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The Fragmentation of Some 2-Pyridones, 2-Pyridthiones, and 2-Alkylthiopyridines Induced by Electron Impact

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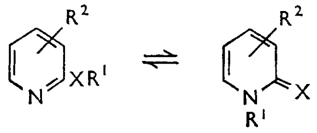
The mass spectra of pyridine-2-thiol, some of its *C*-, *N*-, and *S*-alkyl, -phenyl, and -vinyl derivatives, and some related 2-pyridones have been measured. The principal fragmentation pathways have been elucidated with the aid of deuterium labelling.

MASS spectra of 2- and 4-pyridone and pyridin-3-ol[1] and of a few other pyridones[2] are in the literature. We now discuss the more important fragmentation reactions of pyridine-2-thiol (I; $X = S$, $R^1 = R^2 = H$), some of its alkyl and vinyl derivatives (I and II; $X = S$), and some of the related 2-pyridones (II; $X = O$).

(I)



(II)

EXPERIMENTAL

Mass spectra (Table) were determined with an A.E.I. MS9 instrument using an ionising voltage of 70 ev, trap current 100 μA, and accelerating voltage 8 kv. Samples were introduced through the heated inlet system at 150°. High-resolution measurements were made with heptacosafluorotri-n-butylamine as mass standard.

Compounds examined were mostly prepared by standard methods. *C*-Alkylpyridones were obtained from the appropriate substituted 2-aminopyridine,[3] and *N*-alkylpyridones by treatment of the pyridone in ethanol with potassium hydroxide followed by the alkyl iodide.[4] Pyridthiones were prepared by the action of phosphorus pentasulphide at 130—160° on the pyridone.[5] Alkylthiopyridines were obtained by treatment of 2-pyridthione in N-sodium hydroxide with the alkyl halide.[6] 6-Phenyl-2-pyridone was prepared by the method of Thesing,[7] and the 1-phenyl analogue by the method of Tschitschibabin *et al.*,[8] except that bromobenzene was used instead of iodobenzene.

Mass-to-charge ratios (*m/e*) and relative abundances (%) of the most important ions

2-*Pyridone* (m. p. 107°, ref. *a*)

m/e	95	67	39	28	41	40	38	66	96	37
%	100	50	38·4	21·2	20·6	16·6	12·8	9·1	8·4	8·1
	51	50	27	68						
	7·2	6·6	6·3	5·0						

1-*Methyl*-2-*pyridone* (b. p. 121°/10 mm., ref. *b*)

m/e	109	81	39	80	42	53	44	55	51	28
%	100	43·5	30·2	28·2	26·1	13·1	13·1	13·1	10·9	9·8
	38	50	52	110	31	40	41	27	54	68
	8·7	8·7	8·7	8·7	6·5	6·5	6·5	6·5	6·4	6·3
	108									
	6·3									

1-[$^2H_3$]*Methyl*-2-*pyridone*

m/e	112	84	39	45	82	58	83	57	40	38
%	100	44·8	30·4	25·2	22·0	12·6	9·1	9·1	7·7	7·4
	55	111	113	50	51	41				
	7·0	7·0	7·0	6·3	5·9	5·3				

4-*Methyl*-2-*pyridone* (m. p. 130°, ref. 3)

m/e	109	80	44	31	39	47	53	81	36	41
%	100	73·8	27·8	26·4	22·2	22·2	22·2	22·2	13·9	13·9
	45	55	48	57	69	87	95	97	110	27
	13·9	13·9	12·5	12·5	12·5	11·1	9·7	9·7	9·7	9·1
	28	71	111							
	8·8	8·3	5·6							

[1] G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, 1962, **93**, 1935.

[2] A. M. Duffield, C. Djerassi, G. Schroll, and S. O. Lawesson, *Acta Chem. Scand.*, 1966, **20**, 361.

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[4] D. J. Cook, R. E. Bowen, P. Sorter, and E. Daniels, *J. Org. Chem.*, 1961, **26**, 4949.

[5] M. J. Renault, *Compt. rend.*, 1951, **232**, 77.

[6] M. J. Renault, *Ann. Chim. (France)*, 1955, **10**, 135.

[7] J. Thesing, U.S.P. 2,909,529 (*Chem. Abs.*, 1960, **54**, 2370).

[8] A. E. Tschitschibabin and N. B. Jeletzky, *Ber.*, 1924, **57**, 1158.

6-*Methyl-2-pyridone* (m. p. 158°, ref. 3)

m/e	80	109	39	81	42	28	27	38	66	53
%	100	91·7	53·5	48·5	25·8	25·0	21·0	18·3	15·0	14·2
	40	37	41	51	52	110	50	65	64	63
	9·1	8·3	8·3	8·3	8·3	8·3	6·7	6·3	6·3	5·8
	94									
	5·0									

1,3-*Dimethyl-2-pyridone* (b. p. 78°/0·5 mm., ref. *c*)

m/e	123	94	42	95	53	39	80	27	122	124
%	100	82·5	24·0	20·0	18·5	17·5	12·0	11·5	8·0	8·0
	41	51	52	28	93	54	50	66	55	
	7·5	7·5	7·0	5·5	5·5	5·5	5·0	5·0	5·0	

1,4-*Dimethyl-2-pyridone* (m. p. 59°, ref. 3)

m/e	94	123	95	53	42	39	27	80	124	51
%	100	91·7	21·8	20·9	20·0	17·4	10·9	10·0	8·7	8·3
	41	52	55	50	38	28				
	7·8	7·0	5·7	5·7	5·2	5·2				

1,5-*Dimethyl-2-pyridone* (m. p. 40—41°, ref. *c*)

m/e	94	123	42	95	53	39	27	51	52	41
%	100	49·5	32·6	26·1	17·6	15·7	12·7	9·2	7·7	7·7
	80	50	54							
	6·5	6·1	5·4							

1,6-*Dimethyl-2-pyridone* (m. p. 57°, ref. 3)

m/e	94	123	39	95	108	56	53	124	27	38
%	100	95·0	41·8	30·9	15·6	13·8	10·3	9·1	8·5	7·9
	28	80	65	42	93	54				
	6·8	6·8	6·2	5·9	5·0	5·0				

1,4,6-*Trimethyl-2-pyridone* (m. p. 89°, ref. *d*)

m/e	137	94	109	53	39	56	27	138	41	122
%	100	22·3	22·3	21·3	13·8	12·8	12·1	10·6	9·6	8·5
	42	44	51	52	108	28	67			
	8·5	8·5	7·5	7·5	7·5	6·6	5·3			

1-*Ethyl-2-pyridone* (b. p. 140°/0·5 mm., ref. 10)

m/e	67	123	95	80	39	78	53	122	51	41
%	100	75·0	56·0	40·0	37·5	17·8	16·9	16·9	16·1	15·2
	38	40	50	52	96	69	68	124	94	79
	11·6	10·7	9·8	9·8	8·9	8·9	7·2	7·1	6·3	5·4
	37	42								
	5·4	5·4								

1-*Ethyl-4-methyl-2-pyridone* (m. p. 32°)

m/e	137	109	81	80	136	28	53	94	39	92
%	100	61·5	44·0	40·0	24·6	22·7	22·8	21·0	19·3	19·3
		44	108	138	28	110	93	65	51	52
		15·8	12·3	10·5	10·5	10·5	10·5	10·5	8·8	8·8
	29	55	67	54	66	69	87	95		
	8·3	7·0	7·0	6·1	5·3	5·3	5·3	5·3		

1-*Ethyl*-6-*methyl-2-pyridine* (n_D^{27} 1·5494)

m/e	137	109	81	39	80	94	42	108	92	53
%	100	75·5	64·1	45·3	37·7	29·2	24·5	17·9	16·0	14·2
	65	66	41	138	29	38	110	28	40	93
	13·2	13·2	12·3	10·4	9·4	9·4	8·5	7·5	7·5	7·5
	51	67	91	136	52	82	63			
	6·6	6·6	6·6	6·6	6·1	5·6	5·2			

1-[2,2,2-$^{2}H_{3}$]*Ethyl-2-pyridone*

m/e	126	96	68	80	39	78	124	95	67	53
%	100	57·5	56·0	35·3	27·6	22·0	20·9	20·6	20·0	17·1
	125	29	51	28	32	97	127	123	40	38
	15·6	13·5	12·6	12·1	11·2	9·4	8·5	8·5	8·2	7·9
	41	52	42	47	50	79	81	30	66	
	7·6	7·4	6·8	6·8	6·8	5·3	5·3	5·0	5·0	

1-[1,1-$^{2}H_{2}$]*Ethyl-2-pyridone*

m/e	125	67	95	82	39	124	28	96	78	68
%	100	67·4	56·1	31·6	29·6	22·4	19·4	18·4	17·9	15·3
	29	31	55	40	41	51	38	54	126	66
	12·2	11·2	11·2	11·2	10·2	10·2	9·2	9·2	9·2	8·2
	50	80	52	97	30	42	123			
	8·2	8·2	6·1	6·1	5·1	5·1	5·1			

1-*n-Propyl-2-pyridone* (b. p. 128°/14 mm., n_D^{20} 1·539)

m/e	95	67	137	78	96	39	122	136	80	41
%	100	66·4	59·1	34·7	33·8	32·9	31·6	31·6	28·0	24·4
	53	109	81	51	28	120	52	40	38	79
	21·8	21·4	13·3	12·9	12·0	10·7	9·3	7·6	6·7	6·7
	42	43	68	138	66	50				
	5·8	5·8	5·8	5·8	5·3	5·3				

2-*Pyridthione* (m. p. 125°, refs. 5, *e*)

m/e	111	67	78	51	39	110	28	83	50	52
%	100	78·4	23·3	19·8	15·7	12·4	8·0	7·8	7·5	7·0
	84									
	5·2									

1-*Methyl-2-pyridthione* (m. p. 89°, refs. 5, *f*)

m/e	125	81	80	124	39	78	79	42	126	65
%	100	43·2	35·6	23·7	15·2	14·5	11·8	10·4	9·8	8·6
	45	51	97	52	62·5	69	41	127	84	44
	8·5	7·8	6·9	6·4	6·4	6·3	6·1	5·5	5·5	5·3

1-[$^{2}H_{3}$]*Methyl-2-pyridthione* (ref. *g*)

m/e	128	84	82	126	39	45	80	78	129	83
%	100	47·3	30·8	14·8	13·7	11·3	10·5	9·0	8·6	7·8
	51	127	64	67	44	69	85			
	7·4	7·0	6·6	6·2	5·8	5·1	5·1			

4-*Methyl-2-pyridthione* (m. p. 177°)

m/e	125	80	81	39	65	92	45	53	97	51
%	100	54·5	52·5	35·4	28·2	16·7	13·9	12·8	12·8	11·4
	27	38	126	28	63	50	66	110	52	57
	11·0	10·0	9·9	9·2	8·5	8·5	8·4	8·1	7·1	7·1
	58	69	124	127	37					
	7·1	7·1	7·1	5·7	5·7					

6-*Methyl-2-pyridthione* (m. p. 145°)

m/e	125	81	80	93	76	65	92	66	27	51
%	100	53	37·8	33·8	26·4	25·8	21·8	16·6	9·9	8·6
	126	78	53	40	41	45	63	124	50	52
	8·6	7·9	7·3	6·6	6·6	6·6	6·6	6·6	6·0	6·0
	64	96	97	42	67	127				
	6·0	6·0	6·0	5·3	5·3	5·3				

1,3-*Dimethyl-2-pyridthione* (m. p. 120°)

m/e	139	138	94	93	95	39	92	140	65	69·5
%	100	32·2	31·7	19·5	16·4	12·2	11·9	10·0	9·3	6·9
	42	97	45	78	66					
	6·7	6·7	6·4	6·2	5·0					

1,4-*Dimethyl-2-pyridthione* (m. p. 138°)

m/e	139	94	138	95	39	93	92	140	42	67
%	100	58·0	23·8	20·4	12·9	11·9	11·0	10·5	9·5	8·6
	65	97	53	45	141	66	51	41	77	79
	8·1	8·1	7·6	7·1	6·2	5·7	5·7	5·7	5·7	5·7
	69·5									
	5·2									

1,5-*Dimethyl-2-pyridthione* (m. p. 119°)

m/e	139	94	95	138	93	42	140	97	39	44
%	100	43·0	21·6	19·2	12·2	11·4	10·2	9·8	8·6	8·6
	92	40	65	53	69·5	45	79	66		
	8·2	7·3	7·0	6·5	6·5	6·1	6·1	5·3		

1,6-*Dimethyl-2-pyridthione* (m. p. 104°)

m/e	139	94	138	95	93	39	92	65	140	66
%	100	41·4	27·0	22·2	17·3	13·6	13·3	10·7	10·1	7·2
	69·5	97	45	79	141					
	6·6	5·9	5·1	5·1	5·1					

1,4,6-*Trimethyl-2-pyridthione* (m. p. 127°)

m/e	153	108	152	109	107	106	39	154	77	79
%	100	51·6	32·8	20·6	17·8	13·9	13·4	12·2	11·7	8·9
	94	53	45	56	51	41	76·5	156	42	91
	8·3	7·8	6·7	6·1	5·5	5·5	5·5	5·5	5·0	5·0
	93									
	5·0									

1-*Ethyl-2-pyridthione* (b. p. 182°/15 mm.)

m/e	67	139	111	138	78	39	51	79	80	140
%	100	78·0	53·0	44·0	32·0	16·2	13·0	11·2	10·6	9·4
	52	69	112	45	68	110	83			
	8·6	8·0	8·0	7·2	5·6	5·6	5·0			

1-*Ethyl-4-methyl-2-pyridthione* (m. p. 58°)

m/e	153	81	152	125	92	80	65	39	154	94
%	100	77·7	75·0	72·3	30·6	27·8	25·2	20·3	15·3	12·3
	93	53	45	126	127	66	51	97	41	82
	11·6	11·6	10·6	10·6	10·6	8·4	8·4	7·4	5·8	5·8
	91	44	69							
	5·8	5·2	5·2							

1-*Ethyl-6-methyl-2-pyridthione* (m. p. 88°)

m/e	153	152	125	81	79	44	92	52	39	65
%	100	61·0	52·0	49·0	30·8	27·0	22·6	22·2	19·6	16·2
	80	93	27	51	154	78	29	94	41	68
	13·5	13·5	13·0	13·0	13·0	10·9	9·1	8·7	8·2	7·8
	66	50	53	67	91	36	42	43	126	155
	7·4	7·0	7·0	6·5	6·5	5·6	5·6	5·6	5·6	5·6

1-[2,2,2-^{2}H$_3$]*Ethyl-2-pyridthione*

m/e	142	68	112	140	78	141	67	111	39	80
%	100	91·0	54·5	44·0	35·0	23·6	20·4	15·9	15·0	12·7
	51	139	79	143	29	52	45	113	28	71
	12·3	10·5	9·5	9·5	8·6	8·2	7·7	7·3	6·8	6·8
	27	32	44	69	53					
	6·4	5·9	5·9	5·9	5·4					

1[1,1-^{2}H$_2$]*Ethyl-2-pyridthione*

m/e	141	67	111	140	78	39	51	68	79	28
%	100	95·0	57·6	53·8	36·7	19·0	14·6	13·9	12·7	11·4
		142	112	80	52	29	139	45	31	44
		11·4	10·8	10·1	10·1	8·9	8·2	7·6	7·0	7·0
	69	110	41	70·5	83	113	143	84	82	81
	6·3	6·3	5·7	5·7	5·7	5·7	5·0	5·0	5·0	5·0
	55	50	30							
	5·0	5·0	5·0							

1-*n-Propyl-2-pyridthione* (n_D^{25} 1·655, ref. 5)

m/e	111	67	153	47	78	49	152	39	88	112
%	100	81·6	79·1	42·5	41·6	27·5	25·0	20·0	17·5	17·5
	41	51	138	28	79	80	154	45	52	125
	15·0	11·7	10·8	9·2	9·2	9·2	9·2	7·5	7·5	7·5
	119	113	120	121	95	42	44	53	68	69
	6·7	5·8	5·8	5·8	5·8	5·0	5·0	5·0	5·0	5·0
	81	82	110	155						
	5·0	5·0	5·0	5·0						

2-*Methylthiopyridine* (b. p. 192°/750 mm., refs. 6, *e*)

m/e	125	79	124	52	51	78	80	39	45	126
%	100	75·6	57·5	31·4	24·4	18·4	16·2	14·6	11·3	10·3
	50	92	127							
	8·1	6·5	4·9							

2-*Ethylthiopyridine* (b. p. 205°/750 mm., ref. 6)

m/e	139	106	79	124	67	78	111	51	138	52
%	100	91·5	90·5	60·4	51·0	45·4	38·7	29·2	28·3	26·4
	39	27	80	45	140	29	28	50	107	44
	25·4	22·6	19·8	10·4	10·4	9·5	8·5	8·5	8·5	6·6
	58	57	110	59	53	104	125	112	141	
	6·6	6·6	6·6	5·7	5·7	5·7	5·7	5·7	5·7	

4-*Methyl-2-methylthiopyridine* (n_D^{20} 1·5650)

m/e	139	93	44	138	66	36	87	39	28	65
%	100	82·5	61·0	57·0	32·2	32·2	29·5	28·0	26·5	23·5
	49	94	35	92	140	123	118	123	105	106
	22·4	22·0	20·8	17·8	11·4	7·95	6·4	6·1	5·7	5·3

2-*Ethylthio-6-methylpyridine* (n_D^{21} 1·5600)

m/e	120	153	39	93	138	65	27	81	125	47
%	100	76·6	63·3	62·6	58·6	40·4	37·4	34·6	34·0	33·4
	92	152	66	29	80	94	45	48	87	49
	32·0	22·6	22·0	21·8	16·0	14·7	14·7	14·0	11·3	10·6
	53	121	28	154	41	63	139	51	64	97
	10·0	10·0	8·7	8·7	8·0	8·0	8·0	7·3	7·3	7·3
	40	57	58	78	42	52	59	67	69	
	6·6	6·0	6·0	6·0	5·3	5·3	5·3	5·3	5·0	

2-*Methyl-6-methylthiopyridine* (n_D^{21} 1·5648)

m/e	139	93	39	138	66	65	45	94	92	63
%	100	94·7	82·5	62·1	48·5	45·5	29·6	24·2	17·4	15·2
	64	51	46	140	82	40	50	52	53	27
	14·4	12·1	11·4	11·4	10·6	9·9	9·9	9·9	9·1	8·7
	47	57	41	78	106	67	69	62	79	97
	8·3	8·3	7·6	7·6	7·6	6·8	6·8	6·1	6·1	6·1
	42	80	83	107	141					
	5·3	5·3	5·3	5·3	5·3					

2-*Ethylthio-4-methylpyridine* (n_D^{20} 1·5622)

m/e	153	81	152	125	92	80	27	65	39	154
%	100	77·7	75·0	72·3	30·6	27·8	27·3	25·2	20·3	15·3
	29	94	93	53	45	126	127	28	66	51
	12·7	12·3	11·6	11·6	10·6	10·6	10·6	9·1	8·4	8·4
	97	41	82	91	44	69				
	7·4	5·8	5·8	5·8	5·2	5·2				

2-[2,2,2-^{2}H$_3$]*Ethylthiopyridine*

m/e	79	142	124	108	78	68	51	52	39	112
%	100	74·0	67·5	52·1	43·5	35·6	30·4	29·2	26·6	24·8
	109	141	80	29	67	45	140	32	28	50
	22·6	22·6	20·4	13·5	13·0	11·3	11·3	10·9	9·1	9·1
	106	111	143	83	125	57	30	139	44	
	8·3	8·3	7·4	7·0	6·5	6·1	5·7	5·7	5·2	

2-[1,1-^{2}H$_2$]*Ethylthiopyridine*

m/e	141	108	80	126	67	111	78	51	39	52
%	100	83·5	70·5	57·6	55·0	49·3	48·5	40·8	40·0	24·2
	28	107	27	140	29	50	87	79	139	57
	21·7	20·4	19·1	15·9	15·9	14·1	14·1	14·1	13·3	10·8
	68	110	112	45	53	82	142	81	106	109
	10·8	10·8	10·0	10·0	9·2	9·2	8·3	8·3	7·5	7·5
	58	46	69	84						
	7·5	6·7	6·7	6·7						

2-[1,1-^{2}H$_2$]*Ethylthio-6-methylpyridine*

m/e	155	94	122	140	39	125	81	65	92	66
%	100	93·5	81·5	65·7	52·8	51·0	38·9	36·1	31·4	21·3
	121	154	93	153	80	28	156	31	45	67
	20·4	19·4	15·7	15·7	13·9	12·0	11·1	10·2	10·2	10·2
	95	29	63	53	64	123	126	38	40	96
	10·2	9·2	9·2	8·3	8·3	8·3	8·3	7·4	7·4	7·4
	97	120	141	41	82	30	44	51	52	57
	7·4	7·4	7·4	6·5	6·5	5·5	5·5	5·5	5·5	5·5
	83	157								
	5·5	5·5								

2-[$^2H_3$]*Methylthiopyridine*

m/e	128	80	126	51	52	78	127	39	53	50
%	100	75·0	39·2	19·2	17·6	14·4	12·8	12·8	10·4	9·6
	81	82	129	94	83	79	46			
	9·6	9·6	8·0	7·2	5·6	5·6	5·6			

1-*Phenyl-2-pyridone* (m. p. 128°, ref. 8)

m/e	143	77	51	171	170	115	39	116	50	117
%	100	70·0	69·0	62·5	52·5	47·5	45·5	25·8	24·8	18·8
	38	52	104	144	142	63	78	172	64	65
	13·9	13·9	11·9	11·9	10·9	10·9	9·9	8·9	7·9	6·9
	76	89	40	74	75	90				
	6·9	6·9	5·9	5·9	5·9	5·9				

1-o-*Tolyl-2-pyridone* (n_D^{26} 1·6020)

m/e	184	185	168	65	170	91	39	51	157	158
%	100	93·5	77·7	32·4	29·5	28·8	25·2	18·7	18·0	16·5
	186	169	91·5	63	130	89	77	129	78	28
	13·0	11·5	10·8	10·1	9·4	9·4	9·4	8·7	7·9	7·2
	52	115	50	167	171	64	128	27	41	90
	7·2	7·2	6·5	6·5	6·5	5·8	5·8	5·0	5·0	5·0

4-*Phenyl-2-pyridone* (m. p. 227°, ref. *h*)

m/e	171	170	143	115	172	116	51	39	63	58·5
%	100	55·8	43·5	40·4	13·5	11·5	10·8	10·4	9·6	8·8
	71·5	50	89	77	144	142	65			
	8·5	6·9	6·9	6·1	6·1	6·1	5·0			

6-*Phenyl-2-pyridone* (m. p. 197°, ref. *h*)

m/e	171	143	172	170	39	144	142	72	44	115
%	100	62·0	50·0	49·0	9·2	8·8	7·3	5·4	4·9	4·4
	51	43	77	50	95					
	3·9	2·9	2·9	2·4	2·4					

1-*Vinyl-2-pyridone* (n_D^{20} 1·5960, ref. 10)

m/e	120	121	28	39	66	67	93	27	32	51
%	100	91·5	60·0	30·3	27·1	24·8	19·3	18·7	12·3	11·9
	40	92	65	38	41	26	52	50	54	122
	11·3	11·0	10·3	9·0	8·7	8·4	8·1	7·7	7·7	7·7
	95	46·5	78							
	6·8	6·1	5·8							

1-*Vinyl-2-pyridthione* (m. p. 65·5°)

m/e	136	137	78	39	67	79	51	138	45	52
%	100	67·7	27·1	20·6	17·4	16·8	16·1	12·2	11·0	9·7
	43	93	44	58	69	111	41	50	91	65
	9·0	9·0	7·7	7·7	7·7	7·7	7·1	6·5	5·8	5·2
	92									
	5·2									

[a] H. V. Pechmann and O. Baltzer, *Ber.*, 1891, **24**, 3145.
[b] E. A. Prill and S. M. McElvain, *Org. Synth.*, 1935, **15**, 41.
[c] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 1961, 859.
[d] O. Mumm and G. Hingst, *Ber.*, 1923, **56**, 2301. [e] W. Marckwald, W. Klemm, and H. Trabert, *Ber.*, 1900, **33**, 1556.
[f] M. J. Renault, *Bull. Soc. chim. France*, 1953, 1001. [g] F. S. Babichev and V. N. Bubnovskaya, *Ukrain. khim. Zhur.*, 1964, **30** (8), 848. [h] C. F. H. Allen and W. L. Ball, *J. Amer. Chem. Soc.*, 1937, **59**, 686.

1-*Vinyl-2-pyridthione*.—(*a*) Pyridine-2-thiol (10 g.) was dissolved in methanol (100 ml.) and ethylene oxide (4·5 g.) in methanol (40 ml.) added. The mixture was kept at 20° for 6 hr. and distilled, giving 2-(2-hydroxyethylthio)-pyridine (65%), b. p. 108°/0·8 mm., n_D^{24} 1·5954.

(*b*) Pyridine-2-thiol (150 mg.) was dissolved in N-sodium hydroxide (5 ml.) and 2-chloroethanol (120 mg.) added. The mixture was left for 48 hr., saturated with solid potassium carbonate, and extracted with chloroform. The extract was dried (Na_2SO_4) and distilled, giving 2-(2-hydroxyethylthio)pyridine (80%) (Found: C, 54·3; H, 5·7; N, 9·0; O, 10·3. $C_7H_9NO_5$ requires C, 54·2; H, 5·8; N, 9·0; O, 10·3%).

2-(2-Hydroxyethylthio)pyridine (3·5 g.) and sodium hydride (0·6 g.) in ether (27 ml.) were refluxed for 6 hr. The mixture was cooled in ice, and toluene-*p*-sulphonyl chloride (4·3 g.) in ether (30 ml.) added during 1 hr. Stirring was continued at 0° for 1 hr. and then at 20° for 2 hr. Insoluble material was filtered off and extracted several times with ether. The combined filtrate and extracts were evaporated to dryness, and the solid residue was pyrolysed at 0·5 mm. immediately. The 1-vinyl-2-pyridthione was chromatographed, and crystallised from benzene–petroleum; $\lambda_{max.}$ ($CHCl_3$) 295 and 383 mμ (ε 11,000 and 6000), $\nu_{max.}$ (CCl_4 and CS_2) 1640, 1625, 1460, 1420, 1320, 1275, 1250, 1130, 1090, 1010, 950, 900, 800, and 750 cm.$^{-1}$ (all strong); n.m.r.: τ 2·2 (q), 2·45 (d), 2·65 (d), 3·1 (t), 3·6 (t), 4·8 (d), and 4·7 (d).

1-*Vinyl-2-pyridone*.—1-(2-Hydroxyethyl)-2-pyridone (5 g.)[9] was dissolved in toluene and added to potassium (1·4 g.) in toluene (50 ml.). The mixture was refluxed for 16 hr., cooled in ice, and, after the addition of carbon disulphide (8 ml.), refluxed for a further 18 hr. After cooling, methyl iodide (4·5 ml.) was added and the resulting mixture refluxed with stirring for 4 hr. Low-b. p. material was removed under a vacuum and the residue distilled to remove dimethyl trithiocarbonate (b. p. 50°/0·5 mm.). The fraction, b. p. 170—180°/5 mm., was redistilled to give 1-vinyl-2-pyridone (12%), b. p. 144/0·5 mm., n_D^{20} 1·5960, shown to be pure by gas chromatography (lit.,[10] b. p. 251—252°/750 mm., n_D^{20} 1·5960), $\lambda_{max.}$ (EtOH) 222 and 322 mμ (ε 7000 and 6000); n.m.r.: τ 2·7 (q, J = 17·5 and 9 c./sec.), 4·76 (d, J = 17·5), and 5·05 (d, J = 9), apart from signals due to ring protons.

Analyses.—6-*Methyl-2-pyridthione* (Found: C, 57·7; H, 5·4; N, 10·95. C_6H_7NS requires C, 57·55; H, 5·65; N, 11·2%). 1,4-*Dimethyl-2-pyridthione* (Found: C, 60·4; H, 6·5; N, 10·05. C_7H_9NS requires C, 60·25; H, 6·6; N, 10·15%). 1-*Ethyl-6-methyl-2-pyridthione* (Found: C, 62·5; H, 7·25; N, 8·75. $C_8H_{11}NS$ requires C, 62·7; H, 7·25; N, 9·15%). 1-n-Propyl-2-pyridthione (Found: C, 62·75; H, 7·25; N, 8·9. Calc, for $C_8H_{11}NS$: C, 62·7; H, 7·25; N, 9·15%). 4-*Methyl-2-methylthiopyridine* (Found: C, 60·35; H, 6·4. C_7H_9NS requires C, 60·25; H, 6·6%). 2-*Ethylthio-4-methylpyridine* (Found: C, 62·35; H, 7·15. $C_8H_{11}NS$ requires C, 62·7; H, 7·25%).

RESULTS AND DISCUSSION

Pyridine-2-thiol and its Alkyl Derivatives.—The most important fragmentation of 2-pyridone is the loss of carbon monoxide to give an ion postulated to be the pyrrole molecular ion (*m/e* 67).[1] An analogous loss of carbon monosulphide occurs from the molecular ion of pyridine-2-thiol, the composition of the *m/e* 67 ion being confirmed by high-resolution mass measurement to be $C_4H_5N^+$. In 1-methyl-2-pyridone and 1-methyl-2-pyridthione the abundance of this ion is decreased, relative to the molecular ion, and that of the homologous ion is decreased still further in their *C*-methyl derivatives. In 1-ethyl- and 1-n-propyl-2-pyridthione the (M — 44) ion has only 3 and 1·5% relative abundance, respectively. There is no doubt that loss of CS from the molecular ion does occur, since the fragmentation sequence shown is

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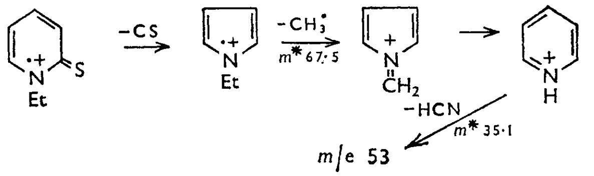
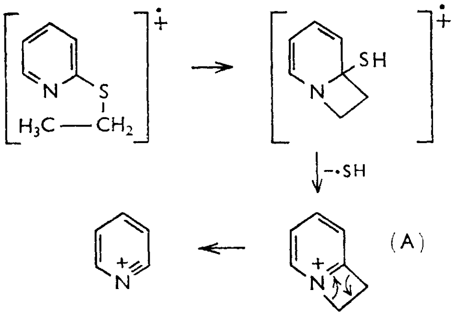
[9] I. L. Knunjanz, *Ber.*, 1935, **68**, 397.
[10] B. I. Kikhant'ev, *Izvest. V.U.Z.M.V.O. S.S.S.R., Khim. i khim. Tekhnol.*, 1959, **2** (3), 390.

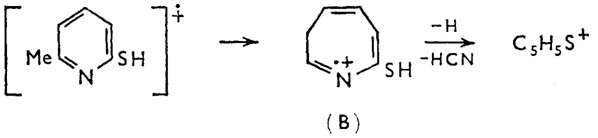
supported by metastable peaks and by deuterium labelling in the ethyl group. An analogous series of fragmentations is particularly clear in 2-pyridones. On the other hand, two fragmentations which are scarcely detectable in 2-pyridone but which are important in pyridine-2-thiol are loss of XH, and loss of hydrogen followed by HCN, from the molecular ion. The relative importance of the two processes and of the loss of CX presumably reflects on the difference in the equilibrium of the tautomerism (I) $\rightleftharpoons$ (II) when X = O and S. However, when the possibility of prototropic rearrangement is removed, as in the 1-alkyl-2-pyridthiones and 2-alkylthiopyridines, $(M - \mathrm{SH})^+$ ions are still observed. The spectra of the [$^2H_3$]methyl compounds show that the hydrogen lost in the SH group is derived from the methyl group, so this fragmentation parallels (in the *S*-alkyl series) that observed in thioanisole,[11] and probably proceeds by a similar mechanism. Loss of SH from the 2-ethylthiopyridine molecular ion is very important. In alkyl phenyl sulphides[11] the abundance of the $(M - \mathrm{SH})^+$ species decreases as the length of the alkyl chain increases, so the different behaviour of 2-alkylthiopyridines seems to be connected with the presence of the nitrogen atom which must be involved in the rearrangement. Deuterium labelling in the ethyl group indicates that ~75% of the SH loss involves hydrogen from the methyl group, the remainder coming from the methylene group. Careful examination of the metastable peaks in the deuteriated and undeuteriated compounds indicates that the $(M - \mathrm{SH})^+$ ion loses ethylene, and structure (A) is postulated for it.





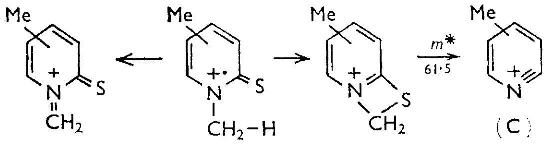
It should be noted that 1-alkyl-2-pyridthiones and 2-alkylthiopyridines are relatively stable to heat, representative examples showing no detectable changes after being kept at 150° for several days. Evidently thermal rearrangements of alkyl groups from nitrogen to sulphur and *vice versa*, such as are observed in 2-alkylthiobenzothiazoles and 3-alkylthiobenzthiazolines,[12] do not occur readily.

The ion, *m/e* 83, in pyridine-2-thiol arises by loss of HCN from the $(M - 1)^+$ ion, as shown by a metastable peak at 62·7 mass units. Replacement of the readily exchangeable hydrogen [*i.e.*, R^1 in (I) or (II)] results in no shift in the ion, *m/e* 83, although the $(M - 1)^+$ and $(M - 2)^+$ ions are of about equal abundance. In 6-methylpyridine-2-thiol the peak at *m/e* 83 (corresponding to $M - \mathrm{H} - \mathrm{CH_3CN}$) is weak, but that corresponding to $(M - 28)$ is as strong as in pyridine-2-thiol. It is postulated that ring-expansion occurs to give the ion (B), which then loses hydrogen followed by HCN.



In pyridine-2-thiol and its 4-methyl derivative the ion $\mathrm{CH_2N^+}$ (*m/e* 28) is observed; it shifts to *m/e* 42 in the 6-methyl compound and in 1-methyl-2-pyridone, and to *m/e* 45 in the 1-[$^2H_3$]methyl-2-pyridthione. Higher homologues of this ion are not found in the spectra of 1-ethyl- and 1-n-propyl-2-pyridthione.

$(M - 1)^+$ ions are more intense in the spectra of the 1-methyl derivative than in pyridine-2-thiol itself. The $(M - 1)^+$ ion loses $\mathrm{CH_2S}$, as shown by the appropriate metastable peak, to give an ion postulated to be an azabenzyne (C). Replacement of the 1-methyl group by trideuteriomethyl confirms that the major part (70%) of the hydrogen lost comes from the 1-methyl group. Both 1-ethyl-2-pyridone and the thio-analogue have large $(M - 1)$ peaks. Deuteriation in the ethyl group leaves no doubt that a hydrogen attached to C-2 of the ethyl group is lost. The $(M - 1)$ peak is less prominent in 1-n-propyl-2-pyridthione, which, however, gives an abundant ion corresponding to loss of methyl from the molecular ion. The $(M - 15)^+$ ion is weak in 1-ethyl-2-pyridthione but does lose $\mathrm{CH_2S}$ ($m^* = 49{\cdot}0$) probably by the mechanism postulated for the 1-methyl compound.



An ion at *m/e* 79 ($\mathrm{C_5H_5N^+}$) is common in the spectra of 1-alkyl-2-pyridones and -2-pyridthiones (II; $R^1 = \mathrm{CH_2Y}$) and is derived from the $(M - \mathrm{CXH})^+$ ion by loss of the radical •Y. The relative abundance of the ion $\mathrm{C_5H_5N^+}$ ($M^+ = 100\%$) is related to the stability of the radical •Y; cf. the following values for the appropriately substituted 2-pyridones: Y = Ph, 55·5; Me, 7·1; H, 2·4%.

Phenyl- and Vinyl-2-pyridones.—The fragmentation patterns of 1-, 4-, and 6-phenyl-2-pyridone are remarkably similar. In each the ion, *m/e* 143, is prominent; it corresponds to the loss of carbon monoxide from the

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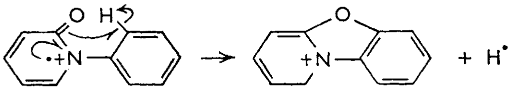
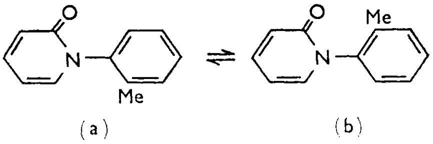
[11] J. H. Bowie, S. O. Lawesson, J. Ø. Madson, G. Schroll, and D. H. Williams, *J. Chem. Soc.* (*B*), 1966, 951.

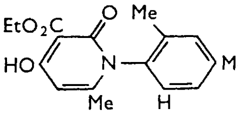
[12] C. G. Moore and E. S. Waight, *J. Chem. Soc.*, 1952, 4237.

molecular ion. Peaks at m/e 115, 116, and 117 correspond to $C_9H_7^+$, $C_9H_8^+$, and $C_8H_7N^+$, the latter two being derived by loss of HCN ($m^* = 94{\cdot}0$) and of C_2H_2 from the $(M - CO)^+$ ion. $C_9H_7^+$ is obtained either by loss of a hydrogen atom from C_9H_8 ($m^* = 114$) or by loss of HCN from the $(M - CO - H)^+$ ion ($m^* = 93$). The only peak which shows any remarkable variation in intensity in the spectra of the three isomers is due to loss of a hydrogen atom from the molecular ion, which is much stronger in the 1-phenyl compound than in the other two. 1-[2,4,6-$^2H_3$]phenyl-2-pyridone has a large $(M - 2)$ peak, showing that the hydrogen lost probably comes from the *ortho*-position of the benzene ring, and it is postulated that this fragmentation involves attack by oxygen on the benzene ring with the formation of an oxazole ring. An $(M - 1)$ peak is also intense (relative abundance 113%, $M^+ = 100\%$) in 1-*o*-tolyl-2-pyridone, which also shows a weaker peak at $(M - 15)$ (32%). This behaviour is distinct from that of the 1-(2,6-dimethylphenyl)-2-pyridone derivative (III), which has an intense $(M - 15)$ peak (142%, $M^+ = 100\%$) but a much weaker $(M - 1)$ peak (6%),[2] and presumably reflects a preference for 1-*o*-tolyl-2-pyridone to exist in conformation (a) rather than (b). In the pyridone (III) the intrinsically more likely elimination of *o*-methyl is conformationally assisted, as the resultant ion then has a relatively weaker interaction between the *o*-hydrogen and the 6-methyl group on the pyridone ring. These fragmentations thus appear to be further examples of the formation of five-membered rings upon electron impact.[13]



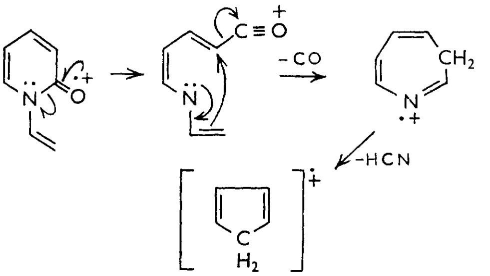


(a) (b)



(III)

The fragmentation of 1-vinyl-2-pyridone shows certain similarities to that of 1-phenyl-2-pyridone. Thus, loss of CO from the molecular ion results in the formation of an ion (m/e 93) which loses hydrogen ($m^* = 91{\cdot}0$), C_2H_2 ($m^* = 48{\cdot}2$), or HCN ($m^* = 45{\cdot}9$). The molecular ion undergoes a McLafferty rearrangement to give a small but significant ion at m/e 95 ($C_5H_5NO^+$), and it also gives a strong $(M - 1)^+$ ion. The peaks at m/e 65, 66, and 67 correspond to C_5H_5, $C_5H_6^+ + C_4H_4N^+$ (a doublet in the ratio 4 : 1), and $C_4H_5^+$. In order to account for the formation of $C_5H_6^+$ it seems necessary to postulate the formation of a seven-membered ring (D). A similar ring-expansion probably occurs in the phenyl-2-pyridones. 1-Vinyl-2-pyridthione has also been examined. The molecular ion and the $(M - 1)^+$ ion are abundant, while loss of acetylene and of carbon monosulphide from the molecular ion also occurs. The $(M - 26)^+$ and $(M - 44)^+$ ions carry 2·0 and 2·3%, respectively, of the ion current (Σ_{26}) which may be compared with 1·35 and 3·85% for the $(M - 26)^+$ and $(M - 28)^+$ ions in 1-vinyl-2-pyridone.



(D)

We are indebted to the S.R.C. for grants to R. L. and to purchase the mass spectrometer. Professor J. A. Elvidge kindly supplied us with 1,3- and 1,5-dimethyl-2-pyridone.

[7/955 *Received, July 31st*, 1967]

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[13] M. A. Baldwin, A. G. Loudon, A. Maccoll, and D. Smith, *Chem. Comm.*, 1967, 350.