The Mass Spectra of 4-, 5-, 6-, and 7-Hydroxy-1-naphthyl Methylcarbamates

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The high resolution mass spectra of 4-, 5-, 6-, and 7-hydroxy-1-naphthyl methylcarbamates have been determined in an effort to provide an alternative method for the identification of these metabolites and potential metabolites of carbaryl insecticide, particularly the 4- and 6-isomers. The results indicate that these latter compounds may be distinguished by this method.

During the study of the metabolism of carbaryl in various plants and animals it was necessary to consider the development of methods other than chromatographic for the identification of various nuclearly hydroxylated 1-naphthyl methylcarbamates. Of particular interest were the 4- and 6-hydroxy isomers, which are not easily distinguished by tlc.

One method which seemed to offer promise involved the elucidation of the mass spectral fragmentation pattern of the isomeric hydroxycarbaryl compounds. If meaningful differences in the various spectra were observed, the mass spectral technique offered the added advantage of being readily adaptable to concentrations of unknown in the order of a few μgl.

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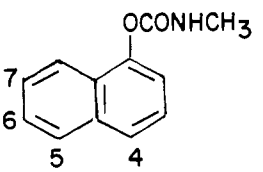
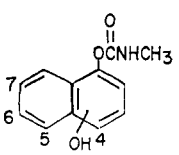
Table I. Tlc Behavior of the Various Compounds Studied

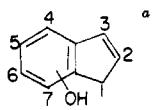
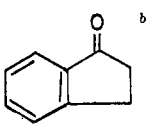


Compound	mp °C	R_f (3:1 ether: hexane)	R_f (4:1 $CHCl_3$: acetone)	Color on Standing
4-OH[a]	163.5–64.5	0.24	0.36	yellow
5-OH[a]	167–68.5	0.31	0.435	brown-yellow
6-OH[b]	163–64.5	0.25	0.36	none
7-OH[b]	205.5–206.5	0.196	0.301	pink-brown yellow

[a] Prepared by the method of Knaak *et al.* (1965). [b] Prepared by the method of Durden (1971).

Table II. Fragmentation Patterns of Isomeric Hydroxy-1-naphthyl Methylcarbamates



OH position	m/e Relative Intensity, % 217	160	144	143	132	131	130	105	104	103	102	101	77
4-	10.2	100.0	1	1.8	13.8	34.6	1.5	17.7	7.4	14.1	6.3	1.4	26.2
5-	5.9	100.0	0.7	0.6	7.0	37.0	0.7	0.7	3.3	6.8	4.9	0.7	10.0
6-	4.4	75.0	3.3	1.0	100.0	20.0	0.74	0.7	4.5	91.0	3.2	2.5	10.0
7-	3.1	100.0	0.5	18.0	21.0	69.5	2.2	2.3	11.7	28.0	21.2	3.0	45.0
 [a]													
4-	...	...	...	...	100	65.3	4.05	...	13.0	24.6	11.6	24.6	24.6
7-	...	...	...	...	100	66.8	4.07	...	13.5	25.0	12.0	25.0	25.0
 [b]	...	...	...	100	36	12.0	9	70	36	15	3	20	

[a] Sharkey (1969). [b] Bowie (1966).

Table III. Metastable Species Encountered in the Table II Spectra

Isomer in Which Detected	Metastable Species, m/e	Transition to Which Assigned	Isomer in Which Detected	Metastable Species, m/e	Transition to Which Assigned
4-	69	160 → 105	4-, 5-, 6-, 7-	109	160 → 132
4-, 5-, 6-, 7-	81	131 → 103	4-, 6-	117.8	217 → 160
4-, 5-, 6-, 7-	107.4	160 → 131			

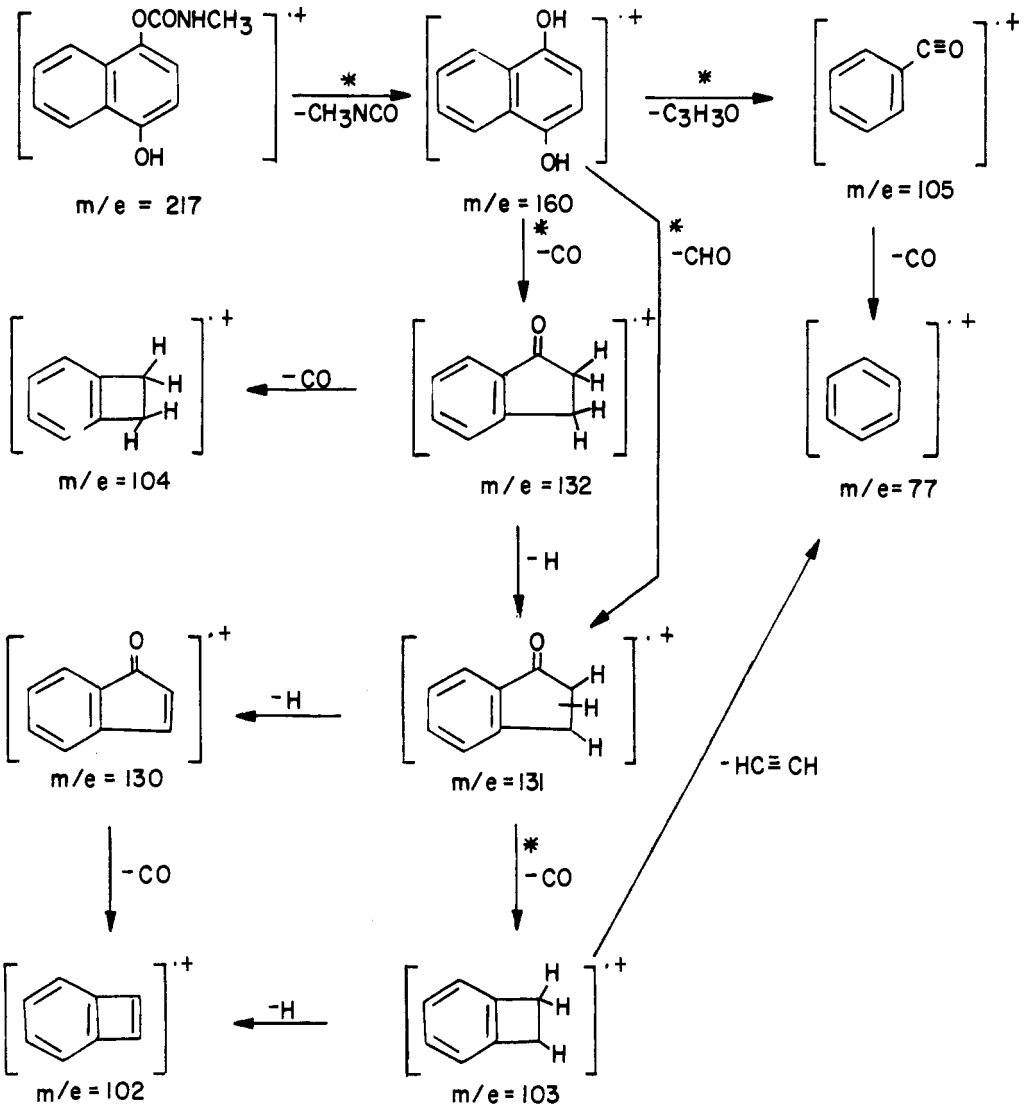
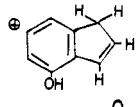
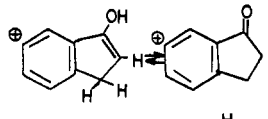
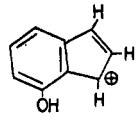
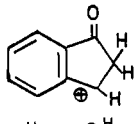
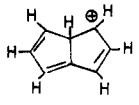
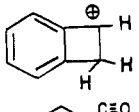
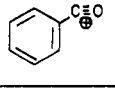


Figure 1. Breakdown of 4-hydroxy-1-naphthyl methylcarbamate. * Supported by a metastable species

Table IV. Mass Measurement of Selected Fragments from 4- and 6-Hydroxy-1-naphthyl Methylcarbamate

Parent	Observed	Calculated	Fragment	Possible Structure
6-	132.057368	132.057611	C_9H_8O	
4-	132.075449	132.057611	C_9H_8O	
6-	131.049646	131.049786	C_9H_7O	
4-	131.049516	131.049786	C_9H_7O	
6-	103.054614	103.054772	C_8H_7	
4-	103.055814	103.054772	C_8H_7	
4-	105.035688	105.034037	C_7H_5O	

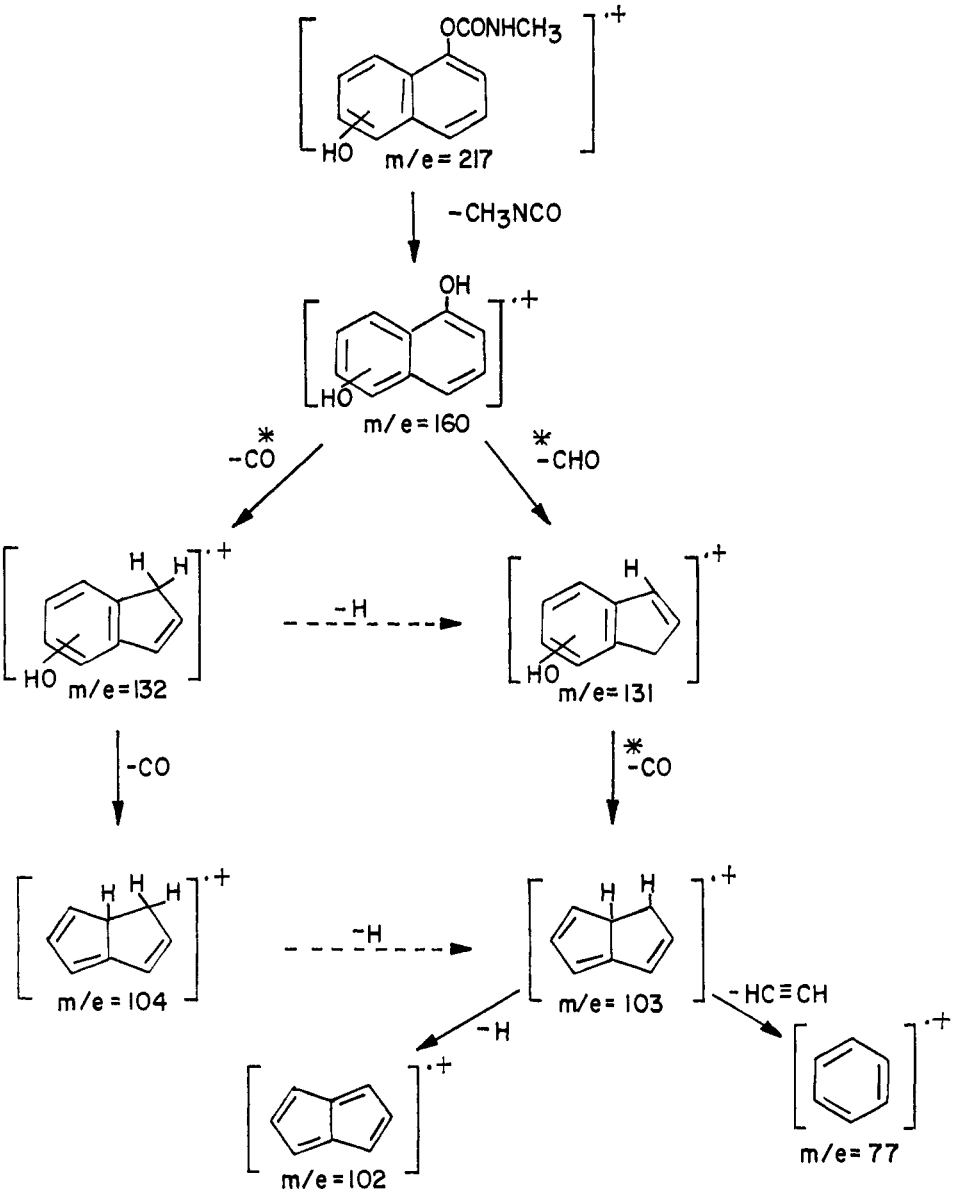


Figure 2. Breakdown of 5-, 6-, and 7-hydroxy-1-naphthyl methylcarbamates. * Supported by a metastable species

EXPERIMENTAL

The nmr spectra were obtained on a Varian 60 or 100 megacycle instrument, infrared spectra were determined on a Baird Atomic 4-55 recording infrared spectrophotometer, and mass spectra were obtained with an A.E.I. MS902b high-resolution mass spectrometer. The tlc studies were carried out on E. Merck Silica Gel-F fluorescent plates. The results are summarized in Table I.

The infrared and nmr results were consistent with high purity (Durden, 1971; Knaak *et al.*, 1965), as were the tlc studies. The mass spectra were obtained under essentially constant conditions; in each case the molecular ion was confirmed by a low-voltage spectrum. The relative intensities of certain of the fragments encountered are summarized in Table II, while the metastable species observed and the processes they define are presented in Table III. Finally, certain of the important fragments in the spectra of the 4- and 6-isomers were mass-measured and these results, together with a possible structure for each fragment measured, are presented in Table IV.

DISCUSSION

The breakdown pathways for these isomeric hydroxycarbaryls are presented in Figures 1 and 2. The specific structures presented for the fragments in Table IV and in Figures 1 and 2 have been assigned to assist in the interpretation of the spectra, and should be regarded only as formal representations.

In each isomer the molecular ion carries a relatively small fraction of the total ion current and, in each case, the P-57 (*m/e* 160) fragment is important (this is the 100% peak in the 4-, 5-, and 7-isomers). The loss of CO from the *m/e* 160 fragment to *m/e* 132 is also a major decomposition in each case, and is supported by the occurrence of a metastable species at *m/e* 109 (in the case of the 6-isomer the *m/e* 132 fragment is the 100% peak). The loss of a CHO fragment from the *m/e* 160 fragment to the *m/e* 121 is apparently important with each isomer and is supported by a metastable species at *m/e* 107.4. The subsequent decomposition of this fragment to *m/e* 103 is supported by a metastable peak at *m/e* 81. The spectrum of 4-hydroxycarbaryl possesses additionally a rela-

tively important *m/e* 105 fragment which apparently arises from the *m/e* 160 fragment, as indicated by a metastable signal at *m/e* 69.

The loss of CO from the *m/e* 160 fragments arising from the 5-, 6-, or 7-hydroxy isomers could be considered to give rise to a fragment which could be formalized as an indenol, while the corresponding fragment from the 4-hydroxy isomer could be formalized as 1-indanone. Various peaks and their relative importance from the mass spectra of 1-indanone (Bowie, 1966) and 4- and 7-indenol (Sharkey, 1969) are recorded in Table II for comparison with the spectra of the hydroxycarbaryl isomers. Although similarities are noted, the spectra of these materials do not offer substantial aid in the understanding of the fragmentation of the hydroxynaphthyl carbamates.

Consideration of the results leads to the conclusion that 4- and 6-hydroxy-1-naphthyl methylcarbamate should be distinguishable by mass spectral techniques. The relative importance of the *m/e* 105 peak and its association with the *m/e* 160 peak in the case of the 4-isomer, the intensity of the *m/e* 103 peak in the 6-isomer, and the fact that the 100% peak is at *m/e* 160 in the 4- and *m/e* 132 in the 6-isomer are unique features in the spectra of these compounds.

ACKNOWLEDGMENT

Gratitude is expressed to W. J. Lambdin and B. E. Wilkes for determining the mass spectra of these materials and for the mass measurement of various fragments.

LITERATURE CITED

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Received for review November 6, 1970. Accepted February 5, 1971.