

from the OH group of the molecular ion (Scheme 1). This is in strong contradiction with the reported (6,7) H-scrambling in the molecular ions of pyridine and α - and β -picolines. It can be assumed therefore that the elimination of HCN from the M-NO ion is preceded by a skeletal rearrangement producing an anilinium type ion *a* (Scheme 1). Indeed, in the case of aniline, the source of the hydrogen eliminated from its molecular ion during HCN loss was shown to be mainly the amino group (8).

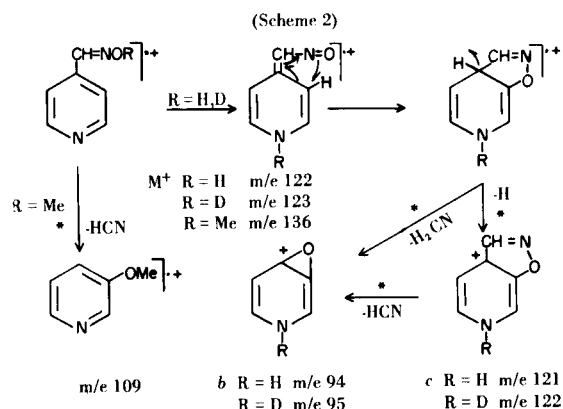
γ -Pyridine Aldoxime (IIa).

The mass spectrum of IIa (Table I) displayed an interesting feature in the elimination of 28 mass units from the molecular ion. It was learned from the high resolution spectrum of IIa that more than 90% of the M-28 peak (*m/e* 94) is due to the M-H₂CN ion (*b*), whereas only 7% corresponds to the elimination of the CO from the molecular ion (Scheme 2).

The expulsion of H₂CN proceeded in a concerted process ($M^{+\cdot} \rightarrow b$) as confirmed by the appropriate metastable peak. An alternative pathway for the formation of this ion *b* is also available through the loss of a hydrogen atom, followed by the elimination of the HCN molecule. This fragmentation sequences ($M^{+\cdot} \rightarrow c \rightarrow b$) was also confirmed by the metastable transitions.

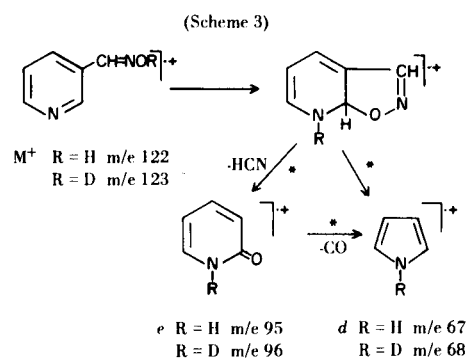
It may be suggested that the H₂CN eliminated from the molecular ion of the aldoxime IIa was made up from the side chain HCN, the ring nitrogen not being involved in this reaction. This could be supported by energetic considerations. Indeed the activation energy for the reaction $M^{+\cdot} \rightarrow (M-HCN)^{+\cdot}$ for *para*-substituted benzaldoxime *O*-methyl ethers was reported to be of about 1.4-2.0eV (9) (appearance-ionization potential differences being used as rough guides to the activation energies) (10). In the case of the oxime methyl ether V the energetical requirements for the reaction $M^{+\cdot} \rightarrow (M-HCN)^{+\cdot}$ were found to be of the same order: about 1.35eV, and the same value was practically obtained for the elimination of H₂CN from the molecular ion of the oxime IIa (Z.V.I. Zaretskii, unpublished results). In sharp contrast with these data the activation energy for the expulsion of HCN from the pyridine ring is more than twice as high: the AP-IP differences in pyridine and the isomeric picolines being of 3,5-4eV (Z.V.I. Zaretskii, unpublished results.) (7,11).

The fragmentation of the oxime IIa may include the tautomeric transformation of the molecular ion into the γ -pyridone form (Scheme 2). The hydroxyl hydrogen seems to play an important role in the suggested rearrangement. Indeed contrary to the oxime IIa, the methyl ether V, in which the tautomerism is prevented, displayed the intense elimination of HCN (Table I, *m/e* 109); the loss of H₂CN (*m/e* 108) was observed to a much lesser extent.



β -Pyridine Aldoxime (IIIa).

The β -isomer IIIa showed the intense formation of the *m/e* 67 ion. The fragment, formulated as the pyrrole ion-radical *d* (Scheme 3), arises both directly from the molecular ion, *via* a concerted process, and from the successive loss of HCN and CO. The last sequence was confirmed by the appropriate metastable peaks but in the case of the process ($M^{+\cdot} \rightarrow d$) such a peak was absent from the spectrum. The suitable metastable transition was, however, recognized by the defocusing technique. In both cases the formation of the ion *d* was accompanied by the retention of the hydroxyl hydrogen in the charged fragment. The unusual formation of the pyrrole ion can be rationalized as shown in Scheme 3.



A possible driving force for this sequence could lie in the initial migration of the hydroxyl H atom to the ring nitrogen. Indeed the methyl ether VI, in which the above rearrangement is precluded, did not show the formation of the ions of this type.

One can assume that the loss of HCN from the aldoxime IIIa molecular ion proceeded through a five-membered transition state (12), and was accompanied by hydroxyl migration to the α -position of the ring. The M-HCN ion can be formulated as an α -pyridone ion-radical *e*, since this daughter ion showed the characteristic fragmentation patterns of α -pyridone itself (5). Indeed, as it was proven by

Table 1 (a)
 Partial Mass Spectra of Oximes (Ia-IIIa) and their Methyl Ethers (IV-VI)

m/e	(Ia)		(IIa)		(IIIa)		(IV)	(V)	(VI)
	70eV	15eV	70eV	15eV	70eV	15eV			
50	11.5		30		23		12	24	18.5
51	23		59		41.5	0.5	32	69	51
52	15.5		14		12.5		19.5	23	14.5
54	--		8	0.5	1		0.5	2	1.5
63	5		10.5		10		5.5	9	9
64	3		2.5		7		5	9	8
65	51	1	14		4		2	5	2.5
66	5		9		5		5.5	18	8.5
67	2	0.5	16	1.5	24	6	1	4	1.5
76	4		7.5		9		4.5	6	6.5
77	3.5		13		40	1	6	15	25
78	19		28		16	0.5	65.5	72	83
79	25	4.5	13.5		12	1.5	100	25	24
92	26	5.5	8.5	0.5	1.5		1	4	1.5
93	3		13	1	4		1	17	3
94	1		30	6	3		1	23	1.5
95	1		9.5		3.5	2	0.5	2	0.5
103	1		1.5		3		0.5	2	3.5
104	1		3.5	1	6	3	2.5	8	14
105	2	2	3		3.5	0.5	5.5	12	16.5
106	--		--		1.5	1	14	3	3
108	--		--		--		1	10	13
109	--		--		--		0.5	23	2
121	4.5	4	3	0.5	2	1	2	2	1
122	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	--	--	--
123	10	9	9.5	9	9	10.5	--	--	--
135							0.5	4	0.5
136							<u>27.5</u>	<u>100</u>	<u>100</u>
137							2.5	10	10

(a) Molecular peaks underlined.

exact mass measurements, the ion *e* decomposed further by the loss of CO to yield a pyrrole ion radical *d* (Table I), the ejection of HCN being absent. Moreover, in the 15eV mass spectrum of IIIa the ion *d* was the main fragment. These facts are in accordance with the behaviour of α -pyridone under electron bombardment: the latter eliminates exclusively CO, whereas its γ -isomer expels both CO and HCN (as the β -hydroxy pyridine does (5)).

EXPERIMENTAL

The mass spectra were recorded at 70 and 15eV on an Atlas CH-4 Mass Spectrometer with TO-4 ion source. The samples were introduced as follows: the aldoximes Ia-IIIa *via* direct inlet system, at about 90°, the *O*-methyl ethers IV-VI *via* double inlet system maintained at 80°.

The high resolution mass spectra were recorded using a Varian MAT 711 Mass Spectrometer in conjunction with a Spectroscopy 100 MS, at the resolving power of 10,000 and electron energy 70 eV. The elemental compositions of the principal fragment ions in the mass spectra of Ia-IIIa and IV were found to be as follows: m/e 121 (C₆H₅N₂O), 106 (C₆H₆N₂), 104 (C₆H₄N₂), 95 (C₅H₅NO),

94 (C₅H₄NO; for IIa: 7% C₅H₆N₂), 92 (C₆H₆N; for IIa: 5% C₅H₄N₂), 79 (C₅H₅N), 78 (C₅H₄N), 77 (C₅H₃N), 67 (C₄H₅N), 65 (C₅H₅), 52 (C₃H₂N/C₄H₄ 1:1).

The measurements of metastable transitions were made using the above instrument as well as a MAT 311. Two different modes of metastable scanning were applied: the "normal defocusing technique" (NDT; MAT 711) and the direct analysis of the daughter ions (DADI; MAT 311) (13). The following metastable transitions were recognized using metastable peaks, when available, or the above techniques: m/e 122 → 95 (IIIa), 95 → 67 (IIIa), 77 → 51 (Ia-IIIa), 104 → 77 (Ia-IIIa), 122 → 121 (IIIa, DADI; Ia, IIa), 122 → 94 (IIa), 92 → 65 (Ia), 79 → 52 (Ia), 122 → 92 (Ia), 122 → 79 (IIIa, DADI), 122 → 67 (IIIa, DADI, NDT), 136 → 135 (V), 136 → 109 (V), 109 → 108 (V, VD), 136 → 106 (IV), 106 → 79 (IV, DADI), 78 → 51 (IV, V), 136 → 79 (IV, DADI), 105 → 78 (V), 93 → 66 (V), 135 → 108 (VI).

The nmr spectra were recorded in DMSO-d₆, at 25° on a Varian A-60 Spectrometer with tetramethylsilane as an internal standard. The pyridine aldoximes Ia-IIIa were commercially available (Fluka AG, pure grade). Their purity was checked by nmr and tlc.

O-Deuterio Analogs of the α -, β - and γ -Pyridine Aldoximes (Ib-IIIb).

The samples of the corresponding aldoxime Ia-IIIa and the deuterium oxide were introduced simultaneously through the high tem-

perature inlet system (90°), and the double inlet system of the Atlas CH-4 Mass Spectrometer, respectively. After 20 to 30 minutes, an equilibrium was attained and the spectrum was recorded. The final isotopic compositions were respectively: Ib, 6% d_0 , 94% d_1 ; IIb, 9% d_0 , 91% d_1 ; IIIb, 8% d_0 , 92% d_1 . The same spectra were obtained with the samples of the Ib-IIIb prepared independently by the heating of Ia-IIIa respectively in perdeuterio-methanol solution.

α -, β - and γ -Pyridine Aldoxime Methyl Ethers (IV-VI).

The ethers IV-VI were prepared by direct interaction of the corresponding pyridine aldehyde and the water solution of the methoxyamine hydrochloride in the presence of sodium acetate, according to a modified procedure (14). The boiling points of the α -, β - and γ -pyridine aldoxime methyl ethers (IV-VI) were $108-110^\circ$, $174-175^\circ$ and $182-184^\circ$ respectively. All ethers gave satisfactory ir spectra (film): nmr (ppm): IV 6.75 (α -CH=N), 3.98 (OCH_3); V 8.55 (γ -CH=N), 4.0 (OCH_3); VI 8.5 (β -CH=N), 3.97 (OCH_3). For the mass spectra of IV-VI see Table I.

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