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Mass Spectral Dehydration and Decarboxylation in Cyclic α-Hydroxy Acids, Alcohols, and Carboxylic Acids

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Synopsis. The relative ease of mass spectral decarboxylation is greater than the ease of mass spectral dehydration as determined from a comparison of the alcohols **1a**—**4a** with acids **1b**—**4b**. However, the relative ease is reversed in α-hydroxy acids **2c**—**4c**; and dehydration predominates over decarboxylation.

The dehydration of alcohols and the decarboxylation of acids are both well known mass spectrometric processes.[1] Alcohol dehydration in the mass spectrometer usually occurs by a 1,4 or 1,3 elimination pathway as opposed to the 1,2 elimination found in solution chemistry. Mass spectrometric decarboxylation of aliphatic acids often occurs by simple α-fragmentation similar to reactions observed in solution. α-Hydroxy acids, although little studied, prefer a fragmentation pathway that favors decarboxylation over dehydration.[2]

A problem of considerable importance is the analysis of hydroxy and carboxy metabolites occurring in natural processes.[3,4] In connection with this problem we have conducted a study designed to determine the preferred mass spectrometric fragmentation pathway, decarboxylation or dehydration, in a series of acyclic and cyclic alcohols, acids, and α-hydroxy acids. The substances studied, shown below, also permit an evaluation of ring size effects on the fragmentation process.

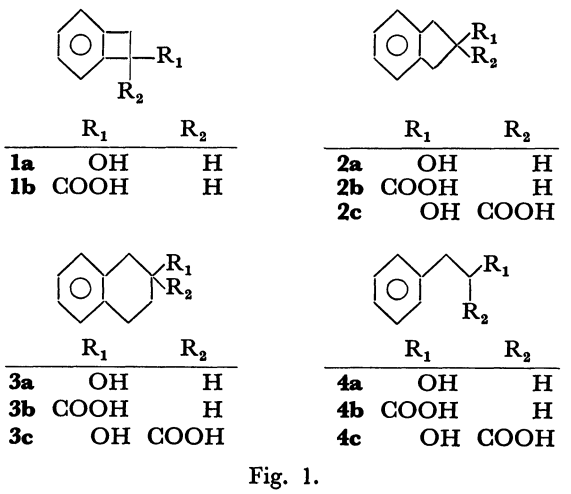
Results and Discussion

The results are summarized in Tables 1 and 2. Dehydration in alcohols **1a**—**4a** occurs with less facility than does decarboxylation in acids **1b**—**4b**. Only 2-hydroxytetralin (**3a**) can dehydrate by a favorable 1,3 elimination pathway whereas a 1,2 elimination is required in **1a** and **2a**. Decarboxylation appears as a very favorable process in the cyclic acids **1b**, **2b**, and **3b**, and is responsible for formation of the base peak in **2b** and **3b**. Decarboxylation can occur by either a thermal reaction or α-fission process. The high abundance of the M−COOH peak is moderately independent of ring size. Both acyclic analogies **4a** and **4b** prefer fragmentation to form the tropylium ion, but the trend of decarboxylation favored over dehydration is still evident in these compounds.

Table 1. Relative ion intensities for the loss of H_2O and COOH in **1a**—**4c**[a)]

Compd	$[M-H_2O]^{+\cdot}$ [b)]	$[M-CO_2H]^+$	Base peak[c)]
1a	0	—	$[T]^+$
2a	23	—	$[CH_3T]^+$
3a	100	—	$[M-H_2O]^{+\cdot}$
4a	4	—	$[T]^+$
1b	—	67	$[M]^{+\cdot}$
2b	—	100	$[M-COOH]^+$
3b	—	100	$[M-COOH]^+$
4b	—	18	$[T]^+$
2c	68	26	$[M-CO_2H, H_2O]^+$
3c	46	26	$[M-CO_2H, H_2O]^+$
4c	11	0	$[T]^+$

a) Intensities are related to the base peak (100%) in each spectrum. b) $[T]^+$ means tropylium ion. c) M means molecular ion.



	R_1	R_2
1a	OH	H
1b	COOH	H

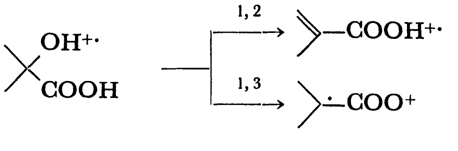
	R_1	R_2
2a	OH	H
2b	COOH	H
2c	OH	COOH

	R_1	R_2
3a	OH	H
3b	COOH	H
3c	OH	COOH

	R_1	R_2
4a	OH	H
4b	COOH	H
4c	OH	COOH

Fig. 1.

Interestingly fragmentation of α-hydroxy acids **2c**—**4c** shows that dehydration is preferred over decarboxylation in contrast to the monosubstituted analogues previously discussed. This phenomenon can be explained by using either a 1,2 thermal elimination process which produces a conjugated acid or a 1,3 elimination which produces a saturated carboxy cation radical as shown below.[5]



The base peak in the cyclic hydroxy acids **2c** and **3c** arises through loss of both COOH and H_2O. The acyclic hydroxy acid shows preference for α-fission to form the tropylium ion, similar to the acyclic compounds **4a** and **4b**.

In conclusion, decarboxylation is preferred over dehydration in the monosubstituted compounds, but the trend reverses in α-hydroxy acids with dehydration preferred over decarboxylation. Furthermore, dehydration and decarboxylation occur in the hydroxy acids, perhaps synergystically, to produce the base peak.

Table 2. Mass spectra (80 eV) of compounds **1a**—**4c**[a]

1a	120 (62, $[M]^{+\cdot}$), 119 (88, $[M-H]^{+}$), 106 (4, $[M-CH_2]^{+\cdot}$), 91 (100, $[\text{tropylium}]^{+}$), 77 (4, $[M-C_2H_3O]^{+}$), 65 (25), 51 (8), 39 (16).
2a	134 (35, $[M^{+\cdot}]$), 116 (23, $[M-H_2O]^{+\cdot}$), 117 (28, $[M-H_3O]^{+}$), 105 (100, $[CH_3-\text{tropylium}]^{+}$), 91 (28, $[\text{tropylium}]^{+}$), 79 (39), 77 (40), 65 (19), 63 (25), 51 (40).
3a	148 (8, $[M]^{+\cdot}$), 130 (100, $[M-H_2O]^{+\cdot}$), 115 (32), 104 (75, $[M-CH_3CHO]^{+\cdot}$), 91 (20, $[\text{tropylium}]^{+}$), 79 (25), 51 (15).
4a	122 (22, $[M]^{+\cdot}$), 104 (4, $[M-H_2O]^{+\cdot}$), 92 (62, $[M-CH_2O]^{+\cdot}$), 91 (100, $[\text{tropylium}]^{+}$), 77 (7, $[M-C_2H_5O]^{+}$), 65 (29), 51 (4), 39 (16).
1b	148 (100, $[M]^{+\cdot}$), 147 (50, $[M-H]^{+}$), 131 (49, $[M-OH]^{+}$), 120 (60, $[M-CO]^{+\cdot}$), 103 (67, $[M-COOH]^{+}$), 91 (51, $[\text{tropylium}]^{+}$), 77 (51), 51 (32).
2b	162 (76, $[M]^{+\cdot}$), 118 (81, $[M-CO_2]^{+\cdot}$), 119 (100, $[M-COOH]^{+}$), 116 (61, $[M-COOH_2]^{+\cdot}$).
3b	176 (1, $[M]^{+\cdot}$), 159 (30, $[M-OH]^{+}$), 148 (18, $[M-CO]^{+\cdot}$), 131 (100, $[M-CO_2H]^{+}$), 104 (10, $[M-CH_2{=}CHCOOH]^{+\cdot}$), 91 (25, $[\text{tropylium}]^{+}$), 77 (8).
4b	150 (56, $[M]^{+\cdot}$), 132 (15, $[M-H_2O]^{+\cdot}$), 106 (11, $[M-CO_2]^{+\cdot}$), 105 (18, $[M-COOH]^{+}$), 91 (100, $[\text{tropylium}]^{+}$), 77 (15), 65 (10), 51 (14).
2c	178 (7, $[M]^{+\cdot}$), 160 (68, $[M-H_2O]^{+\cdot}$), 134 (22, $[M-CO_2]^{+\cdot}$), 135 (26, $[M-CO_2H]^{+}$), 116 (98, $[M-CO_2, H_2O]^{+\cdot}$), 115 (100, $[M-CO_2H, H_2O]^{+}$), 105 (58, $[M-HOCCO_2]^{+}$), 104 (60, $[M-HOCCOOH]^{+\cdot}$), 91 (13, $[\text{tropylium}]^{+}$), 77 (50), 65 (30).
3c	192 (3, $[M]^{+\cdot}$), 174 (46, $[M-H_2O]^{+\cdot}$), 148 (12, $[M-CO_2]^{+\cdot}$), 147 (26, $[M-CO_2H]^{+}$), 129 (100, $[M-H_2O, CO_2H]^{+\cdot}$), 105 (10, $[M-HOCCO_2]^{+}$), 104 (54, $[M-HOCCO_2H]^{+\cdot}$), 77 (12).
4c	166 (12, $[M]^{+\cdot}$), 148 (11, $[M-H_2O]^{+\cdot}$), 91 (100, $[\text{tropylium}]^{+}$), 77 (12), 65 (19), 51 (11).

[a] *m/e* (relative abundance [probable genesis]). The genesis is based on standard mass spectrometric fragmentations.

Experimental

The compounds used in this study have been previously described.[6,7] Mass spectra were recorded on a low-resolution Varian MAT-111 magnetic sector instrument at 80 eV. All samples were introduced into the ionization chamber by the use of a direct probe at ambient temperature. The mass spectra are reported in Table 2.

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5) A referee has suggested the elimination of OH from COOH in the H_2O loss as an alternative to the 1,3 elimination. A test of this interesting possibility requires labeling experiments which have not yet been performed.

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