficult to estimate.

Table XV. Peak Distributions Showing the Loss of Propyl from d_0- and d_4-Heptan-4-one

	Transition							
	$M^+ - 44$	$M^+ - 43$	$M^+ - 42$	$M^+ - 47$	$M^+ - 46$	$M^+ - 45$	$M^+ - 44$	$M^+ - 43$
	m/e							
	70	71	72	71	72	73	74	75
	Heptan-4-one ($MW = 114$)			3,3,5,5-d_4-Heptan-4-one ($MW = 118$)				
70 eV	0	100	0	0	0	100	0	0
10 eV	0	100	0	0	8	86	6	0
$^1m^*$ (70 eV)	0	100	0	0	19	54	22	5
$^2m^*$ (70 eV)	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*

[a] Intensity too low to be detected. [b] Intensity too low to be detected.

Table XVI. Peak Distributions Showing the Loss of Ethylene from d_0- and d_4-Heptan-4-one by the McLafferty Rearrangement

	Transition							
	$M^+ - 29$	$M^+ - 28$	$M^+ - 27$	$M^+ - 31$	$M^+ - 30$	$M^+ - 29$	$M^+ - 28$	$M^+ - 27$
	m/e							
	85	86	87	87	88	89	90	91
	Heptan-4-one ($MW = 114$)			3,3,5,5-d_4-Heptan-4-one ($MW = 118$)				
70 eV	11[a]	89	0	0	0	17	83	0
10 eV	0	100	0	0	0	17	83	0
$^1m^*$ (70 eV)	0	100	0	0	3	39	58	0
$^2m^*$ (70 eV)	0	100	0	0	6	43	51	0

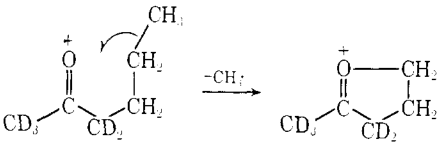
[a] Origin of peak uncertain; probably from β cleavage.

vation energy E_0 (see Table I) but a higher frequency factor than the rearrangement process, and hence it is understandable that at 70 eV it gives the larger peak (see Figure 1). At a nominal 10 eV,[7] the loss of C_2H_4 increases in importance relative to the loss of C_2H_5. In addition, in ions of even lower internal energies and hence longer lifetimes, such as those decomposing in the first and second field-free regions,[8] the loss of C_2H_4 is more important than the loss of C_2H_5. The ratios for $[M^+ - C_2H_4]/[M^+ - C_2H_5]$ are 2:1 and 3.3:1 for the two field-free regions, respectively (Table II).

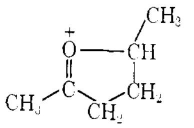
In the 70-eV mass spectrum of 2,2,4,4-d_4-hexan-3-one (**2**), the loss of the ethyl radical by α cleavage and the loss of ethylene by the McLafferty rearrangement give rise to peaks at *m/e* 73 and 76, respectively, in the same ratio as in the undeuterated compound. However, at 10 eV, this loss of CH_3CD_2 (31 mass units) and C_2H_4 (28 mass units) is accompanied by the loss of 30 and 29 mass units (Table II). These must be due to the loss of CH_3CHD or $C_2H_2D_2$ (or a combination of both) and CH_3CH_2 or C_2H_3D (or a combination of both), indicating that the deuteriums from the α positions have scrambled to the β- and/or γ-carbon atoms of the propyl chain, since the loss of ethylene by the McLafferty rearrangement involves only the loss of these carbon atoms.[9] Ions of longer lifetimes giving rise to ^{1}m* and ^{2}m* peaks show progressively greater loss of 29 and 30 mass units indicating greater degrees of internal hydrogen rearrangement prior to fragmentation (Table II). It is of course true that lifetimes weighted in spectra obtained at a nominal 10 eV will also be weighted in 70-eV spectra. However, since the nominal 10 eV is very near threshold for the reactions under consideration, the ion abundances need only be 10^{-2} or of 10^{-3} of the intensities in 70-eV spectra (*cf.* typical ionization efficiency curves). Hence, if fast reactions occurring in the source preceded hydrogen scrambling, it is perfectly understandable that $M^+ - 30$ and $M^+ - 31$ intensities are negligible relative to $M^+ - CD_2CH_3$ and $M^+ - C_2H_4$ intensities in the 70-eV spectrum of 2,2,4,4-d_4-hexan-3-one (Table II).

Heptan-3-one and octan-3-one both exhibit also the loss of an ethyl radical from the molecular ion by α cleavage. In these compounds, the loss of an ethyl radical can also occur *via* γ cleavage[10] and δ cleavage, respectively (see **3** and **4**). In the 70-eV spectra, there is no significant contribution from the γ and δ cleavages since there is no peak for the loss of 29 mass units in the spectra of the corresponding 2,2,4,4-d_4 analogs of these compounds, **3** and **4** (see Tables III and V). For ions of longer lifetimes (especially those giving rise to ^{1}m* and ^{2}m* peaks), where such γ and δ cleavages are usually of importance (*vide infra*), it is not possible o estimate their contribution to the loss of ethyl because the loss of ethyl from these ions of low internal energies for compounds **3** and **4** is preceded by extensive H/D randomization (Tables III and V). As in the case of 2,2,4,4-d_4-hexan-3-one (**2**), both 2,2,4,4-d_4-heptan-3-one (**3**) and 2,2,4,4-d_4-octan-3-one[11] (**4**) lose CH_3CD_2 with a high degree of specificity at 70 eV.[11]

In the spectrum of hexan-2-one, the loss of a methyl radical has been attributed to a simple α cleavage at both 70 and 10 eV.[12] The 70-eV spectrum of 1,1,1,3,3-d_5-hexan-2-one (**5**) shows, in addition to the expected loss of 18 mass units (CD_3), the loss of 15 (CH_3) and 16 (CH_2D) mass units from the molecular ion. The ratio of $M^+ - CD_3 : M^+ - CD_2H : M^+ - CDH_2 : M^+ - CH_3$ is 18:0:1:6 (Table VIII). It is interesting to note that while δ cleavage contributes only about one-third to the M^+ − methyl peak in the 70-eV hexan-3-one spectrum, it is the dominant cleavage at 10 eV, far more important than the α cleavage. Indeed, for decompositions in the field-free regions, no α cleavage (as evidenced by the total absence of $M^+ - CD_3$) is detected (Table VIII). The δ cleavage must have a lower activation energy and lower frequency factor than the α cleavage, assuming that these are competing unimolecular reactions. It is unlikely therefore that this δ-cleavage process involves just the simple cleavage of the δ bond, as the name implies; on the contrary this process probably involves a rearrangement and the transition **5** → **8** represents an attractive possibility. This formulation is strongly supported by the observed cyclization of hex-5-en-2-one to the 2,5-dimethyl-1-oxoniacyclopent-1-enyl cation **9** in sulfuric acid.[13] It is therefore not surprising (given the relatively low activation energy and assumed low-frequency factor of the δ cleavage), that a slight degree of H/D scrambling is observed prior to the formation of the δ-cleavage daughter ions in the source at 70 eV (Table VIII). Scrambling is, as expected, progressively more pronounced in the ions giving rise to ^{1}m* and ^{2}m* peaks (Table VIII).



5 **8**



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In 1,1,1,3,3-d_5-heptan-2-one (**6**), the loss of CD_3 by α cleavage is not accompanied by the loss of CH_3 either in the 70-eV spectrum or the ^{1}m* spectrum, *i.e.*, ϵ cleavage does not occur in this compound. The peak at *m/e* 102 is slightly bigger than is expected from ${}^{13}C$ contribution and probably arises from the loss of CD_2H after some H/D scrambling (Table XI; *cf.* also the loss of ethyl from 2,2,4,4-d_4-octan-3-one (**4**), Table V). Increase in H/D scrambling is observed, as expected, in ions of low internal energies such as those in the 10-eV, ^{1}m*, and ^{2}m* spectra (Table XI).

3,3,5,5-d_4-Heptan-4-one exhibits specific loss of $CH_3CH_2CD_2$ by α cleavage at 70 eV, and loss of C_3H_6D, $C_3H_5D_2$, $C_3H_4D_3$, and $C_3H_3D_4$ in the first field-free region (Table XV). The loss of almost equal amounts of C_3H_6D and $C_3H_4D_3$ (Table XV) in the 10-eV and ^{1}m* spectra shows that the two α cleavages are almost

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[7] All low electron voltages given in this paper are nominal only.

[8] The "metastable peaks" arising from decompositions in the first and in the second field-free regions are referred to as ^{1}m* and ^{2}m* respectively, in the tables as well as in the Discussion.

[9] See, for example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 155.

[10] Reference 9, p 138.

[11] The peak at *m/e* 102 ($M - C_2H_4D$, 7% of *m/e* 101, $M - C_2H_3D_2$, Table V) for the loss of 30 mass units from the molecular ion of 2,2,4,4-d_4-octan-3-one (**4**) indicates a small contribution to the daughter ion abundance from molecular ions of relatively long lifetimes even at 70 eV.

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

[13] C. U. Pittman, Jr., and S. P. McManus, *Chem. Commun.*, 1479 (1968).

equally favored (*i.e.*, after internal H/D rearrangement which renders the deuterium distribution between the two propyl chains unequal, no significant secondary isotope effect favors loss of one propyl group over the other). Ions undergoing decomposition in the second field-free region are of too low an abundance to be detected even at very high multiplier gain.

B. The McLafferty and "McLafferty + 1" [1] **Rearrangements.** The H/D scrambling in the McLafferty rearrangement in 2,2,4,4-d_4-hexan-3-one (**2**) has already been considered together with α cleavage in section A.

At 70 eV, 2,2,4,4-d_4-heptan-3-one (**3**) loses predominantly C_3H_6 from the molecular ion by the McLafferty rearrangement, giving rise to a peak at *m/e* 76. In addition, a small peak present at *m/e* 75 indicates the loss of C_3H_5D. At 10 eV, loss of $C_3H_4D_2$ is also observed and in ions decomposing in the first field-free region, the loss of $C_3H_3D_3$ is detected. It is even possible to observe a small "metastable peak" for the loss of $C_3H_2D_4$ for the molecular ion decomposing in the second field-free region (Table IV).[14] The sampling of ions of progressively longer lifetimes shows clearly the corresponding progressive increase in H/D scrambling.

Octan-3-one gives at 70 eV a small peak at *m/e* 73 in addition to the familiar peak at *m/e* 72 due to the McLafferty rearrangement. This "McLafferty + 1" rearrangement process has a lower activation energy than the McLafferty rearrangement (see Table I), and is dominant in ions of relatively long lifetimes. The ^{2}m* peak for the process $M^+ \rightarrow$ *m/e* 73 is greater than the corresponding peak for the process $M^+ \rightarrow$ *m/e* 72 (58:42, Table VI). Slight H/D scrambling is observed for 2,2,4,4-d_4-octan-3-one (**4**) in the 70-eV daughter peaks due to the McLafferty and "McLafferty + 1" rearrangements. In ions of longer lifetimes, progressive increase in internal hydrogen rearrangement is encountered (Table VI).

Hexan-2-one also exhibits both the McLafferty and the "McLafferty + 1" rearrangements (Table IX), in contrast to heptan-3-one which exhibits only the McLafferty rearrangement (Table IV). The "McLafferty + 1" rearrangement in hexan-2-one is only important for ions of relatively low internal energies and long lifetimes (Table IX). 1,1,1,3,3-d_5-Hexan-2-one (**5**) loses C_3H_5D as well as C_3H_6 at 70 eV in the McLafferty rearrangement. Extensive H/D scrambling is again evident in ions of low internal energies such as those giving rise to ^{1}m* peaks. It is, unfortunately, not possible to measure the relative abundances of the ^{2}m* peaks because of their low intensities. The low intensity of the ^{2}m* peaks reflects the scrambling in that the total ^{2}m* intensity is smeared out among five or six ^{2}m* peaks.

Heptan-2-one loses both C_4H_8 and C_4H_7 by the McLafferty and the "McLafferty + 1" rearrangements at 70 eV, as does octan-3-one. In the ^{2}m* spectrum of heptan-2-one, the "McLafferty + 1" rearrangement gives a peak about 3.3 times that due to the McLafferty rearrangment (Table XII). It appears from comparison of hexan-2-one and heptan-3-one, and heptan-2-one and octan-3-one (Tables IX and IV, and XII and VI), that the methyl ketones have a greater tendency to give "McLafferty + 1" rearrangement than the ethyl ketones for an alkyl chain, R, of a given length in $RCOCH_3$ and $RCOC_2H_5$. As with the other deuterated ketones giving these rearrangements, 1,1,1,3,3-d_5-heptan-2-one (**6**) shows slight H/D scrambling when 70-eV daughter peaks are considered, and extensive scrambling when ions of relatively long lifetimes (^{1}m* peaks) are considered (Table XII). The relative abundances of the ^{2}m* peaks are not measurable, owing to the interference of other processes giving rise to ^{2}m* peaks in the same mass region.

Heptan-4-one loses ethylene by the McLafferty rearrangement in the 70-eV, 10-eV, ^{1}m*, and ^{2}m* spectra. However at 70 eV, there is a small peak for the loss of 29 mass units, the origin of which is uncertain.[15] This process has a relatively high activation energy since the M − 29 peak is not detected at all in the 10 eV, ^{1}m*, and ^{2}m* spectra. 3,3,5,5-d_4-Heptan-4-one undergoes the McLafferty rearrangement with loss of C_2H_4 and a small amount of C_2H_3D at 70 eV. More extensive H/D scrambling occurs prior to the rearrangement when ions of longer lifetimes (^{1}m* and ^{2}m* peaks) are sampled. These show greater loss of C_2H_3D and $C_2H_2D_2$ (Table XVI).

C. The γ-Cleavage and "γ-Cleavage + 1" Processes. In the three ketones, octan-3-one, hexan-2-one, and heptan-2-one, where γ cleavage can be observed, there is always a peak one mass unit higher than the γ-cleavage peak, though it is less intense than the γ-cleavage peak at 70 eV (Tables VII, X, and XIII). The intensity of this peak increases very rapidly relatively to that of the γ-cleavage peak for ions of longer lifetimes. For octan-3-one and heptan-2-one, the γ-cleavage process is not observed at all when ions decomposing in the first and second field-free region are sampled (Tables VII and XIII), while for hexan-2-one the "γ-cleavage + 1" process gives a peak three times as intense as that due to the γ-cleavage process in the second field-free region. These observations are consistent with the fact that "γ-cleavage + 1" reaction is a rearrangement process having a lower activation energy (see Table I) than the γ-cleavage process. The γ-cleavage process has been suggested to involve a rearrangement process giving a rearranged four-membered cyclic oxonium ion.[10] While the present observations do not give any strong support to such a formulation, they do not preclude it. Attempts made to determine the site specificity of the "γ-cleavage + 1" process for various deuterated octan-3-ones were unsuccessful;[1] a plausible pathway for the rearrangement was nevertheless suggested. Also, from a 70-eV study of various deuterated octan-2-ones it was shown that in the γ-cleavage process, some deuterium originating from the 5, 6, and 7 positions was found in the γ-cleavage ion, although the γ-cleavage ion contains only carbons 1, 2, 3, and 4 of the original molecule. Deuteriums originating from the 1 and 3 positions were also partially lost. A mechanistic rationalization invoking a reciprocal hydrogen transfer process for the formation of some of γ-cleavage ions was given.[1] It seems from our results that the processes considered (*i.e.*, γ-cleavage and "γ-cleavage + 1") have relatively low-activation energies and low-frequency factors and

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(14) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968).

(15) The possibility of a β cleavage cannot be ruled out, particularly in the light of the relatively high activation energy of this process.

Table XVII. Comparison of the Calculated and Observed Peak Distributions for the Loss of Ethyl and Ethylene from 2,2,4,4-d_4-Hexan-3-one (**2**)

	Calcd, %		
m/e	No randomization	Complete randomization	Obsd, % ^{2}m*
76	77	10.8	16
75		36.5	44
74		34.3	24
73	23	14.7	16
72		3.5	0
71		0.2	0

Table XVIII. Comparison of the Calculated and Observed Peak Distributions for the Loss of Ethyl from 2,2,4,4-d_4-Heptan-3-one (**3**)

	Calcd, %		Obsd, %	
m/e	No randomization	Complete randomization	^{1}m*	^{2}m*
89		12.5	19	32
88		42.0	55	52
87	100	36.0	26	16
86		9.0	0	0
85		0.5	0	0

Table XIX. Comparison of the Calculated and Observed Peak Distributions for the Loss of Propylene from 2,2,4,4-d_4-Heptan-3-one (**3**)

	Calcd, %		Obsd, %	
m/e	No randomization	Complete randomization	^{1}m*	^{2}m*
76	100	7.0	38	20
75		33.4	50	34
74		42.0	9	26
73		16.0	3	18
72		1.5	0	2

Table XX. Comparison of the Calculated and Observed Peak Distributions for the Loss of Ethyl from 2,2,4,4-d_4-Octan-3-one (**4**)

	Calcd, %		Obsd, %	
m/e	No randomization	Complete randomization	^{1}m*	^{2}m*
103		18.2	23	27
102		45.2	53	53
101	100	30.2	24	20
100		6.2	0	0
99		0.2	0	0

Table XXI. Comparison of the Calculated and Observed Peak Distributions for the Loss of C_4H_8 and C_4H_7 and Deuterated Analogs from 2,2,4,4-d_4-Octan-3-one (**4**)

	Calcd, %		
m/e	No randomization	Complete randomization	Obsd, % ^{1}m*
77	43.0	3.0	8
76	57.0	16.4	24
75		31.7	32
74		31.9	26
73		23.9	10
72		2.2	0

Table XXII. Comparison of the Calculated and Observed Peak Distributions for the Loss of Propylene from 2,2,4,4-Octan-3-one (**4**)

	Calcd, %		Obsd, %	
m/e	No randomization	Complete randomization	^{1}m*	^{2}m*
90	100	11.5	2	0
89		39.6	13	17
88		37.1	39	52
87		11.0	46	31
86		0.8	0	0

hence ions of relatively long lifetimes are involved even in the 70-eV spectra. Extensive H/D scrambling is therefore expected prior to fragmentation in all ions undergoing these processes. This is borne out by the results (Tables VII, X, and XIII). It is therefore not possible to determine the site specificity of these processes in conventional instruments, since the fragment ions always come from molecular ions of relatively long lifetimes.

D. The δ-Cleavage and "δ-Cleavage + 1" Processes. The δ-cleavage process occurring in hexan-2-one has been discussed in connection with α cleavage and has been shown to have a relatively low-frequency factor and low activation energy. This suggests that a rearrangement process might be involved. It is therefore expected that in heptan-2-one (where δ cleavage is observed together with a slight contribution from a "δ-cleavage + 1" process), some internal hydrogen rearrangement should occur prior to the formation of the daughter peaks at 70 eV. This is evident in the 70-eV spectrum of 1,1,1,3,3-d_5-heptan-2-one, where the loss of ethyl and ethylene from the molecular ions involves the loss of 28, 29, 30, and 31 mass units. H/D scrambling must obviously have preceded the fragmentation processes. Scrambling is again more extensive in ions of longer lifetimes (Table XIV).

E. Extent of Randomization. Calculations were made for the three ethyl ketones 2,2,4,4-d_4-hexan-3-one (**2**), 2,2,4,4-d_4-heptan-3-one (**3**), and 2,2,4,4-d_4-octan-3-one (**4**), for the hypothetical case of complete randomization of the deuterium atoms in the α positions prior to the loss of the various radicals and neutral molecules. For convenience, it is assumed in these calculations that no primary or secondary deuterium isotope effect is operative. The calculated values are compared in Tables XVII–XXII with the ^{1}m* and ^{2}m* values, observed in the first and in the second field-free regions, respectively.[16] In some cases the deviations from statistical distributions are relatively small, but it is interesting to note that the loss of CH_3CD_2 from $CH_3CD_2COCD_2CH_2CH_2CH_3$ (**3**), of CH_3CD_2 from $CH_3CD_2COCD_2CH_2CH_2CH_2CH_3$ (**4**), and of C_3H_6 from $CH_3CD_2COCD_2CH_2CH_2CH_2CH_3$ (**4**) ("γ-cleavage + 1" process) is *less* than that calculated on the basis of complete randomization of H and D. It seems that in these cases primary and/or secondary isotope effects must be operating. Since ions decomposing in the field-free regions have internal energies only slightly in excess of the necessary activation energies, isotope effects may well be pronounced.

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(16) In Table XVII, the observed values for ^{1}m* are not given because the relative contributions of the peaks for the loss of ethyl and ethylene are different from those for ^{2}m*; in Table XXI, the observed ^{2}m* values are not available owing to their low intensities.

Conclusion

We have shown from our study of the various specifically deuterated aliphatic ketones that internal hydrogen rearrangement in the alkyl chains of the ketones occurs at a relatively slow rate in ions of high internal energy, and is therefore evident only when ions of long lifetimes are considered. For single bond cleavages, such as α-cleavage reactions, there is little evidence of H/D scrambling at 70 eV, simply because the rate of fragmentation of the bond is much faster than that of the scrambling process. However, at low electron voltage, where ions of low internal energies and hence longer lifetimes are present in much higher proportion, scrambling becomes evident. In fragment ions formed from rearrangement processes such as the "McLafferty +1" and "γ-cleavage +1" rearrangements, H/D scrambling is evident even in the 70-eV spectra, because such rearrangements occur with k *vs.* E curves that are comparable to those of the scrambling processes. When ions of relatively long lifetimes are sampled, such as those decomposing in the first field-free region ($\sim$5–10 μsec) and in the second field-free region ($\sim$10–15 μsec), H/D scrambling is observed for all fragmentations, regardless of whether the process is a single-bond cleavage or rearrangement. The relationship between the lifetimes and the extent of H/D scrambling observed in the various fragment ions requires that care must be exercized[17] in the interpretation of deuterium-labeling experiments, particularly when rearrangement processes are implicated.

Experimental Section

The mass spectra of all the ketones were obtained with an AEI MS-9 double focussing mass spectrometer. Samples were introduced *via* the heated inlet system, with an operating source temperature of about 200°. The 70-eV, nominal 10-eV, and ^{2}m* (70 eV) spectra were obtained at an accelerating voltage of 8 kV while the ^{1}m* (70 eV) spectra (obtained with the aid of a "metastable defocusser"[6]) were obtained at an accelerating voltage of 4 kV. The ^{1}m* and ^{2}m* spectra were recorded using a high gain on the multiplier at 70 eV.

Appearance potential measurements were obtained by the use of semilogarithm plots.[18] Krypton and xenon were used as internal standards. The estimated accuracy of the appearance potential measurements is ±0.3 eV.

All the undeuterated ketones used were commercially available. They were purified by glpc, using a 6-ft 10% Apiezon L column operating at a column temperature set at about 30° below the normal boiling point of the ketone to be purified. The flow of the carrier gas was regulated such that the retention time was about 3–5 min. All deuterated ketones were prepared by the same method—the undeuterated ketone (1 g) was refluxed for 24 hr with D_2O (1 g) with a trace of potassium carbonate as catalyst. The water was removed and the refluxing repeated with a fresh portion of D_2O. Three or four such exchanges were usually necessary to give a high incorporation of the label. The deuterated ketones were then purified by glpc before use. The isotopic purities are listed in Table XXIII.

Table XXIII. Isotopic Purity of Deuterated Ketones

Ketone	Isotopic purity, %
2,2,4,4-d_4-Hexan-3-one (**2**)	d_4, 91; d_3, 9
2,2,4,4-d_4-Heptan-3-one (**3**)	d_4, 89; d_4, 11
2,2,4,4-d_4-Octan-3-one (**4**)	d_4, 87; d_3, 13
1,1,1,3,3-d_5-Hexan-2-one (**5**)	d_5, 93; d_4, 7
1,1,1,3,3-d_5-Heptan-2-one (**6**)	d_5, 92; d_4, 8
3,3,5,5-d_4-Heptan-4-one (**7**)	d_4, 93; d_3, 7

In correcting for small amounts of d_3 contaminants (7–13%, see Table XXIII) in the d_4 compounds, or for d_4 contaminants (7–8%, see Table XXIII) in d_5 compounds, it was assumed that in cleavages involving, for example, the loss of a whole alkyl chain, the extra hydrogen atom was distributed proportionally in the two alkyl chains. For example, in 2,2,4,4-d_4-hexan-3-one (**2**), it was assumed that d_1-ethyl and d_1-propyl chains were each present to the extent of 4.5%. In general, for each fragmentation process, an m/e value one unit less than an m/e value under consideration was corrected by subtraction of the appropriate percentage, this procedure being undertaken starting with the highest m/e value of the group and then operated repeatedly in sequence toward lower mass. This method is only approximate, but any errors introduced by the approximation will be small compared with the magnitudes of the effects under consideration. For metastable transitions, such isotopic impurity corrections are not of course necessary, since the position of the "metastable peak" could be used to uniquely define the masses ofthe precursor and daughter ions.

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(17) See also W. A. Bryce and P. Kebarle, *Can. J. Chem.*, **34**, 1249 (1956); W. Benz and K. Biemann, *J. Am. Chem. Soc.*, **86**, 2375 (1964); for earlier calls for caution. For some previous examples of H/D scrambling in aliphatic systems see (a) D. P Stevenson and C. D. Wagner, *J. Chem. Phys.*, **19**, 11 (1951); (b) S. Meyerson, *ibid.*, **42**, 2181 (1965); (c) W. H. McFadden, *J. Phys. Chem.*, **67**, 1074 (1963); (d) W. H. McFadden and M. Lounsbury, *Can. J. Chem.*, **40**, 1965 (1962); (e) B. J. Millard and D. F. Shaw, *J. Chem. Soc., B*, 664 (1966); (f) J. Collin and F. P. Lossing, *J. Am. Chem. Soc.*, **80**, 1568 (1958); (g) W. A. Bryce, *Advan. Mass Spectry.*, **2**, 392 (1959); (see also S. Meyerson, *J. Chem. Phys.*, **34**, 2046 (1961)); (h) W. H. McFadden and A. L. Wahrhaftig, *J. Am. Chem. Soc.*, **78**, 1572, (1956); (i) S. Sample and C. Djerassi, *ibid.*, **88**, 1937 (1966); (j) A. G. Harrison and E. G. Jones, *Can. J. Chem.*, **43**, 960 (1965);

(18) See, for example, F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, p 14.