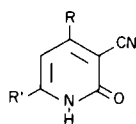


## Mass Spectra of Selected Alkyl- and Dialkyl-3-cyano-2-pyridones

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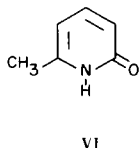
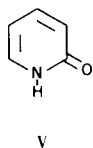
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6-Alkyl- and 4,6-dialkyl-3-cyano-2-pyridones are readily available compounds (I) whose mass spectra appear not to have been determined. It seemed of interest to obtain such spectra and to compare them with related 2- and 4-pyridones whose fragmentation patterns have been published. This paper describes the mass spectra of four cyanopyridones, namely, 6-methyl-3-cyano-2-pyridone (I), 4,6-dimethyl-3-cyano-2-pyridone (II), 6-(2-phenylethyl)-3-cyano-2-pyridone (III), and a cyanopyridone whose structure at the outset was either IVa or IVb (2), but which is shown below to actually be IVb.



- I. R = H, R' = CH<sub>3</sub>  
 II. R = R' = CH<sub>3</sub>  
 III. R = H, R' = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 IVa. R = CH<sub>3</sub>, R' = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>  
 IVb. R = CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>

The results are summarized in Table I. This Table shows that the mass spectrum of each of the cyanopyridones contained a molecular ion. This ion was the most abundant one in the spectra of I and II, but it constituted only 22.9% and 19.8% of the base peak (mass 91) in the spectra of III and IVa or IVb, respectively. The large abundance of the molecular ions of I and II are similar to those observed in the spectra of the parent 2-pyridone (V) (3,4) and in 6-methyl-2-pyridone (VI) (5). That the 2-phenylethyl derivatives III and IVa or IVb afforded only small parent ions may be ascribed to the great propensity for cleavage of bonds β- to a benzene ring to afford tropylium ion (mass 91) (6).



Next, Table I shows that less than 1% of parent minus one (M-1) was observed in the spectra of I and II while 9.5% and 2.3% of such ions were observed in the spectra of III and IVa or IVb, respectively. In the case of the latter pyridones, the hydrogen lost is apparently that on the nitrogen atom since the structurally similar 1,2-diphenylethane affords less than 1% of M-1 (7). However, the lower value in the spectrum of the unknown (IVa or IVb) suggests the *N*-hydrogen atom is in a different environment than in III as would be the case if the unknown were IVb.

Table I also shows that the loss of carbon monoxide followed by the loss of a hydrogen atom was a major fragmentation mode in methyl derivatives I and II. Thus, M-28 and M-29 fragments constituted 32.4% and 72.8% of the base peak, respectively, in the spectrum of compound I. Corresponding ions in the spectrum of II were present to the extent of 26.5% and 66.8%, respectively. These results are analogous to methylpyridone VI where the M-29 peak was the most abundant one in the spectrum (5). In contrast, the spectra of the 2-phenylethyl derivatives III and IVa or IVb did not contain M-28 and M-29 fragments presumably because of the above mentioned scission of the external β-carbon-carbon bond.

In the case of dimethyl derivative II, the loss of carbon monoxide (M-28) followed by loss of a hydrogen atom (M-29) was confirmed by the presence in the spectrum of metastable peaks at masses 97.3 and 118.1, respectively (eq. 1). Further verification for this sequence was obtained by exact mass measurement of the ions of

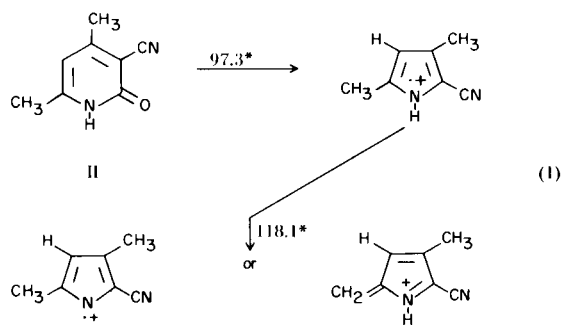


TABLE I

Relative Intensities of Selected Fragments in the Mass Spectra of Alkyl- and Dialkyl-3-cyano-2(1)-pyridones

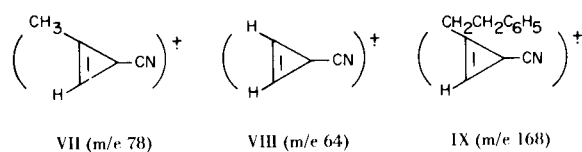
m/e	I	II	III	IV b
M <sup>+</sup>	100	100	22.9	19.8
M-1	<1	<1	9.5	2.3
M-28	32.4	26.5	0	0
M-29	72.8	66.8	0	0
M-77	0	0	4.0 (C <sub>8</sub> H <sub>7</sub> ON <sub>2</sub> )	1.2
M-78	0	0	1.7 (C <sub>8</sub> H <sub>6</sub> ON <sub>2</sub> )	0
91	0	0	100	100
78 (C <sub>6</sub> H <sub>6</sub> )	0	0	7.3	6.8
78 (C <sub>5</sub> H <sub>4</sub> N)	5.9	10.0	3.7	0
77 (C <sub>6</sub> H <sub>5</sub> )	0		14.0	12.0
77 (C <sub>5</sub> H <sub>3</sub> N)	1.7	(2.5)	0	0
64 (C <sub>5</sub> H <sub>4</sub> )	0		2.0	2.8
64 (C <sub>4</sub> H <sub>2</sub> N)	28	(3.6)	14.0	2.8
51	5.3	7.8	4.7	3.5
43	6.2	1.1	1.0	0.2
42	4.9	12.6	0	4.0
40	9.3	2.1	0	0.4

mass 120 and 119. The structures of these ions are apparently pyrroles (eq. 1), but this assignment may be open to question (8).

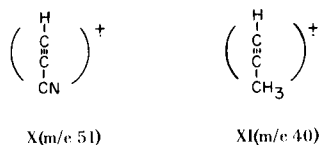
Next, fragments in the spectrum of the 2-phenylethyl derivative III which arise from the parent ion minus 77 (phenyl) and the parent ion minus 78 (phenyl plus hydrogen) were identified by exact mass measurement as C<sub>8</sub>H<sub>7</sub>ON<sub>2</sub> and C<sub>8</sub>H<sub>6</sub>ON<sub>2</sub>, respectively. Interestingly, the 2-phenylethyl derivative IVa or IVb likewise lost 77 mass units from the parent ion but at a suppressed level; in addition, compound IVa or IVb did not exhibit a rearrangement corresponding to the parent ion minus 78 mass units.

Table I further shows that abundant ions arising from the top half of the cyanopyridone rings were observed in the spectra of compounds I-III. Thus, ions of mass 78 from the 4,6-dimethyl derivative II were established by exact mass measurement to be C<sub>5</sub>H<sub>4</sub>N. Ions of mass 64 in the spectra of pyridones I and III (which do not contain a methyl group in the 4-position) were similarly established to be C<sub>4</sub>H<sub>2</sub>N. Based on earlier results with 2-pyrone (9) the structures of these ions (78 and 64) may tentatively be assigned to cyclopropenyl derivatives VII and VIII, respectively. It is noteworthy that an ion of mass 78 in the spectrum of IVa or IVb was absent. This

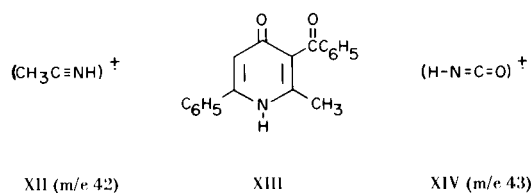
further suggests that the actual structure of pyridone IV is IVb since IVa would be expected to afford such an ion. On the other hand, the spectrum of IVa or IVb did contain an ion of mass 168 which is presumably due to the cyclopropenyl derivative IX; this fragment could arise from IVb, but not from IVa.



Finally, cyanopyridones I-IV exhibited two fragmentations which now appear to occur in most 2- and 4-pyridones. First, the spectra of each of these compounds contained an ion of mass 51 which may be assigned to the acetylene derivative X; this fragment can arise from scission of the right side of the respective ring systems. Similarly, the spectra of pyridones I and II contained an ion of mass 40 which would result from cleavage of the left side of the ring systems; this ion may be ascribed to methylacetylene XI. Such extrusions of substituted acetylenes in the spectra of various 4-pyrone and 3-acyl-4-pyridones have previously been demonstrated (10, 11).



Second, the spectra of the 6-methyl derivatives I and II contained ions of mass 42 which can be assigned to the imine derivative XII. Similar fragments arising from cleavage of the lower portion of the ring systems have also been observed in the spectra of acyl-pyridone XIII and related compounds (11). That the spectrum of the unknown pyridone IVa or IVb also afforded an ion of mass 42 appears to be proof that the actual structure of the compound is IVb since IVb, but not IVa, contains a 6-methyl group. Incidentally, the spectra of cyanopyridones I-IVb each contained an ion of mass 43 which can be ascribed to isocyanic acid derivative XIV. Such a fragmentation also would arise from cleavage of the lower portion of the ring systems.



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- (12) The mass spectra were obtained on a Consolidated Electrostatics Corp. Model 21:110 double-focusing mass spectrometer using a 100  $\mu\text{a}$  ionizing current, 70 volt ionizing voltage, and 8 KV accelerating voltage. In each case, the cyanopyridones were introduced directly into the source which was then gradually heated to 160-235° until a steady beam was obtained.

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