

## A Study of the Fragmentation Processes of Some Pyridones on Electron Impact\*

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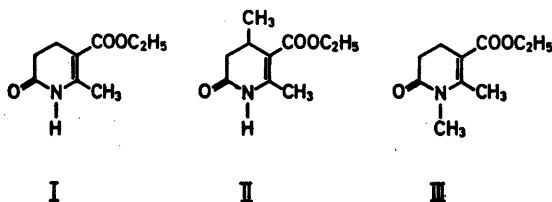
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The mass spectra of three 3,4-dihydro-5-carbethoxy-2-pyridones, six 4-hydroxy-5-carbethoxy-2-pyridones, 3-carbethoxy-4-hydroxy-6-methyl-2-pyridone, 4-hydroxy-6-methyl-2-pyridone, and 5-acetyl-6-methyl-3,4-dihydro-2-pyridone are reported and discussed. Upon electron impact the pyridones break down in a well defined manner and different fragmentation paths are suggested.

As a part of an investigation<sup>1,2</sup> on the behaviour of lactams upon electron impact, it was thought desirable that the mass spectra of some available pyridones should be determined and interpreted. This paper gives details of the mass spectra of twelve pyridones I—XII, which are summarized in Figs. 1—5. As seen below, certain fragmentations were observed, for which alternative paths are postulated. Further considerations will be made when suitably labeled compounds have been prepared.

### Substituted 3,4-dihydro-5-carbethoxy-2-pyridones



\* Part XCV of a series of papers on "Mass Spectrometry in Structural and Stereochemical Problems"; for paper XCIV see L. Tökes and C. Djerassi, *Steroids*, in print.

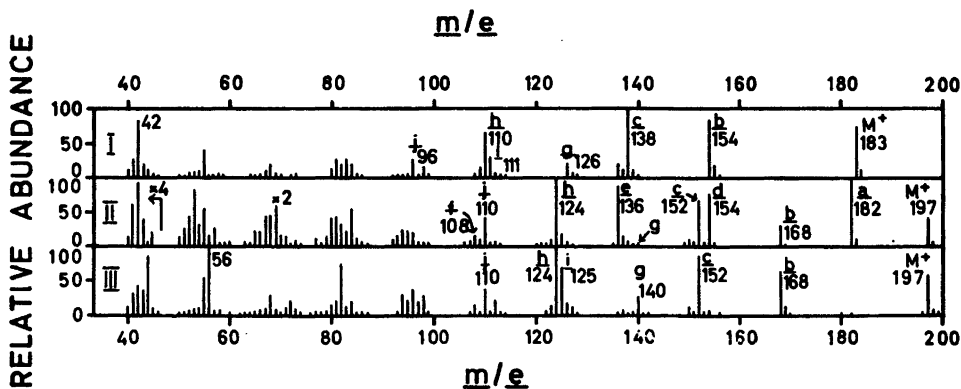
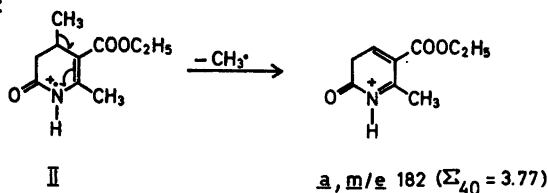
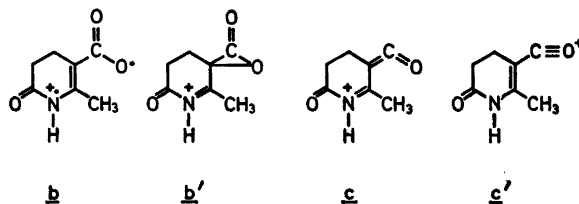


Fig. 1.

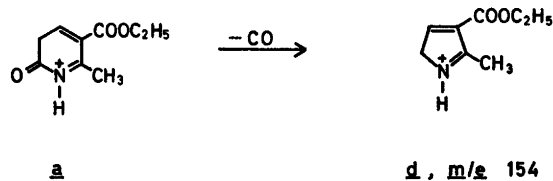
All three spectra (Fig. 1) display prominent molecular ions ( $\Sigma_{40} = 7.55$ , 1.54, and 4.12 for compounds I, II, and III, respectively). The molecular ion may be formed by removal of a non-bonding electron from either nitrogen or oxygen.<sup>1,3</sup> Compound II shows an abundant ion at  $m/e$  182 ( $M-15$ ) and this facile expulsion of a methyl radical ( $II \rightarrow a$ ) is due to its position  $\beta$  to the double bond:



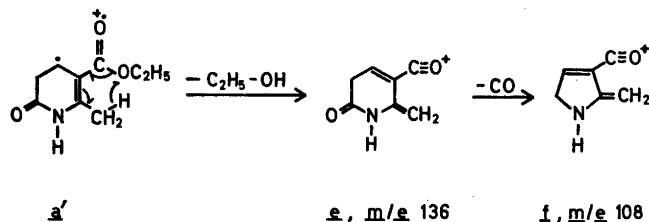
Fragmentation of the carboxy-group results in loss of both ethyl and ethoxy radicals, and all three spectra (I–III) exhibit peaks corresponding to  $M-29$  ions ( $\Sigma_{40} = 8.81$ , 1.21, and 4.74, respectively). The  $M-29$  ion, in the case of compound I, may be represented by either  $b$  or  $b'$ ; the  $M-45$  ion by  $c$  or  $c'$ :



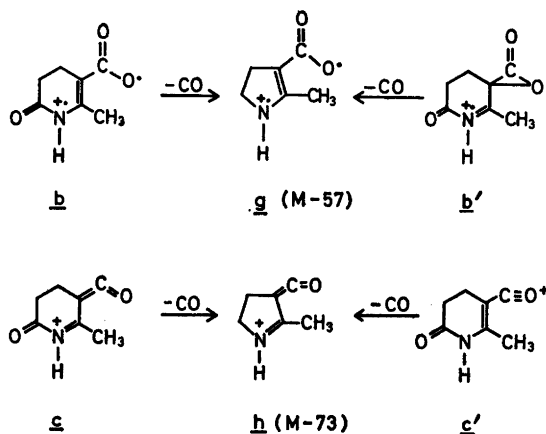
The mass spectrum of II differs from the spectra of I and III by abundant peaks corresponding to  $M-43$  ( $\Sigma_{40} = 2.49$ ) and  $M-61$  ( $\Sigma_{40} = 3.35$ ). The  $M-43$  peak may be due to loss of carbon monoxide from the  $M-\text{CH}_3$  ion  $a$ . (Loss of carbon monoxide in connection with ring contraction in the fragmentation of various aromatic and heteroaromatic compounds has recently been discussed<sup>4</sup>).



The M—61 ( $m/e$  136) ion can arise from loss of ethanol from the ion  $a'$  (about the "ortho effect"<sup>5</sup>). The subsequent expulsion of carbon monoxide from the ion  $e$  producing the ion  $f$  may be responsible for the peak at  $m/e$  108 ( $\Sigma_{40}=0.60$ ).



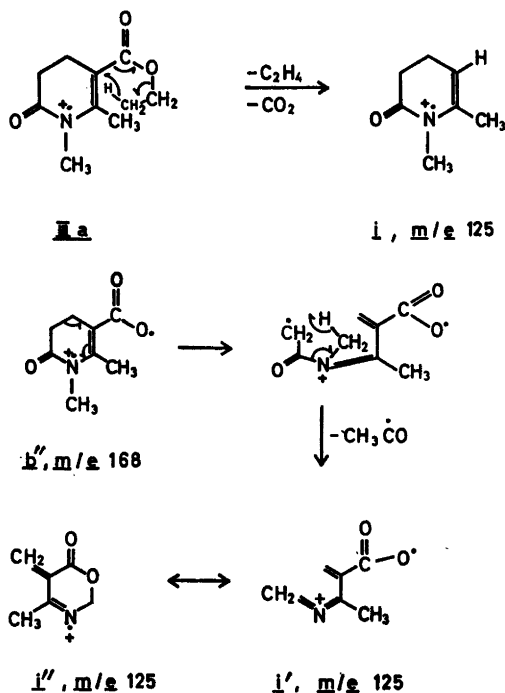
Peaks corresponding to loss of carbon monoxide from the M—Et and M—OEt ions ( $b$  and  $c$ ) are found in all three spectra (I—III) at M—57 ( $\Sigma_{40} = 2.03, 0.15,$  and  $1.51,$  respectively) and at M—73 ( $\Sigma_{40} = 6.39, 3.77,$  and  $6.67,$  respectively). In the case of I these ions may be represented by the structures  $g$  and  $h$  which could be formed by expulsion of carbon monoxide from either  $b$  or  $b'$  and  $c$  or  $c'$ .



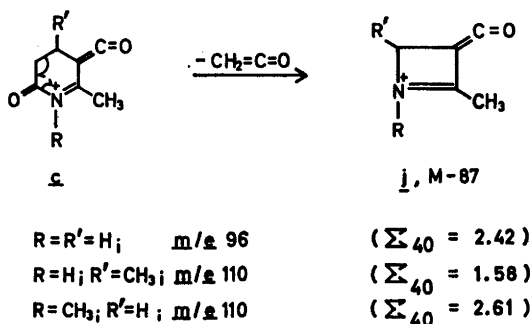
The formation of the M—57 ion by loss of carbon monoxide from the M—Et ion of compound III is confirmed, at least in part, by a metastable ion at  $m/e$  117.0 ( $140^2/168 = 116.7$ ).

All the spectra I—III display peaks corresponding to M—72 ( $\Sigma_{40} = 2.90, 0.68,$  and  $4.81,$  respectively). As illustrated for compound III, this fragmentation would correspond to a concerted loss of ethylene and carbon dioxide

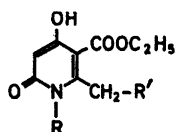
from the molecular ion *IIIa* to give *i*. The appearance of a metastable ion in the spectrum of compound III at mass 93.0 ( $125^2/168 = 93.0$ ) implies that at least a portion of the ion *i* at mass 125 ( $M-72$ ) arises from the  $M-Et$  species by loss of 43 mass units, and the mechanism  $b'' \rightarrow i'$  ( $m/e$  125) could be involved in this ion's genesis.



Finally, loss of ketene from the  $M-OEt$  ion *c* may be responsible for the  $M-87$  ion. This hypothesis receives support from the presence of a metastable ion at  $m/e$  79.6 ( $110^2/152 = 79.6$ ) in the spectrum of compound III.



## 4-Hydroxy-5-carbethoxy-2-pyridones



IV : R' = H ;	R = H ;
V : R' = CH <sub>3</sub> ;	R = H ;
VI : R' = CH <sub>2</sub> -CH <sub>3</sub> ;	R = H ;
VII : R' = H ;	R = C <sub>6</sub> H <sub>5</sub> ;
VIII : R' = H ;	R =  O-CH <sub>3</sub> ;
IX : R' = H ;	R =  CH <sub>3</sub> ;

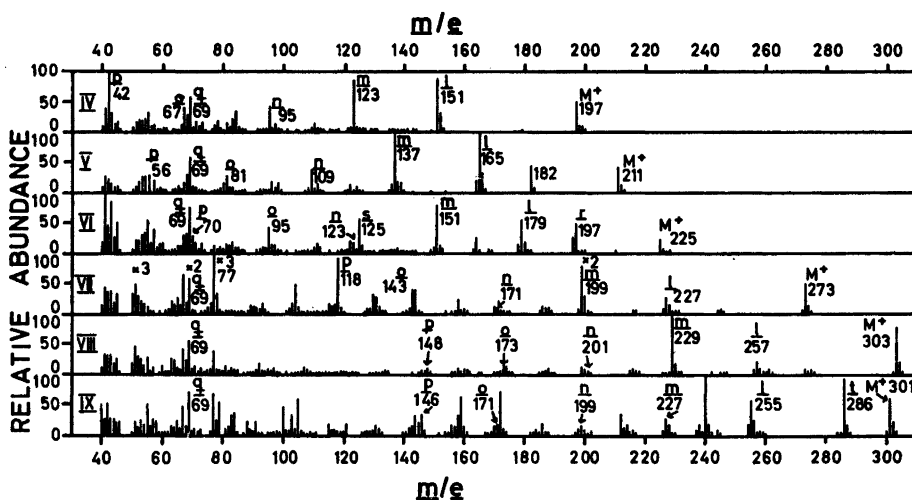


Fig. 2.

The mass spectra (Fig. 2) of the pyridones (IV–IX) resemble each other and the abundant peaks at  $M-45$ ;  $M-46$ ;  $M-74$ ;  $M-102$ ;  $M-130$ ;  $M-155$ , and  $m/e$  69 are found in all spectra. The corresponding  $\Sigma_{40}$ -values are listed in Table 1.

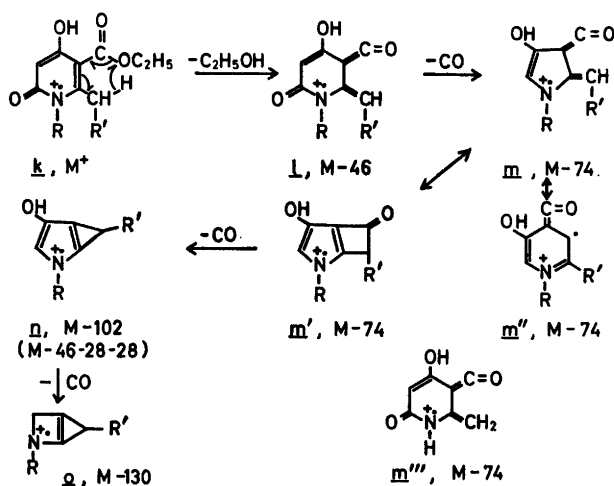
As seen from the table the  $\Sigma_{40}$ -values of the molecular ions are of the same magnitude as that of the pyridones I–III. Further the  $M-45$  peaks are considered to be due to loss of an ethoxy radical from the carbethoxy group and structures similar to *c* and *c'* are suggested for these ions.

The  $M-46$ ,  $M-74$ ,  $M-102$ , and  $M-130$  peaks can be explained by assuming the initial loss of ethanol from the molecular ion *k* ( $k \rightarrow l$ ) followed

Table 1.

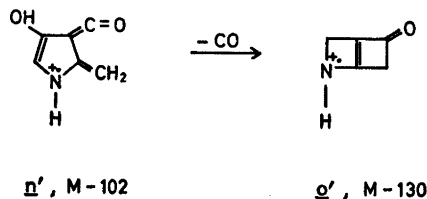
	IV	V	$\Sigma_{40}$ VI	VII	VIII	IX
M <sup>+</sup>	4.16	3.98	1.33	2.36	5.77	2.67
M-45	2.63	2.94	1.01	0.64	0.75	1.02
M-46	7.39	9.47	3.41	1.23	1.57	2.40
M-74	7.73	9.19	4.93	7.68	7.49	1.07
M-102	3.48	3.50	0.73	0.44	0.45	0.58
M-130	3.40	2.46	2.59	1.82	1.20	0.62
M-155	8.49	2.75	1.45	4.48	0.67	1.42
<i>m/e</i> 69	4.84	5.51	4.61	5.61	3.97	3.07

by a subsequent step-wise loss of three moles of carbon monoxide giving the ions *m*, *n*, and *o*, as depicted below.



In the case of compound VI the origin of the M-74 species could be visualized as an initial loss of ethanol from the molecular ion followed by either the expulsion of carbon monoxide (formation of *m* ( $R' = C_2H_5, R = H$ )) or alternatively ethylene (formation of  $m'''$ ). High-resolution mass spectrometry indicated that the species *m* ( $C_8H_9NO_2$ ) and  $m'''$  ( $C_7H_8NO_3$ ) each contribute one half of the ion yield at mass 151.

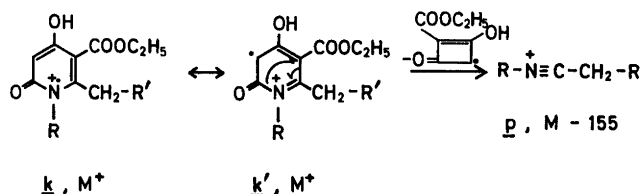
High-resolution mass measurements were made on the peaks at *m/e* 123 (M-102) and *m/e* 95 (M-130) in the spectrum of compound VI. Both were multiplets having the composition listed in Table 2. The genesis of these ions can be visualized as:  $m''' \xrightarrow{-CO} n'' (m/e 123)$ ;  $m' \xrightarrow{-CO} n (R = H; R' = CH_2CH_3; m/e 123)$ ;  $n' \xrightarrow{-CO} o' (m/e 95)$ ;  $n \xrightarrow{-CO} o (R = H; R' = CH_2CH_3; m/e 95)$ ;



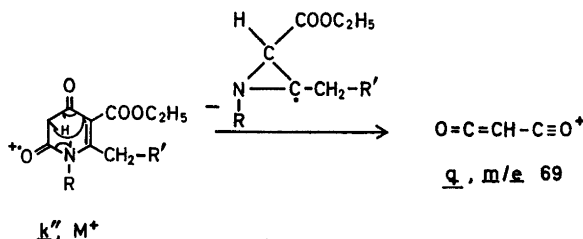
The M-155 peak may be due to the loss of a 4-membered cyclic radical resulting in the stable quaternary ammonium ion *p* as shown below and is apparently associated with the energy gained in forming a stable ion *p* as well as a resonance stabilized radical.

Table 2. High-resolution mass spectral measurements of some ions of 4-hydroxy-5-carbomethoxy-6-propyl-2-pyridone (VI).

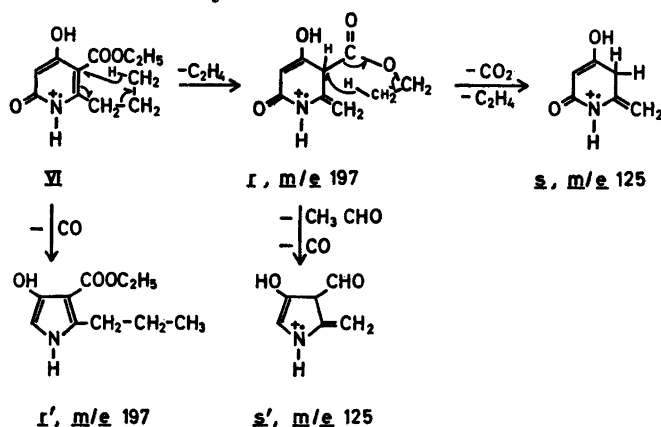
<i>m/e</i>	observed	calculated	composition	
151	151.0268	151.0269	C <sub>8</sub> H <sub>9</sub> NO <sub>3</sub> (50 %)	M-C <sub>4</sub> H <sub>10</sub> O
	151.0634	151.0633	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub> (50 %)	M-C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>
125	125.0466	125.0477	C <sub>6</sub> H <sub>7</sub> NO <sub>2</sub>	M-C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>
123	123.0312	123.0320	C <sub>6</sub> H <sub>7</sub> NO <sub>2</sub> (60 %)	M-C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>
	123.0676	123.0684	C <sub>7</sub> H <sub>9</sub> NO (40 %)	M-C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>
95	95.0361	95.0371	C <sub>6</sub> H <sub>7</sub> NO (90 %)	M-C <sub>6</sub> H <sub>10</sub> O <sub>3</sub>
	95.0486	95.0497	C <sub>6</sub> H <sub>7</sub> O (5 %)	M-C <sub>5</sub> H <sub>8</sub> NO <sub>3</sub>
	95.0726	95.0735	C <sub>6</sub> H <sub>7</sub> N (5 %)	M-C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>
69	68.9976	68.9977	C <sub>3</sub> HO <sub>2</sub>	M-C <sub>8</sub> H <sub>14</sub> NO <sub>2</sub>



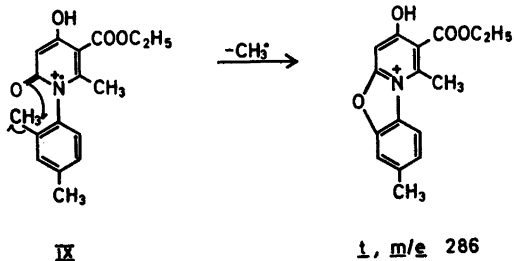
The rather abundant peak at *m/e* 69 found in all six spectra (IV-IX), regardless of substitution at C-6 or on the nitrogen atom, may be assigned to *q*, and high-resolution mass spectrometry established C<sub>3</sub>HO<sub>2</sub> as the composition of this ion in the spectrum of compound VI.



By comparing the mass spectra of IV, V, and VI it is found that the spectrum of VI exhibits abundant ions corresponding to  $M-28$  and  $M-100$  ( $\Sigma_{40} = 2.91$  and  $3.47$ , respectively) in contrast to the spectra of IV ( $\Sigma_{40} = 0.08$  and  $1.02$ ) and V ( $\Sigma_{40} = 0.57$  and  $1.23$ ). The  $M-28$  fragment could arise from the expulsion of ethylene from the propyl group resulting in the ion  $r$  ( $m/e$  197) or from the loss of carbon monoxide from the lactam carbonyl group and formation of  $r'$  ( $m/e$  197). Rearrangement of the ion  $r$  by a simultaneous loss of carbon dioxide and ethylene would lead to the  $M-100$  ion  $s$  ( $m/e$  125). If acetaldehyde and carbon monoxide (the latter from the lactam carbonyl group) were eliminated from the species  $r$  then the charged species produced would correspond to  $s'$  ( $m/e$  125). In the absence of the appropriately deuteriated analogs no distinction can be drawn between the representations  $s$  and  $s'$  for the ion of mass 125 in the spectrum of VI. High-resolution mass spectrometry demonstrated the homogeneity and composition of the peak at  $m/e$  125 as  $C_6H_7NO_2$  in agreement with this ion's designation as  $s$  and  $s'$ . An alternative mode of formation for the ion  $s'$  ( $m/e$  125) would be *via* the loss of ethylene and acetaldehyde from  $r'$ .



The three compounds of this group (VII, VIII and IX) which contain either phenyl or a substituted phenyl group attached to the ring nitrogen atom, display ions in their respective spectra corresponding to the charged aromatic moiety. Compound IX is unique amongst those investigated in respect to the presence of a very strong  $M-15$  peak ( $\Sigma_{40} = 4.09$ ) in its spectrum. The origin of this ion can be depicted by  $IX \rightarrow t$ , ( $m/e$  286).





## 3-Carbethoxy-4-hydroxy-6-methyl-2-pyridone (X)

From the spectrum (Fig. 3) of the only 3-carbethoxy derivative investigated it is apparent that it shows a striking difference from the 5-carbethoxy derivatives IV–IX. Thus the base peak in the 3-carbethoxy derivative occurs at  $m/e$  125 (M–72) and the presence of a metastable ion at mass 102.1 ( $125^2/153 = 102.1$ ) indicates that at least a portion of the ion yield at  $m/e$  125 arises by the loss of 28 mass units from the ion of mass 153 (M–44).

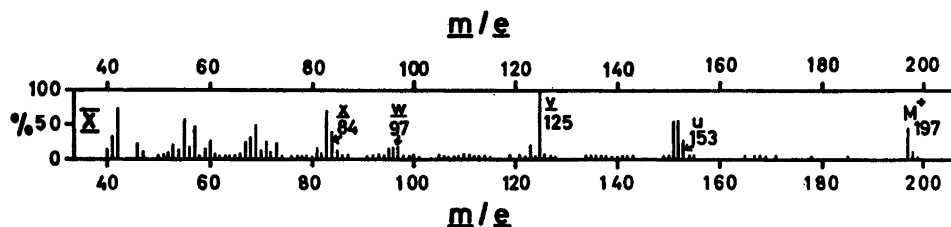


Fig. 3.

The latter peak was of some interest as it could arise from the molecular ion (verified by the observation of a metastable ion at mass 118.8 ( $153^2/197 = 118.8$ ) according to either of two mechanisms  $X \rightarrow u$ , ( $m/e$  153) or  $X \rightarrow u'$  ( $m/e$  153), the latter postulate requiring an alkyl (ethyl) migration, examples of which are relatively few in mass spectrometry.<sup>6-9</sup>

High-resolution mass spectrometry unequivocally eliminated the species  $u'$  from consideration in establishing the composition of the peaks at  $m/e$  153, 152, 151, 125, and 123 to correspond to the elimination of  $\text{CH}_3\text{CHO}$ ,  $\text{OEt}$ ,  $\text{EtOH}$ , ( $\text{CH}_3\text{CHO} + \text{CO}$ ), and ( $\text{EtOH} + \text{CO}$ ), respectively.

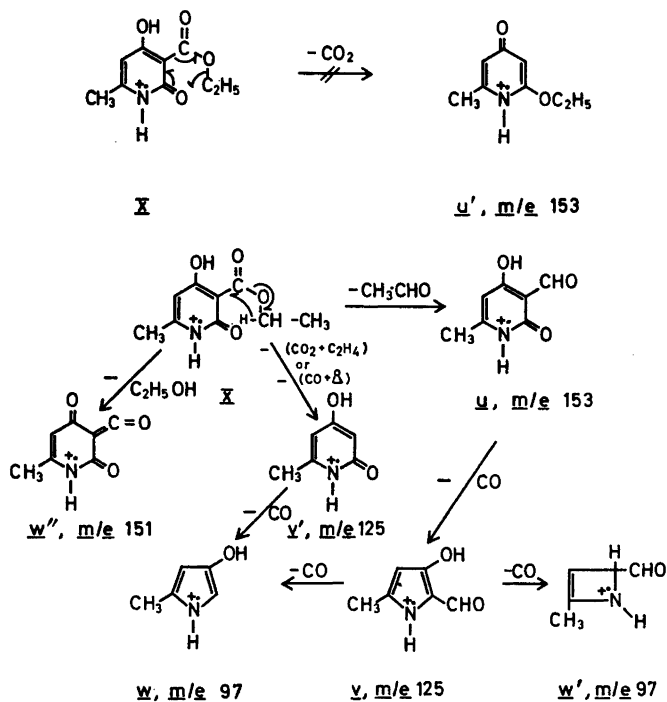
Elimination of carbon monoxide from the lactam carbonyl group of  $u$  would yield the fragment  $v$ ,  $m/e$  125. Portion of the ion yield at  $m/e$  125 could also arise from the molecular ion of X *via* a synchronous mechanism with the formation of  $v'$  ( $m/e$  125) and either carbon dioxide and ethylene or alternatively carbon monoxide and ethylene oxide as neutral entities. Deuterium labeling of the terminal methyl of the carbethoxy group will be required to test the validity of this proposal.

Table 3. High-resolution mass spectral measurements of some ions of 3-carbethoxy-4-hydroxy-6-methyl-2-pyridone (X).

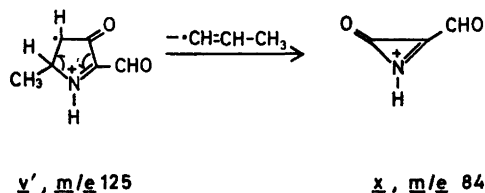
$m/e$	observed	calculated	composition
153	153.0426	153.0418	$\text{C}_7\text{H}_7\text{NO}_3$ $\text{M} - \text{C}_2\text{H}_4\text{O}$
152	152.0348	152.0343	$\text{C}_7\text{H}_6\text{NO}_3$ $\text{M} - \text{C}_2\text{H}_5\text{O}$
151	151.0269	151.0269	$\text{C}_7\text{H}_5\text{NO}_3$ $\text{M} - \text{C}_3\text{H}_4\text{O}$
125	125.0460	125.0460	$\text{C}_6\text{H}_5\text{NO}_2$ $\text{M} - \text{C}_5\text{H}_4\text{O}_2$
123	123.0320	123.0320	$\text{C}_6\text{H}_5\text{NO}_2$ $\text{M} - \text{C}_5\text{H}_4\text{O}_2$

The appearance of a metastable ion at mass 75.3 ( $97^2/125 = 75.3$ ) in the spectrum of compound X showed that the further loss of carbon monoxide from the ion *v* generates the ion *w*, (*m/e* 97) or *w'* (*m/e* 97).

The "ortho effect"<sup>5</sup> can be invoked to explain the expulsion of ethanol from X — the product being formulated as *w''* (*m/e* 151). This latter species can then expel carbon monoxide (from either of the carbonyl groups) to produce the ion of mass 123 (*M*−74). Finally, inspection of the spectrum shows, that the sequence *M*−74 → *M*−102 → *M*−130, found in the spectra of compounds IV–IX, also is observed although in this instance the peaks are not so intense.



The presence of a metastable ion at mass 56.5 ( $84^2/125 = 56.4$ ) in the spectrum of X indicates the transition *v'* → *x*:



## 4-Hydroxy-6-methyl-2-pyridone (XI)

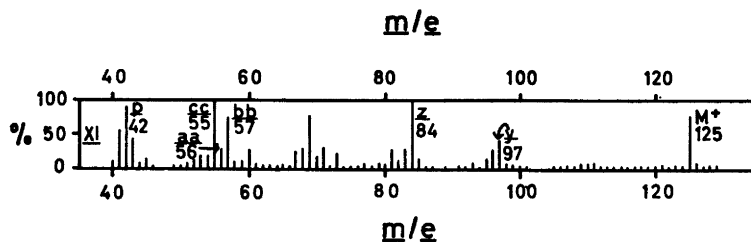
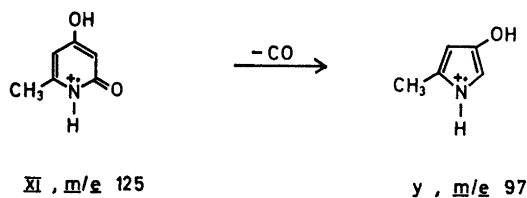
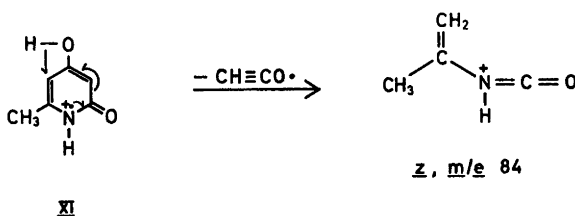


Fig. 4.

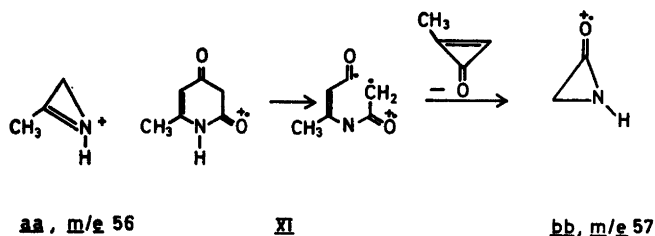
The spectrum of this compound (Fig. 4) displays a strong molecular ion peak ( $\sum_{40} = 5.92$ ) while the loss of 28 mass units (carbon monoxide) also affords an ion of high yield ( $\sum_{40} = 3.19$ ), which can be assigned structure *y* ( $m/e$  97).



The base peak in the spectrum occurs at  $m/e$  84 ( $M-41$ ) which may have its origin according to  $XI \rightarrow z$ , ( $m/e$  84) and this postulate is in agreement with the composition  $C_4H_6NO$  determined for this fragment by high-resolution mass spectrometry.



The ion at mass 69 ( $\sum_{40} = 5.49$ ) in the spectrum of compound XI can be assigned structure *g*, on the basis of its composition ( $C_3HO_2$ ) which was determined by high-resolution mass spectrometry. A peak at  $m/e$  56 ( $\sum_{40} = 2.20$ ) may arise by expulsion of carbon monoxide from the ion *z* and this species may correspond to *aa*,  $M-69$ . A possible genesis for the ion of mass 57 ( $M-68$ ) is given by the sequence  $XI \rightarrow bb$ , ( $m/e$  57) and high-resolution mass spectrometry established its composition as  $C_2H_3NO$  (80%) contaminated with a  $C_3H_7N$  species.



An ion of high yield at mass 55 ( $M-70$ ) in the spectrum of compound XI was shown by high-resolution precision to consist of a multiplet of the composition  $C_3H_3O$  (70%),  $C_2HNO$  (20%), and  $C_3H_5N$  (10%). The preponderant ion probably corresponds to *cc* representing carbon atoms 3, 4, and 5 of the pyridone ring. It is difficult to present an explanation for the formation of the species  $C_2HNO$  while the minor constituent of the mixture may be *cc'* representing C-5, C-6 plus its methyl group, and the ring nitrogen atom.



Table 4. High-resolution mass spectral measurements of some ions of 4-hydroxy-6-methyl-2-pyridone (XI).

<i>m/e</i>	observed	calculated	composition	
84	84.0453	84.0449	$C_4H_6NO$	$M-C_2HO$
69	68.9975	68.9977	$C_3HO_2$	$M-C_3H_2N$
57	57.0212	57.0215	$C_2H_2NO$ (80%)	$M-C_2H_4O$
	57.0577	57.0578	$C_3H_7N$ (20%)	$M-C_3O_2$
55	55.0187	55.0184	$C_3H_3O$ (70%)	$M-C_2H_4NO$
	55.0122	55.0058	$C_2HNO$ (20%)	$M-C_4H_6O$
	55.0424	55.0422	$C_3H_5N$ (10%)	$M-C_3H_2O_2$

5-Acetyl-6-methyl-3,4-dihydro-2-pyridone (XII)

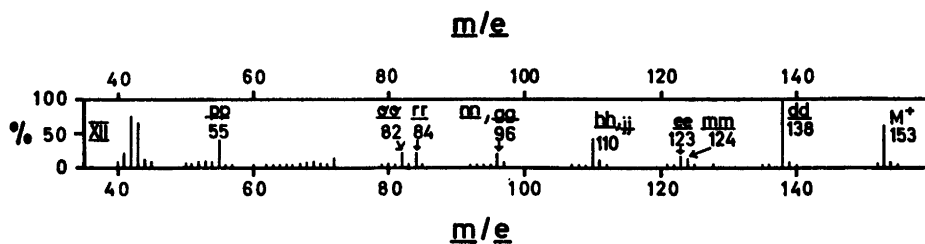


Fig. 5.

Compound XII, (Fig. 5) as would be predicted, showed an intense peak in its spectrum corresponding to the elimination of the methyl group of the methyl ketone and the resulting ion would be *dd*, ( $m/e$  138) ( $\Sigma_{40} = 13.35$ ). The less abundant ion *ee* ( $\Sigma_{40} = 2.14$ ) at mass 123 ( $M-30$ ) probably arises from the loss of a C-6 methyl radical from *dd*. A metastable ion at mass 67.0 ( $96^2/138 = 66.8$ ) testifies to the loss of 42 mass units from the ion *dd* ( $m/e$  138) and this elimination can be attributed to the elimination of ketone and generation of *gg* ( $m/e$  96) by a retro-Diels-Alder reaction.<sup>10</sup> High-resolution mass spectrometry (Table 5) is consistent with 80 % of the ion yield at mass 96 being assigned structure *gg* while the remainder corresponds to  $C_6H_{10}N$  and a mechanistic interpretation of this fragment is attempted below.

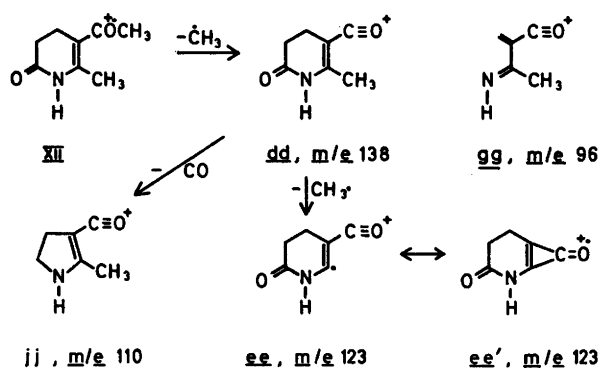
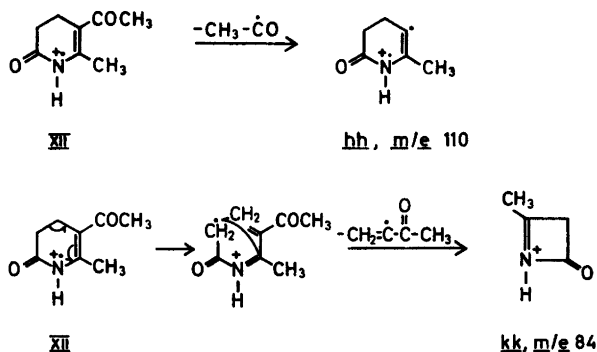


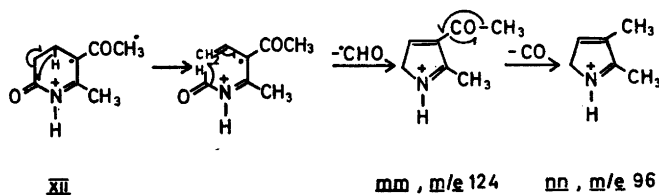
Table 5. High-resolution mass spectral measurements of some ions of 3,4-dihydro-2-pyridone (XII).

$m/e$	observed	calculated	composition
125	125.0830	125.0841	$C_7H_{11}NO$ M-CO
124	124.0753	124.0762	$C_7H_{10}NO$ M-CHO
110	110.0611	110.0606	$C_6H_9NO$ M- $C_2H_5O$
96	96.0435	96.0449	$C_5H_7NO$ (80 %) M- $C_3H_5O$
	96.0800	96.0813	$C_6H_{10}N$ (20 %) M- $C_2HO_2$
84	84.0424	84.0449	$C_4H_6NO$ M- $C_2H_5O$
82	82.0639	82.0657	$C_5H_7N$ M- $C_2H_5O_2$
55	55.0184	55.0184	$C_3H_3O$ M- $C_2H_5NO$
43	43.0184	43.0184	$C_2H_2O$ M- $C_2H_5NO$
42	42.0344	42.0344	$C_2H_4N$ (90 %) M- $C_2H_7O_2$
	42.0106	42.0106	$C_2H_2O$ (10 %) M- $C_2H_7NO$

The intense ion peak at mass 110 ( $M-43$ ) can be visualized as arising via the process  $\text{XII} \rightarrow hh$  ( $m/e$  110) while the peak at  $m/e$  84 ( $M-69$ ) may arise according to the mechanism  $\text{XII} \rightarrow kk$ , ( $m/e$  84). Both postulates were supported by the results from high-resolution mass spectrometry which established the compositions  $C_6H_9NO$  and  $C_4H_6NO$ , respectively, for these fragment ions.



The composition (from high-resolution mass measurement) of the peak at  $m/e$  124 ( $M-29$ ) in the spectrum of compound XII corresponds to  $\text{C}_7\text{H}_{10}\text{NO}$  ( $M-\text{CHO}$ ). Furthermore, 20 % of the ion yield at mass 96 ( $M-57$ ) consisted of the species  $\text{C}_6\text{H}_{10}\text{N}$  ( $M-\text{C}_2\text{HO}_2$ ). Although a plausible mechanistic interpretation of the  $M-\text{CHO}$  peak can be presented (XII  $\rightarrow$   $mm$  ( $m/e$  124) no obvious reason exists for the expulsion of the elements  $\text{C}_2\text{HO}_2$  from the molecular ion. This latter fragment could be explained by the loss of carbon monoxide from the  $M-\text{CHO}$  species ( $mm$ ) — such a rationale involves the postulate of a methyl migration<sup>6-9</sup> — and the charged species is represented by  $nn$  ( $m/e$  96).



The peak at  $m/e$  82 ( $M-71$ ) in the spectrum of compound XII could arise from the loss of carbon monoxide from the fragment  $hh$  ( $m/e$  110) such that it can be represented by  $oo$ , ( $m/e$  82). High-resolution mass spectrometry showed this ion to have the empirical composition  $\text{C}_5\text{H}_8\text{N}$  which is in agreement with its assigned structure.

Fragment ions at mass 55 and 43 in the spectrum of compound XII were shown by high-resolution mass measurements (Table 5) to have the composition  $\text{C}_3\text{H}_3\text{O}$  and  $\text{C}_2\text{H}_3\text{O}$ , respectively. The former can be assigned structure  $pp$  ( $m/e$  55) while the latter would correspond to the acetyl cation ( $\text{CH}_3\text{C}\equiv\text{O}^+$ ). The composition of the peak at  $m/e$  42 corresponded to  $\text{C}_2\text{H}_2\text{O}$  (10 %) and  $\text{C}_2\text{H}_4\text{N}$  (90 %).



## EXPERIMENTAL

The low resolution mass spectra were obtained with a CEC 21-103 C instrument using an ionizing energy of 70 eV and ionizing current 50 mA and using a direct inlet system.<sup>11</sup> High resolution mass measurements were performed by Mr. R. G. Ross of Stanford University using an A. E. I MS-9 double focussing mass spectrometer.

The pyridones were prepared according to known methods.<sup>12-14</sup>

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