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REACTIONS OF ALIPHATIC ALDEHYDES UNDER ELECTRON-IMPACT*

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Abstract—The mass spectra of hexanal, heptanal and nonanal variously labeled with deuterium confirm γ-hydrogen migration and β cleavage as the mechanism leading to $[C_2H_4O]^{+\cdot}$ and $[M - C_2H_4O]^{+\cdot}$, although the data on the latter are complicated by contributions from other, related paths. In addition, they show that three other major primary decomposition products, $[M - C_2H_4]^{+\cdot}$, $[M - H_2O]^{+\cdot}$ and $[C_3H_5O]^{+}$, all arise in large part by processes involving γ-hydrogen migration to the oxygen atom. The ethylene lost to yield the first of these products consists of the α and β methylene groups. The loss of ethylene most likely occurs by way of a cyclobutanol intermediate, which, via alternative reaction paths, may well contribute to the yields of the other two products as well. These findings further extend the range of parallelism between photochemical and electron-impact-induced reactions.

THE DOMINANT features of the mass spectra of *n*-aldehydes were defined in a 1957 correlation study:[1] (a) an intense $[C_2H_4O]^{+\cdot}$ peak; (b) an intense $[M - C_2H_4O]^{+\cdot}$ peak; (c) an $[M - 28]^{+\cdot}$ peak, attributed to loss of C_2H_4, assumed to be derived from the terminal C_2H_5 group; and (d) loss of H_2O from aldehydes with six or more carbon atoms. The $[C_2H_4O]^{+\cdot}$ and $[M - C_2H_4O]^{+\cdot}$ ions were viewed as complementary products arising via γ-hydrogen migration and β carbon-carbon bond cleavage,[1] and the proposed mechanism was subsequently extensively documented.[2,3] This reaction, which parallels the Norrish Type II photolysis down to fine mechanistic detail insofar as is known, is characteristic of a wide variety of carbonyl compounds provided they have the requisite structural features. The oxygenated product appears to have the

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* Organic Ions in the Gas Phase—XXIV. For paper XXIII in this series, see reference 22b.

structure of vinyl alcohol and the complementary hydrocarbon that of a 1-olefin. The high intensity of the latter in the spectrum presumably stems from its ability to compete effectively with vinyl alcohol for the charge—a consequence of the near-equality of the ionization potentials of the two products.[2]

Chiefly to clarify the reactions leading to primary loss of C_2H_4[4] and H_2O, we prepared and studied the mass spectra of hexanal unlabeled, -4-d_2, -5-d_2 and -6-d_3; heptanal unlabeled, -2-d_2, -3-d_2, -4-d_2, -5-d_2 and -6-d_2; and nonanal unlabeled and -1-d. In addition, the spectra also confirmed the origin of $[C_2H_4O]^{+\cdot}$ and $[M - C_2H_4O]^{+\cdot}$, but revealed contributions to the latter via additional related paths. They also threw some light on yet another apparently characteristic product, $[C_3H_5O]^+$. To aid the interpretation of the aldehyde spectra, especially with respect to primary loss of C_2H_4,[4] we prepared 2-propylcyclobutanol and included its mass spectrum in the study.

The work was started and in large part carried out as three separate and independent investigations, spread over a time scale of several years. The instruments used and the procedures followed in sample handling and data collection varied among the participating laboratories. Since the fall of 1968, when we learned of each other's work and agreed to combine our efforts, we have become acutely aware of additional experimental data that would have been helpful, but many of the samples were no longer in existence. The limitations arising from such gaps are counterbalanced by the internal consistency of the data on hand, however, and the extent to which they complement each other.

As this report was being prepared to go to press, and following submission of a preliminary communication,[4] we learned of a similar study by R. J. Liedtke and Carl Djerassi, whose results are generally in agreement with ours. We thank Drs Liedtke and Djerassi and their associates for making their paper[5] and a related preliminary communication* available to us before publication.†

RESULTS AND DISCUSSION

Conventional 70- or 80 eV spectra were supplemented by low-voltage spectra, by high-resolution precise-mass measurements on selected peaks, and by a survey of metastable peaks in conventional spectra.

Most of the work on the heptanals was done on the derived bisulfite salts, which offered advantages in ease of handling and of transport between laboratories and in reduced susceptibility to inadvertent oxidation and other reactions. The bisulfite spectra were indistinguishable from those of the free aldehydes except for additional peaks evidently due to $[SO]^{+\cdot}$, $[SO_2]^{+\cdot}$ and perhaps a trace of $[CS_2]^{+\cdot}$ ions, suggesting that the bisulfites had undergone thermal decomposition in the spectrometer to regenerate the aldehydes.[6] The hexanals and nonanals were handled as the free aldehydes.

Isotopic analysis of the aldehydes is made difficult by a combination of factors–low sensitivity of the molecular ions and interference from both bimolecular reaction products and fragment ions, even at reduced ionizing voltage. N.m.r. spectra and

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* C. A. Brown, W. A. Faul, A. F. Gerrard, R. L. Hale and R. Liedtke, private communication.

† Following submission of the present paper for publication, we learned of yet another study of the mass spectra of aliphatic aldehydes, by A. G. Harrison, whose results are also generally in agreement with ours. We thank Dr Harrison for sending us a copy of his manuscript, published in *Org. Mass Spectrom.* **3**, 549 (1970).

indirect mass-spectral evidence indicate isotopic purities close to 100% for the labeled nonanal and hexanals. Mass spectra of the heptanals measured at high multiplier gain, with sample pressure low enough to essentially eliminate the bimolecular contribution to the $[M + 1]^+$ intensity, gave estimates of isotopic purity of $\geq 99\%$ for the 3-d_2 species and 90 to 93% for the other labeled species (See Experimental Section).

Partial 70- or 80 eV spectra of the hexanals, heptanals and nonanals are shown in Tables 1, 2 and 3, respectively. Intensities, corrected approximately for naturally occurring heavy-isotopic contributions, are expressed as percents of total ion intensity at masses 39 and above, uncorrected for natural heavy isotopes, but minus the $[SO]^{+\cdot}$, $[SO_2]^{+\cdot}$ and $[CS_2]^{+\cdot}$ contributions in the case of the heptanals. Table 4 lists ion formulae derived from precise mass measurements on heptanal and nonanal. Table 5 lists metastable peaks and the indicated transitions in the mass spectrum of heptanal.

Ions of neighboring–and, in the spectra of the labeled species, potentially overlapping–masses interfere with the calculation of label retentions in all the ions of

TABLE 1. PARTIAL SPECTRA OF HEXANALS*

Mass	Ion†	Unlabeled	4-d_2	5-d_2	6-d_3
43		11·6	7·74	8·59	8·21
44	$[C_2H_4O]^{+\cdot}$	18·1	6·99	20·9	20·9
45		3·17	21·2	5·64	6·14
46		—	2·91	2·52	4·84
47		—	0·07	0·05	0·06
54		0·49	0·50	0·40	0·25
55		3·10	1·11	0·84	1·01
56	Mainly $[C_4H_8]^{+\cdot}$	13·4	1·64	1·32	0·60
57	Mainly $[C_3H_5O]^+$	7·41	10·1	10·3	6·05
58		1·17	8·97	9·56	3·72
59		0·05	2·90	4·24	12·9
60		0·01	0·34	0·41	3·08
61		0·04	0·05	0·05	0·51
71		1·29	0·18	0·75	0·67
72	$[C_4H_8O]^{+\cdot}$	2·88	0·15	0·85	0·23
73		0·02	1·72	0·39	0·52
74		0·01	2·75	2·73	0·65
75		—	0·01	0·01	2·53
81		0·23	0·03	0·02	0·02
82	$[C_6H_{10}]^{+\cdot}$	2·13	0·16	0·12	0·04
83		0·09	1·37	0·54	0·16
84		0·01	1·05	1·18	0·16
85		0·07	0·05	0·06	1·89
86		—	0·01	0·01	0·05
99		0·06	—	0·02	—
100	$[C_6H_{12}O]^{+\cdot}\equiv[M]^{+\cdot}$	0·10	—	—	0·01
101		0·02	0·05	0·05	—
102		—	0·14	0·08	0·05
103		—	0·02	0·02	0·15
104		—	0·02	0·01	0·02

* Measured with 70 eV electrons on a Consolidated model 21-103 instrument, with the source and inlet system at 250°.

† Formulae listed correspond to unlabeled ions of indicated masses.

TABLE 2. PARTIAL SPECTRA OF HEPTANALS*

Mass	Ion†	Unlabeled	2-d_2	3-d_2	4-d_2	5-d_2	6-d_2
43		11·8	8·4	7·8	8·0	10·0	8·9
44	$[C_2H_4O]^{+\cdot}$	16·8	2·4	15·3	6·8	16·5	15·5
45		3·2	3·8	6·1	14·4	4·8	4·6
46		—	13·8	0·4	2·9	2·1	0·7
47		—	2·8	—	—	0·1	0·2
54		1·0	0·6	0·8	0·6	0·8	1·6
55		7·9	7·1	3·1	2·3	1·8	2·1
56	Mainly $[C_4H_8]^{+\cdot}$	0·6	1·6	3·0	5·2	3·9	2·7
57	$[C_4H_9]^+$ and $[C_3H_5O]^+$	6·3	1·8	5·8	6·7	6·3	8·7
58		0·8	3·4	1·5	2·4	3·0	2·2
59		—	2·4	5·0	1·4	1·6	1·2
60		—	0·3	0·4	—	0·1	0·2
69		0·6	1·7	1·3	2·1	1·7	1·8
70	$[C_5H_{10}]^{+\cdot}$	11·6	12·0	1·9	0·9	1·1	0·8
71		2·7	2·2	1·4	4·5	6·3	3·9
72		1·2	0·7	12·6	8·5	8·5	7·8
73		—	0·8	2·4	2·3	2·3	2·4
74		—	0·8	1·3	0·9	0·2	0·4
85		0·5	0·3	0·5	0·1	0·2	0·3
86	$[C_5H_{10}O]^{+\cdot}$	2·1	2·1	2·5	0·1	0·3	0·3
87		0·2	0·3	0·5	1·0	0·5	0·8
88		—	—	—	2·4	2·3	1·7
95		0·3	—	—	—	—	—
96	$[C_7H_{12}]^{+\cdot}$	1·7	—	0·3	0·3	0·2	0·3
97		0·2	0·6	1·2	1·2	0·7	0·8
98		—	1·4	0·8	0·9	1·1	1·2
99		—	—	0·1	—	0·1	0·2
114	$[C_7H_{14}O]^{+\cdot}\equiv[M]^{+\cdot}$	0·2	—	—	—	—	—
116		—	0·1	0·2	0·1	0·2	0·2

* Measured with 80 eV electrons on a Hitachi model RMU-7 instrument, using direct injection of the bisulfite salts on a probe at 180°, with the source at 250°.

† Formulae listed correspond to unlabeled ions at indicated masses.

interest, and in all cases except the $[M - H_2O]^{+\cdot}$ ion from hexanal, such interferences persist even in the low-voltage measurements. We have made semiquantitative estimates where possible, however, and in all the cases studied these values are essentially independent of ionizing voltage down to voltages slightly above the appearance potentials. The low-voltage intensity distributions in the $[M - H_2O]^{+\cdot}$ region of the hexanal spectra are shown in Table 6.

$[C_2H_4O]^{+\cdot}$

Essentially the entire yield of this ion remains at mass 44 in the 3-d_2, 5-d_2, and 6-d_2 and 6-d_3 species and is displaced to 45 in the 1-d and 4-d_2 species and to 46 in heptanal-2-d_2. The ion thus contains the hydrogen atoms originally on C-1 and C-2 plus one hydrogen derived from C-4, in full accord with expectation from prior work.[1,2,3]

TABLE 3. PARTIAL SPECTRA OF NONANALS*

Mass	Ion†	Unlabeled	1-*d*
43		8·4	7·8
44	$[C_2H_4O]^{+\cdot}$	6·4	1·6
45		1·8	7·4
46		—	2·2
54		1·5	0·8
55		7·0	6·0
56	Mainly $[C_4H_8]^{+\cdot}$	8·3	7·4
57	$[C_4H_9]^+$ and $[C_3H_5O]^+$	13·7	6·9
58		0·5	4·8
59		0·1	0·6
97		0·1	0·8
98	$[C_7H_{14}]^{+\cdot}$	4·9	4·2
99		0·4	0·4
100		0·1	0·3
113		0·1	—
114	$[C_7H_{14}O]^{+\cdot}$	1·2	0·1
115		—	1·0
123		0·1	—
124	$[C_9H_{16}]^{+\cdot}$	1·6	0·1
125		—	1·5
126		—	0·1
142	$[C_9H_{18}O]^{+\cdot}\equiv[M]^{+\cdot}$	0·11	—
143		0·04	0·16
144		—	0·04

* Measured with 70 eV electrons on a Bendix model 12 instrument, with the source and inlet system at 150°.

† Formulae listed correspond to unlabeled ions at indicated masses.

$[M - C_2H_4O]^{+\cdot}$

This product has the formulae and masses $[C_4H_8]^{+\cdot}$, 56; $[C_5H_{10}]^{+\cdot}$, 70; and $[C_7H_{14}]^{+\cdot}$, 98, respectively, in the spectra of unlabeled hexanal, heptanal and nonanal. In the 70 eV hexanal spectra, the $[C_4H_8]^{+\cdot}$ ion is subject to severe interference from $[C_3H_5O]^+$. The bulk of the $[C_4H_8]^{+\cdot}$ yield derived from hexanal-6-d_3, however, is evidently displaced to mass 59 and thus retains all three labels. The $[C_3H_5O]^+$ interference is substantially reduced at low voltage (7·0 eV, nominal), where the greater part of the $[C_4H_8]^{+\cdot}$ yield is displaced to masses 57, 58 and 59, respectively, in the 4-d_2, 5-d_2 and 6-d_3 species. In the heptanal spectra, interferences with the $[C_5H_{10}]^{+\cdot}$ ion are minor at 70 eV, where essentially the entire yield remains at mass 70 in the 2-d_2 species and is displaced to 72 in the 3-d_2 species; in the 4-d_2, 5-d_2 and 6-d_2 species, the $[C_5H_{10}]^{+\cdot}$ isotopic distribution is nearly constant–about 65% at mass 72 and 35% at 71. Essentially the entire yield of $[C_7H_{14}]^{+\cdot}$ in nonanal-1-*d* remains at mass 98, as in the unlabeled species.

The hydrogen atoms on C-1 and C-2 are lost cleanly, as expected if this product is complementary to $[C_2H_4O]^{+\cdot}$. On the other hand, the lack of specificity in the position

TABLE 4. ION FORMULAE FROM PRECISE MASS MEASUREMENTS

Aldehyde	Nominal Mass	Formula	Percent of Multiplet Intensity
Heptanal*	86	$[C_5H_{10}O]^{+\cdot}$	
	85	$[C_6H_{13}]^{+}$	15
		$[C_5H_9O]^{+}$	85
	81	$[C_6H_9]^{+}$	
	72	$[C_5H_{12}]^{+\cdot}$	9
		$[C_4H_8O]^{+\cdot}$	91
	71	$[C_5H_{11}]^{+}$	67
		$[C_4H_7O]^{+}$	33
	70	$[C_5H_{10}]^{+\cdot}$	
	57	$[C_4H_9]^{+}$	17
		$[C_3H_5O]^{+}$	83
	56	$[C_4H_8]^{+\cdot}$	90
		$[C_3H_4O]^{+\cdot}$	10
	55	$[C_4H_7]^{+}$	93
		$[C_3H_3O]^{+}$	7
	45	$[C_2H_5O]^{+}$	
	44	$[C_2H_4O]^{+\cdot}$	
	43	$[C_3H_7]^{+}$	92
		$[C_2H_3O]^{+}$	8
Nonanal†	124	$[C_9H_{16}]^{+\cdot}$	
	98	$[C_7H_{14}]^{+\cdot}$	
	96	$[C_7H_{12}]^{+\cdot}$	
	82	$[C_6H_{10}]^{+\cdot}$	
	70	$[C_5H_{10}]^{+\cdot}$	
	68	$[C_5H_8]^{+\cdot}$	
	58	$[^{13}CC_3H_9]^{+}$	41
		$[C_3H_6O]^{+\cdot}$	59
	57	$[C_4H_9]^{+}$	61
		$[C_3H_5O]^{+}$	39
	56	$[C_4H_8]^{+\cdot}$	95
		$[C_3H_4O]^{+\cdot}$	5
	55	$[C_4H_7]^{+}$	93
		$[C_3H_3O]^{+}$	7
	45	$[C_2H_5O]^{+}$	
	44	$[C_2H_4O]^{+\cdot}$	96
		$[^{13}CC_2H_7]^{+}$, $[CO_2]^{+\cdot}$	4
	43	$[C_3H_7]^{+}$	92
		$[C_2H_3O]^{+}$	8
	42	$[C_3H_6]^{+\cdot}$	84
		$[^{13}CC_2H_5]^{+}$	10
		$[C_2H_2O]^{+\cdot}$	6

* Measured by peak-matching on Consolidated model 21-110 and Hitachi model RMU-7 instruments.

† Measured by peak-matching on a Nuclide model 12-90-DF instrument.

TABLE 5. METASTABLE PEAKS IN MASS SPECTRUM OF HEPTANAL*

Apparent Mass	Transition
80·9	$114^+ \rightarrow 96^+ + 18$
68·4	$96^+ \rightarrow 81^+ + 15$
64·8	$114^+ \rightarrow 86^+ + 28$
63·4	$114^+ \rightarrow 85^+ + 29$
58·6	$86^+ \rightarrow 71^+ + 15$
53·8	$86^+ \rightarrow 68^+ + 18$
46·8	$96^+ \rightarrow 67^+ + 29$
45·4	$114^+ \rightarrow 72^+ + 42$
45·0	$72^+ \rightarrow 57^+ + 15$
44·2	$114^+ \rightarrow 71^+ + 43$
43·3	$70^+ \rightarrow 55^+ + 15$
	or $114^+ \rightarrow 70^+ + 44$ (Uncertain; calcd. mass 43·0)
38·3	$85^+ \rightarrow 57^+ + 28$
37·7	$86^+ \rightarrow 57^+ + 29$
36·5	$83^+ \rightarrow 55^+ + 28$
28·2	$114^+ \rightarrow 57^+ + 57$ (Uncertain; calcd. mass 28·5)
27·6	$114^+ \rightarrow 56^+ + 58$

* From conventional spectra measured on AEI model MS-9 and Consolidated model 21-110 instruments.

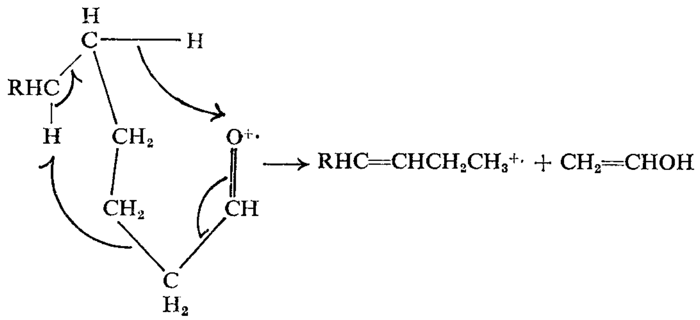
TABLE 6. LOW-VOLTAGE INTENSITIES IN $[M - H_2O]^{+\cdot}$ REGION OF HEXANAL SPECTRA*

Mass	Unlabeled	4-d_2	5-d_2	6-d_3
82	100	4	2	—
83	—	53	27	—
84	—	43	71	13
85	—	—	—	87

* Measured at 8·5 nominal ionizing volts; corrected for naturally occurring heavy isotopes; intensities normalized to a total of 100 in the mass region shown.

from which the final hydrogen is lost raises two questions. First, if the heptanal ion breaks down to $[C_5H_{10}]^{+\cdot}$ via δ- or ε-hydrogen migration to oxygen and β carbon-carbon cleavage, why do we not observe more extensive incorporation of δ or ε hydrogens into the complementary $[C_2H_4O]^{+\cdot}$ ions? Second, one might expect δ- and ε-hydrogen migration to be accompanied to some extent by γ and δ carbon-carbon cleavage, respectively, to produce $[C_3H_6O]^{+\cdot}$ and $[C_4H_8O]^{+\cdot}$, the next higher homologs of $[C_2H_4O]^{+\cdot}$. Is there evidence for such products?

A plausible answer to the first question can be made in terms of charge competition between the complementary products. The more nearly equal yields of the complementary ions in the mass spectra of aldehydes than of the corresponding ions derived from ketones, acids, or esters are accounted for by the near equality of the ionization potentials of the products, about 9·5 eV for both vinyl alcohol and 1-olefins longer than propylene.[2] The structures of the hydrocarbons arising via δ- or ε-hydrogen migration are not known, but concomitant 1,3- or 1,4-hydrogen migration to produce an olefin seems likely and the thermochemically more stable internal olefin would presumably be preferred to the terminal olefin. One such process might be pictured as



The ionization potentials of internal olefins with no branching on the vinyl carbons are about 9·1 eV,[2] and the 0·4 eV difference between the ionization potentials of the olefin and vinyl alcohol would be expected to favor retention of the charge on the olefin by perhaps an order of magnitude.[2] Lengthening the chain beyond six carbons facilitates the process by increasing the number of positions at which hydrogens, and particularly secondary hydrogens, are available for migration.

In reply to the second question, there is indeed evidence for the higher homologs of $[C_2H_4O]^{+\cdot}$. The spectra of hexanal, heptanal and nonanal all contain ions of masses 58 and 72, and precise-mass measurements, available for five of the six ions (See Table 4 and reference 5), establish their identities as $[C_3H_8O]^{+\cdot}$ and $[C_4H_8O]^{+\cdot}$ (The $[C_4H_8O]^{+\cdot}$ ion derived from hexanal, however, arises mainly by another process, discussed below.) The low intensities of these ions and interferences from neighboring species combine to preclude confirmation of the mechanistic path, such as one might otherwise hope to find in the spectra of labeled compounds. On the other hand, the interpretation advanced here is supported by the analogous products in the mass spectra of ketones,[7] acids[8] and nitriles.[8,9]

$[M - 28]^{+\cdot 4}$

This product has the formulae and masses $[C_4H_8O]^{+\cdot}$, 72; $[C_5H_{10}O]^{+\cdot}$, 86; and $[C_7H_{14}O]^{+\cdot}$, 114, respectively, in the spectra of unlabeled hexanal, heptanal and nonanal. High-resolution mass measurement confirms the ionic composition at mass 86 in the spectrum of heptanal as $[C_5H_{10}O]^{+\cdot}$ (See Table 4 and reference5) and that at 72 in the spectrum of hexanal as $[C_4H_8O]^{+\cdot}$,[5] in agreement with the earlier assignment, which was based on ^{18}O labeling.[1] These ions are comparatively free of interferences, and the spectra present a clear picture. The deuterium labels on C-1, C-4, C-5 and C-6 are retained and those on C-2 and C-3 are lost, nearly quantitatively. Thus, the ethylene lost clearly consists mainly of the methylene groups originally in the α and β positions.

Especially in light of the close parallels between reactions of acyclic carbonyl compounds under electron-impact and u.v. irradiation,[2,10] this finding suggested that the reaction may occur via a cyclobutanol intermediate, as in a photochemical reaction path of aliphatic ketones[11] and aldehydes.[12] Subsequent rupture of the ring, characteristic of cyclobutane and its derivatives,[13] would then effect loss of the α and β methylene groups as ethylene. To test this surmise, we compared the mass spectrum of heptanal with that of the suspected intermediate, 2-propylcyclobutanol. These spectra (the heptanal was introduced as the free aldehyde in this case), including all peaks at mass 39 and above, with no isotopic corrections, are shown in Table 7.

The spectra of the two isomers are qualitatively similar, in accord with the proposal of such a common intermediate. They both contain metastable peaks corresponding to the primary loss of C_2H_4 and competing secondary processes by which $CH_3^{\cdot}$ and

TABLE 7. SPECTRA OF HEPTANAL AND 2-PROPYLCYCLOBUTANOL*

Mass	Ion†	Heptanal	2-Propylcyclobutanol
39		2·1	3·3
40		0·4	0·7
41		6·2	5·6
42		6·2	5·6
43		8·8	5·7
44	$[C_2H_4O]^{+\cdot}$	11·9	9·5
45		3·0	3·4
50		—	0·2
51		0·2	0·2
52		—	0·2
53		0·5	1·1
54		0·9	0·8
55		7·1	7·5
56		1·0	1·0
57	$[C_4H_9]^+$ and $[C_3H_5O]^+$	6·8	16·4
58		1·1	1·3
59		—	0·2
63		—	0·2
65		—	0·3
66		—	0·2
67		1·1	1·0
68		2·6	2·1
69		0·9	0·8
70	$[C_5H_{10}]^{+\cdot}$	18·8	10·2
71		4·1	2·6
72		2·8	1·3
81		3·0	1·5
82		0·4	0·2
83		0·4	0·3
84		—	0·3
85		0·8	0·5
86	$[C_5H_{10}O]^{+\cdot}$	3·8	11·8
87		0·2	0·7
95		0·5	0·2
96	$[C_7H_{12}]^{+\cdot}$	3·3	1·8
97		0·3	0·3
112		—	0·2
113		0·1	0·4
114	$[C_7H_{14}O]^{+\cdot}\equiv[M]^{+\cdot}$	0·7	0·3
115		0·1	0·2

* Measured with 70 eV electrons on a Consolidated model 21-110 instrument, with the source and inlet system at 160° and 170°, respectively.

† Formulae listed correspond to unlabeled ions at indicated masses.

H_2O are lost:

$$64{\cdot}9\quad 114^+ \rightarrow 86^+ + 28;\quad [C_7H_{14}O]^{+\cdot} \rightarrow [C_5H_{10}O]^{+\cdot} + C_2H_4$$

$$58{\cdot}6\quad 86^+ \rightarrow 71^+ + 15;\quad [C_5H_{10}O]^{+\cdot} \rightarrow [C_4H_7O]^+ + CH_3\cdot$$

$$53{\cdot}8\quad 86^+ \rightarrow 68^+ + 18;\quad [C_5H_{10}O]^{+\cdot} \rightarrow [C_5H_8]^{+\cdot} + H_2O$$

Moreover, the mass-64·9:mass-86 and mass-53·8:mass-58·6 intensity ratios are nearly the same in the two spectra, as expected if the ions involved have the same structures and energy contents and distributions.[14] The first ratio has the values 0·0076 in heptanal and 0·0081 in 2-propylcyclobutanol; corresponding values of the second are 2·0 and 1·9.

To what extent the paths proposed here can be taken as characteristic of the entire class of aliphatic aldehydes is not known. In the vapor-phase photolysis of 2-pentanone, the quantum yield of 1-methylcyclobutanol, unlike those of acetone and ethylene, is highly dependent on pressure, temperature and wave length;[11c] cyclobutanol formation seems to occur only in molecules in low vibrational levels. In the mass spectra of aldehydes, the relative abundance of products formed via a cyclobutanol intermediate, similarly, may well be influenced both by structural factors such as alkyl chain length and the number, size and position of branches, and by operating variables[15] such as source temperature and repeller field strength, as well as electron energy.

For example, a cyclobutanol might be an intermediate in the process leading to $[CH_2{=}CHOH]^{+\cdot}$ and the olefinic coproduct, and such intervention could not be detected by labeling in an aldehyde longer than butanal with no branching on C-2. The mass spectrum of 2-methylpentanal-5-d_3, in which a cyclobutanol intermediate, if formed, would have twofold symmetry except that one of the methyl groups is labeled, ruled out such an intermediate.[*] 2-methylbutanal and 2-ethylbutanal show no loss of C_3H_6 and C_4H_8, respectively, however, analogous to the loss of C_2H_4 from unbranched aldehydes.[1] [†] Thus, branching on C-2 may well interfere with cyclobutanol formation. Possible cyclobutanol formation in ketones has been rejected on the basis of similar evidence in 3-methylhexan-2-one-6-d_3.[*] Methyl alkyl ketones with no α branching show loss of 28 mass units,[16] presumably ethylene, but 3-methylpentan-2-one does not show the analogous loss of 42 mass units.[16] Neither the available ethyl alkyl[16] nor phenyl alkyl[‡] ketones show loss of C_2H_4. Thus, these classes of ketones show no characteristic behavior pointing to a cyclobutanol intermediate. Even if formed, the 1-ethyl- or 1-phenyl-2-alkylcyclobutanol may decompose preferentially by other routes. For example, the loss of C_2H_4 that seems to generally characterize cyclopentanols and cyclohexanols is not observed in the mass spectra of 1-alkylcyclopentanols and 1-alkylcyclohexanols.[17]

A mechanism paralleling precisely that offered here can account for the loss of ethylene consisting of the α and β methylene groups from 5-methylhexanenitrile[9a] and heptanenitrile[9b] and for the respective loss of CH_2O and CH_3CHO from 1-butyl and 2-butyl esters.[18] It cannot, without modification, account for the seemingly similar loss of CH_2O from neopentyl esters.[19]

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[*] C. A. Brown, W. A. Faul, A. F. Gerrard, R. L. Hale and R. Liedtke, private communication.

[†] Harrison, in the work referred to in the footnote on page 690, reports weak peaks corresponding to loss of C_3H_6 from 2-methylbutanal and of C_4H_8 from 2-ethylbutanal.

[‡] S. Meyerson, unpublished spectra.

Our data furnish no clear evidence for loss of ethylene from positions farther removed from the functional group, which has been reported to be a major process in nitriles[9] and a minor one in aldehydes.[5]

$[M - H_2O]^{+\cdot}$

None of the labeled aldehydes loses more than perhaps a few percent of D_2O (See Table 6 for the pertinent hexanal low-voltage data). The split between ^1HDO and ^1H_2O loss can be estimated fairly well from the spectra; the values are listed in Table 8, in which approximate corrections have been made for the isotopic impurities in the labeled heptanals.

TABLE 8. LOSS OF ^1HDO AND ^1H_2O FROM LABELED ALDEHYDES

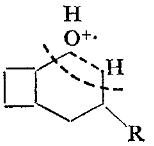
Aldehyde	^1HDO, %	^1H_2O, %
Hexanal-4-d_2	57	43
-5-d_2	31	69
-6-d_3	8	92
Heptanal-2-d_2	~0	~100
-3-d_2	60	40
-4-d_2	57	43
-5-d_2	33	67
-6-d_2	36	64
Nonanal-1-d	~0	~100

C-1 and C-2 contribute essentially no hydrogen atoms to water formation. The H_2O hydrogens come entirely from the more distant positions. The deuterium losses from C-3 to C-6 in the appropriately labeled heptanals account for 186 atoms per 100 molecules. The material balance is thus *ca.* 93%. The small discrepancy probably stems in the main from isotope effects; it apparently also reflects some contribution from C-7.[5] The similarly calculated material balance for hexanal is 48%, reflecting a large contribution from C-3.[5] Losses from C-4, and likewise from C-5, in the two aldehydes are very similar. The large difference at C-6, which appears even larger if it is expressed in terms of loss per available hydrogen atom, is presumably caused by the greater difficulty of abstracting a primary hydrogen than a secondary one.

The fact that hydrogens from four different positions in the original aldehyde molecule are incorporated into H_2O molecules requires that either (a) some measure of loss of position identity of hydrogens precede or intervene in the formation of H_2O or (b) loss of H_2O occur via two or more contributing reaction paths. The first possibility, paralleling the hydrogen scrambling that is prominent in ketones at reduced ionizing voltage,[7] seems unlikely in aldehydes in view of the sharp distinction between the behavior of hydrogens on C-1 and C-2 and of those on the subsequent four carbons. Likewise, quantitative retention of the hydrogen atoms on C-2 rules out any appreciable keto-enol tautomerization, in agreement with a conclusion drawn from a study of piperitone and related compounds[20] but contrary to suggestions proposed for other similar systems.[7,21] This conclusion accords with–and, conversely, is reinforced by–the substantial evidence against the reverse tautomerization in other unimolecular ionic reactions in the mass spectrometer.[22]

Loss of H_2O from the molecular ion is extensive only in *n*-aldehydes with six or more carbon atoms.[1] Thus, a hydrogen atom on C-6–or possibly on C-5, if a primary hydrogen is too inactive to perform the necessary function but a secondary one is satisfactory–must be assigned a crucial role in any proposed mechanism. A number of possible contributing paths can be suggested:

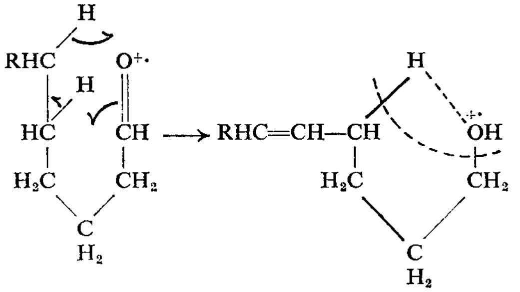
(a) γ-Hydrogen migration to the oxygen and cyclobutanol formation as proposed above, followed by 1,3- or 1,4-elimination,[23] in which a hydrogen from C-5 or C-6, respectively, would be lost along with the one from C-4, e.g.



(R = H or alkyl)

In accord with this proposal is the substantial $[M - H_2O]^{+\cdot}$ intensity in the spectrum of 2-propylcyclobutanol, although cyclobutanol itself shows no more than a possible trace of such a product.[13a,24]

(b) Concerted migration of hydrogens from C-6 and C-5 to the oxygen and carbonyl carbon, followed by migration of an activated hydrogen from C-4 to the oxygen and loss of H_2O:



If hydrogen from C-5 is assigned the crucial role, the initial migrations would occur from C-5 and C-4 and the final one from C-3. This path is patterned after that by which 6-substituted alkanoic acids lose H_2O and CH_2CHOH, and methyl 6-substituted alkanoates lose CH_3OH and CH_2CHOH.[25]

(c) Hydrogen migration to the oxygen from C-6–or, again, from C-5–accompanied or followed by carbon-carbon bonding to form a cycloalkanol ion, by analogy with 6-methylhept-5-en-2-one, another system in which the hydrogen on C-6* is activated.[26] Loss of H_2O would then be expected to occur by 1,4- or 1,3-elimination in a cyclohexanol[27] or by 1,3-elimination in a cyclopentanol.[28]

Available data do not permit an estimate of the relative contributions of these and other possible paths.

$[C_3H_5O]^+$ *and the isobaric* $[C_4H_9]^+$

The $[C_3H_5O]^+$ ion comprises a large part of the observed ion intensities at mass 57 in the unlabeled aldehydes, 83% in heptanal and 39% in nonanal. Estimates of label retentions in this ion in the spectra of the labeled aldehydes must take into account interferences from $[C_4H_9]^+$, $[C_4H_8]^{+\cdot}$ and other species.

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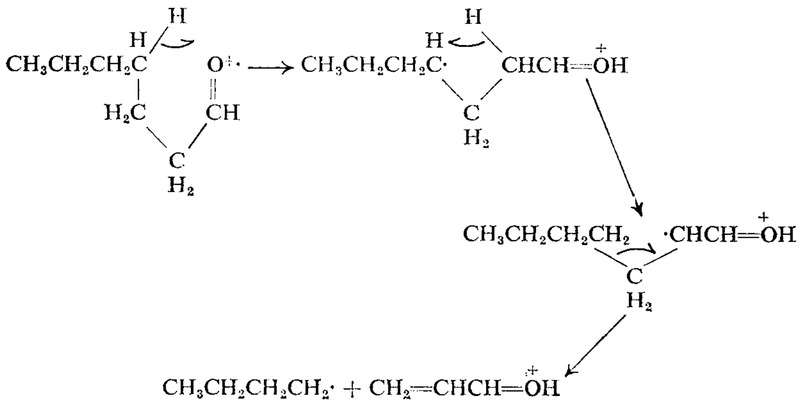
* Referred to the carbonyl carbon as C-1.

We estimated the retention of both labels in the combined yield of $[C_3H_5O]^+$ and $[C_4H_9]^+$ simply from the ratio of the intensity at 59 in each labeled heptanal in turn to that at 57 in the unlabeled compound. We made a second estimate similarly after reducing the intensity at 59 by the difference between the intensity of the unlabeled heptanal at 58 and that of the labeled one at 60. Both estimates were then corrected for the isotopic impurities in the labeled heptanals. The values so arrived at are: 2-d_2, 42 and 34%; 3-d_2, 80 and 73%; 4-d_2, 24 and 10%; 5-d_2, 28 and 16%; and 6-d_2, 20 and 10%. In heptanal-3-d_2, where interferences are at a minimum, retention of the two labels in $[C_3H_5O]^+$ is high and it may well be quantitative. In heptanal-2-d_2, it is substantial, but about half the ions have lost one deuterium atom. In heptanal-4-d_2, -5-d_2 and -6-d_2, retention of both labels is low, and it may be zero in $[C_3H_5O]^+$; retention of one label in the combined yield is appreciable, but probably less than 50% in all cases.

In nonanal-1-*d*, the $[C_4H_8]^{+\cdot}$ yield is concentrated at mass 56 and so does not interfere. Thus, label retention in the combined yield of $[C_3H_5O]^+$ and $[C_4H_9]^+$ can be calculated directly from intensities at 58 and 57, implicitly taking into account the over-all isotope effect on the combined yield. The value so arrived at is 41%. This is so nearly equal to the fraction that $[C_3H_5O]^+$ comprises of the combined yield, as determined by precise mass measurements on the unlabeled compound, that it suggests quantitative retention in $[C_3H_5O]^+$ and quantitative loss of the label in $[C_4H_9]^+$.

In the labeled hexanals, the interference from $[C_4H_9]^+$ is unknown; that from $[C_4H_8]^{+\cdot}$ is severe but can be approximated by assuming that this ion arises solely by γ-hydrogen migration and β cleavage. On this basis, the $[C_4H_8]^{+\cdot}$ yield in hexanal-4-d_2 is at mass 57, and the bulk of the combined yield of $[C_3H_5O]^+$ and $[C_4H_9]^+$ is at 58 and so retains one label. In hexanal-5-d_2, $[C_4H_8]^{+\cdot}$ falls at 58; therefore, the bulk of the combined yield of $[C_3H_5O]^+$ and $[C_4H_9]^+$ must be at 57 and is thus unlabeled. In hexanal-6-d_3, $[C_4H_8]^{+\cdot}$ is at 59; by analogy with heptanal, one might suspect that $[C_3H_5O]^+$ is in the main unlabeled and thus concentrated at 57. Intensity at 58 would seem to be due largely to $[C_4H_7]^+$-d_3. The excess intensity at 59 in hexanal-4-d_2 and -5-d_2 and at 60 in hexanal-6-d_3, beyond that at 58 in the unlabeled compound, is plausibly attributed to $[C_4H_9]^+$. This excess corresponds to 23%, 41% and 26% of the combined intensity of $[C_3H_5O]^+$ and $[C_4H_9]^+$ as observed at 57 in the unlabeled hexanal. The near equality of two of the three values suggests that these values are in fact measures of the yields of $[C_4H_9]^+$, in which label retention is complete. If so, about 25% of the intensity of unlabeled hexanal at 57 can be attributed to $[C_4H_9]^+$ and 75% to $[C_3H_5O]^+$, in rough agreement with the distribution reported by Liedtke and Djerassi[5] and only slightly different than the measured distribution in heptanal.

Taken *in toto*, the data thus indicate that $[C_4H_9]^+$, at least in hexanal and heptanal, consists mainly of the terminal butyl group from the original aldehyde; some 40% of the $[C_3H_5O]^+$ ions from heptanal retain all the C-1, C-2 and C-3 hydrogens and thus consist of the original CH_2CH_2CHO group, complementary to $[C_4H_9]^+$; but the greater part of the $[C_3H_5O]^+$ ions retain the hydrogens originally on C-1 and C-3, one of the two from C-2, and one from all the farther removed positions together. The latter labeling pattern in $[C_3H_5O]^+$ is most simply accounted for by a decomposition path generally characteristic of cycloalkanols,[13a,24] although not found in unsubstituted cyclobutanol.[13a,24] The first step in this path in cycloalkanols is rupture of the ring at the hydroxyl-substituted carbon; the aldehydes may react via a cycloalkanol intermediate, or they may follow essentially the same path but omit both initial ring closure and subsequent rupture, thus:



In this form, our proposed process is indistinguishable from that of Liedtke and Djerassi.[5] This path may also be responsible for some part of the $[C_4H_9]^+$ yield, which would, again, be formed as a complementary product to $[C_3H_5O]^+$. The lack of specificity of hydrogen retention from C-4 in $[C_3H_5O]^+$ suggests substantial contributions to this ion by way of cyclopentanol and cyclohexanol as well as cyclobutanol intermediates, as described above in path (c) leading to loss of H_2O.

Metastable peaks, listed in Table 5, show other paths leading to ions of mass 57, but the precise reactions and their relative contributions are obscure.

General considerations

The reaction paths leading to the five fragment ions with which we have been concerned remain subject to some uncertainties because of numerous interferences, including some converging paths. More extensive labeling has helped sort out the components of other complex reaction networks,[29] and it may well permit better definition of the reactions of aldehydes also. For example, deuterium labeling on the various carbon atoms taken two at a time could reveal which hydrogens are paired in H_2O molecules lost from the molecular ions.

At the same time that our findings reveal some competing paths, they extend the range of parallelism between the reactions of aliphatic carbonyl compounds under light irradiation and those induced by electron-impact. In particular, they emphasize the pervasive role of γ-hydrogen migration in the primary reactions of aldehydes. A growing body of evidence indicates that such γ-hydrogen migration in photochemical processes occurs, at least in large part, as a discrete step.[30] Our findings suggest that hydrogen migration under electron-impact also occurs largely as a discrete primary step, which may be followed by a choice of secondary steps.[33]

An argument to the contrary is implied in Rol's study of the competition among (i) γ-hydrogen migration and β cleavage, (ii) δ-hydrogen migration and γ cleavage, and (iii) ε-hydrogen migration and δ cleavage in aliphatic acids and nitriles.[8] Reaction (ii) is greatly enhanced by alkyl substitution on C-4, and reaction (iii) by substitution on C-5. The connecting link between the position of substitution and the reaction that is enhanced by the substitution is presumably the weakening of the carbon-carbon bond to be cleaved. If so, this cleavage and the associated hydrogen migration–if Rol's model is valid–must be concerted. The molecule just prior to reaction may perhaps be pictured with more than one hydrogen bridged to the heteroatom and thus poised to make the jump as the carbon-carbon bond ruptures.

The widespread occurrence of γ-hydrogen migration in these systems in turn adds plausibility to a proposal made 30 years ago by Smith and McReynolds.[32] These workers plotted several quantities–rate constants of catalyzed esterification of normal and methyl- and phenyl-substituted aliphatic acids in methanol; rate constants of alkaline hydrolysis of saturated aliphatic esters; ionization constants of aliphatic acids; and optical rotatory power of a number of series of alcohols, esters, azides, aldehydes, and acids–against chain length of members of homologous series. In all these curves they found sharply defined structure that they rationalized in terms of intramolecular hydrogen bonding from γ carbon to the oxygen or nitrogen atom. The favorable geometry thus seems to promote bond formation between the γ hydrogen and the heteroatom even without the high-energy activation implicit in photolysis and electron-impact. This and other evidence point to a widespread preference for six-membered quasicyclic orientations of formally acyclic molecules, leading variously to intramolecular elimination reactions[33] and to steric interference with addition reactions.[34]

EXPERIMENTAL

Hexanals

The labeled and unlabeled hexanols corresponding to the desired hexanals were initially prepared as described earlier[23b] from the appropriate 1-bromopropanes and trimethylene oxide. Subsequently, the yields of alcohol were nearly doubled by using a 1 mole excess of trimethylene oxide, as was done in the synthesis of labeled 6-phenylhexanols.[25] The excess trimethylene oxide tends to react with magnesium bromide to give 3-bromopropanol as a byproduct.

Several methods of oxidizing the alcohols to the aldehydes were considered. Oxidation in the vapor phase over a copper chromite catalyst[35] proved unpromising because of the possibility of unwanted exchange at the temperature required. An attempted oxidation of unlabeled hexanol with chromic acid in water[36] gave a poor yield and was therefore abandoned. N-Bromosuccinimide has been reported to give good yields of ketones from secondary alcohols[37] but hexanol produced only tars. Di-*t*-butyl chromate, which is reported to give high yields of aldehyde from cetyl alcohol,[38] gave only a poor yield with hexanol. The problem was finally solved by employing the method of Kornblum, Jones and Anderson,[39] which consists in heating the alkyl halides or, preferably, the tosylates in dimethyl sulfoxide with sodium bicarbonate at 150°. An hour's heating on the steam bath was sufficient to achieve complete oxidation. The tosylates were prepared from the hexanols by the method of Marvel and Sekera.[40] The procedure is illustrated by the detailed description of the synthesis of hexanal.

Hexyl tosylate was prepared from the alcohol (1·6 g, 0·0157 mole), pyridine (5·0 ml), and *p*-toluenesulfonyl chloride (3·4 g, 0·0180 mole).[40] Bulb-to-bulb distillation at 1 torr and 135° after work-up gave 3·0 g of pure product (75% yield). The tosylate (7·7 g, 0·033 mole) was heated for 1 hour on the steam bath in 100 ml of dimethyl sulfoxide containing 20 g of suspended sodium bicarbonate. The reaction mixture was then distilled in a current of steam, and the colorless, pungent, oily distillate (100 ml) was extracted with 25 ml of pentane. The pentane extract was washed with water, transferred to a Späth bulb and freed of solvent on the steam bath. Bulb-to-bulb distillation of the residue at 0·1 torr yielded 2·1 g of colorless distillate (70% yield). Analysis by gas chromatography on a silicone-coated firebrick at 90° indicated it was over 95% pure.

Some deterioration took place during the time spent in the mails between laboratories. To remove contaminants and protect the purified material, the hexanals were isolated by gas chromatography on a 15-ft column of 30% diethyleneglycol sebacate on Chromosorb W, trapped from the column effluent, and transferred under a nitrogen atmosphere to indium tubes,[41] which were sealed immediately and stored under liquid nitrogen for about a day until we were ready to introduce them into the mass spectrometer.

Despite these precautions and the apparently successful removal of impurities, persistent $[M + 1]^+$ peaks, coupled with very low parent-peak sensitivity, precluded isotopic analysis from the spectra. The spectra suggest high isotopic purities, however; moreover, the isotopic purities of the 4-d_2 and 5-d_2 6-phenyl-hexanoic acids (and derived methyl esters) prepared by a similar synthetic route were 96 to 98%.[25] The bimolecular origin of the $[M + 1]^+$ peak in the spectrum of the unlabeled hexanal was confirmed by observing the expected dependence of the $[M + 1]^+ : [M]^+$ intensity ratio on sample pressure and on repeller voltage.

The spectra were measured on a Consolidated model 21-103 instrument with the source and inlet system at 250°. 70 eV spectra were supplemented by low-voltage measurements over a range of electron energies starting slightly above the appearance potentials of the ions under study. For the low-voltage measurements, the repellers were maintained at an average potential of 3 volts, with actual settings adjusted for maximum ion current.

Heptanals and 2-Propylcyclobutanol

Heptanal, purchased from Aldrich Chemical Co, was collected from an FFAP* gas-chromatographic column and stored under argon. The bisulfite was made as described by Vogel,[42] collected by suction filtration, and the feathery crystals were washed several times with ether.

Deuterium labels intended for positions 4, 5 and 6 in heptanal were introduced by exchanging propyl-, ethyl- and methyl-substituted diethyl malonate, respectively, in deuterium oxide and sodium deuteroxide. Saponification and acid-catalyzed decarboxylation[43] led to pentanoic, butanoic and propanoic acids, which were reduced with lithium aluminum hydride to the corresponding alcohols. These were converted to bromides and the carbon chains were extended by Grignard reaction with formaldehyde or ethylene oxide. By suitable combination of these two Grignard sequences the three compounds were lengthened to hexanol-3-d_2, -4-d_2 and -5-d_2. Conversion to 1-bromohexane was followed by Grignard reaction with triethyl orthoformate and the aldehyde products were recovered as bisulfites.[42] The bisulfites were dissolved in 1 N aqueous sodium hydroxide and heptanal-4-d_2,-5-d_2 and -6-d_2 were recovered by immediate ether extraction. The heptanals were purified by gas chromatography on a 6-ft 6% terephthalate-terminated Carbowax 400 column. Small samples were stored in capillary tubes sealed under dry argon. Larger samples were stored as the bisulfite salts.

Heptanal-2-d_2 and -3-d_2 were synthesized by reduction of hexanoic and pentanoic acids with lithium aluminum deuteride, and elaboration of the chain to bromohexane. Grignard reaction with triethyl orthoformate led to the labeled heptanals, which were collected and stored as bisulfite salts. Attempts to introduce deuterium into the 2-position by acid- or base-catalyzed enolization of heptanal were unsuccessful. For example, no more than one-half atom of deuterium was introduced by enolization exchange in deuterium oxide heated for six days under reflux with 0·5 N sodium hydroxide.

Mass spectra were measured with 80 eV and 13 eV electrons on a Hitachi model RMU-7 instrument. Spectra of liquid samples of heptanal-d_0, -4-d_2, -5-d_2 and -6-d_2 were obtained with the source and inlet at 200° and 150°, respectively. Spectra of the bisulfites of the entire heptanal series[7] were obtained by direct injection into the source, with the source and probe at 250° and 180°, respectively. As with the hexanals, persistent $[M + 1]^+$ peaks in excess of naturally occurring heavy isotope, in the spectra of both the free aldehydes and the bisulfites, interfered with attempts at isotopic analysis. The spectra were also measured on a Consolidated model 21-110 instrument, as described below, and here we succeeded in reducing the $[M + 1]^+$ intensity to that expected for natural isotope. Isotopic analyses were estimated from 70 eV spectra

	2-d_2	3-d_2	4-d_2	5-d_2	6-d_2
d_2, %	90	≥99	92	90	93
d_1, %	10	—	8	9	7
d_0, %	—	—	—	1	—

on the assumption that the $[M - 1]^+$ intensity in the spectra of all the labeled species equals 11% that of the molecular ion, as observed in the unlabeled species. If this assumption is valid, it implies

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* Free Fatty Acid Phase, a reaction product of Carbowax 20 M and 2-nitroterephthalic acid, developed and sold by Varian-Aerograph.

that primary loss of H occurs solely from the formyl group. The $[M - 1]^+$ and $[M - 2]^+$ peaks in the spectrum of nonanal-1-*d* (not shown in Table 3 because of their low relative intensities) confirm the formyl group as the major site of this process. An estimated 70% of the hydrogen lost from the molecular ion of this compound consists of deuterium atoms.

2-Propylcyclobutanol was obtained by u.v. irradiation with a medium pressure mercury lamp of a 5% solution of heptanal in pentane.[11d,12,44] Carbonyl compounds were removed from the reaction mixture by aqueous extraction of bisulfite salts. The product was collected as a single peak by preparative gas chromatography on two columns, 6% terephthalate-terminated Carbowax 500 and diethyleneglycol succinate. Elemental analysis found: C, 73·99; H, 12·41; calculated: C, 73·68; H, 12·28.

Spectra of heptanal and 2-propylcyclobutanol were measured with 70 eV electrons on a Consolidated model 21-110 mass spectrometer with the source and inlet at 160° and 170°, respectively. Precise-mass measurements of selected peaks in the spectrum of heptanal were made by peak matching on the 21-110 and RMU-7. Metastable peaks in the 70 eV spectra of heptanal and 2-propylcyclobutanol were recorded on an AEI model MS-9 instrument with the multiplier at high gain. The source and inlet were at 250° and 100°, respectively.

Nonanals

Unlabeled nonanal was separated by preparative gas chromatography from the products of ozonolysis of soybean oil and further purified by fractional distillation at 13 torr: b.p. 79 to 83°; lit.[45] 80 to 82° at 13 torr. Nonanal-1-*d* was prepared by reducing nonanoyl chloride with lithium tri-*t*-butoxyaluminodeuteride.[46] The nonanal was separated from the reaction mixture (mostly diglyme) with an Adsorbosil CAB column using hexane:ether (95:5) as the wash solution. The solvent was distilled off and the nonanal further purified by gas chromatography on an SE-30 column. Gas chromatography revealed no impurities in either of the two products. Proton n.m.r. showed the nonanal-1-*d* to be labeled quantitatively (estimated $\geq 98\%$) on the carbonyl carbon. The samples were stored in vials under nitrogen in a freezer. The vial was continuously flushed with nitrogen whenever a sample was withdrawn.

Mass spectra were measured with 70 eV electrons on a Bendix TOF model 12 instrument equipped with a model 14 source, and on a Nuclide model 12-90-DF instrument, both with the source and inlet at 150°. The spectra measured on the two instruments are in good qualitative agreement, and only those from the Bendix are reported here. Precise-mass measurements on selected peaks were made by peak matching on the Nuclide instrument.

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