Mass Spectrometry of 2-Methylpyrimidines
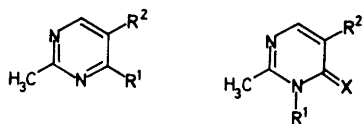
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Hydroxy- and mercapto-2-methylpyrimidines and derivatives thereof fragment with loss of HCN or CH_3CN from the nucleus besides fragmentations directed by the oxygen or sulphur substituents. 5-Ethoxypyrimidines show loss of ethylene $(M - 28)$ as the dominant fragment. With an additional 4-substituent, however, which can exert an *ortho* effect, expulsion of a methyl group from the ethoxy function becomes important. γ-Cleavage occurs in substituents *ortho* to the annular nitrogen.

Mass spectrometry of pyrimidines is largely restricted to biologically important uracil, cytosine, and thymine derivatives [1–4] and to derivatives of 2- and 4-aminopyrimidines.[5,6] We now report on the behaviour of 2-methylpyrimidine and its derivatives.

The compositions of the discussed fragments have been determined by high resolution. The relative contribution of different species to multiplets is given in brackets. Metastable transitions marked "m" have been determined by the defocusing technique.[7] The following compounds were studied:

Comp.	R^1	R^2	Comp.	R^1	R^2	X
I	H	H	XII	H	H	O
II	H	OH	XIII	H	OH	O
III	H	OC_2H_5	XIV	H	OC_2H_5	O
IV	OCH_3	H	XV	H	H	S
V	OCH_3	OC_2H_5	XVI	H	OH	S
VI	SCH_3	H	XVII	H	OC_2H_5	S
VII	SCH_3	OH	XVIII	CH_3	H	O
VIII	SCH_3	OC_2H_5	XIX	CH_3	OC_2H_5	O
IX	Cl	H				
X	Cl	OC_2H_5				
XI	SCH_2CH_2OH	OH				

The dominating fragments in pyrimidine arise by loss of two molecules of HCN.[1] In 2-methylpyrimidine (I) (Fig. 1) the most intense fragment is formed by loss of HCN (m/e 67). Appropriate metastable peaks confirm further expulsion of either HCN, C_2H_2 or CH_3CN from the m/e 67 fragment besides the loss of 25 mass units to the prominent fragment at m/e 42, formulated as protonated acetonitrile. The loss of 25 mass units, corresponding to the radical
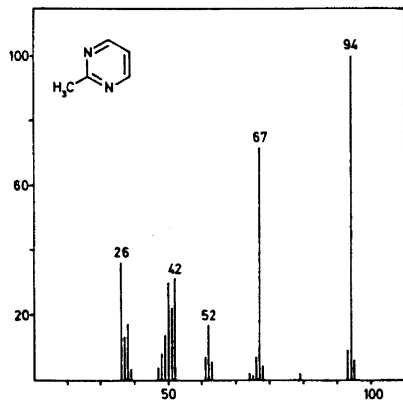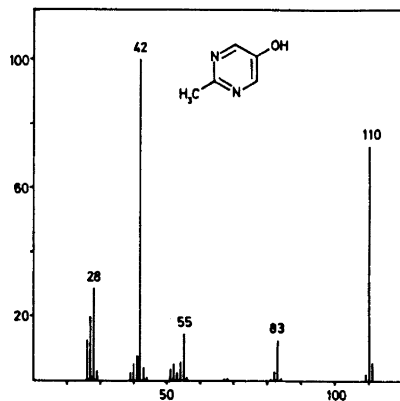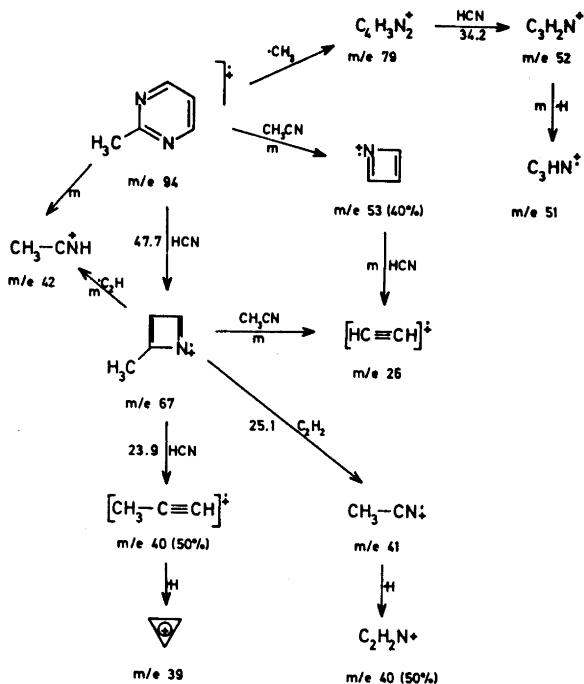

Fig. 1.

Fig. 2.

Scheme 1.

C_2H is unusual, but the transition is confirmed by a narrow and well defined metastable peak by the defocusing technique. The probable driving force for the reaction is the high stability of the even electron ion formed. This agrees with observations in aliphatic nitriles where the $(M+1)$ peak in some cases exceeds the intensity of the molecular ion.[8] The m/e 52 ions arise by expulsion of HCN from the $(M-15)$ species.

The 5-hydroxy derivative (II) (Fig. 2) has an intense peak at m/e 42. 35 % of the intensity is due to initial expulsion of HCN followed by loss of CH_3CN. The remainder is due to C_2H_4N. Metastable defocusing shows two transitions to m/e 42. An intense peak corresponds to loss of 41 mass units from m/e 83 and a very weak peak to a transition from the molecular ion. The composition of the fragment lost, however, cannot be determined by metastable defocusing because of very low resolution. By analogy to compound I, however, C_2H_4N is probably formed by both processes while C_2H_2O arises from m/e 83 by loss of acetonitrile. At low electron voltages m/e 42 is greatly reduced. An intense metastable shows that m/e 55 is formed directly from the molecular ion, presumably by simultaneous loss of CO and HCN. A transition from m/e 83 could not be determined accurately because the peak was broad and unsymmetrical, probably caused by interaction with the loss of HCN from m/e 82. Deuteration of the phenolic proton caused the discussed fragments to appear at one higher mass unit.

Scheme 2.
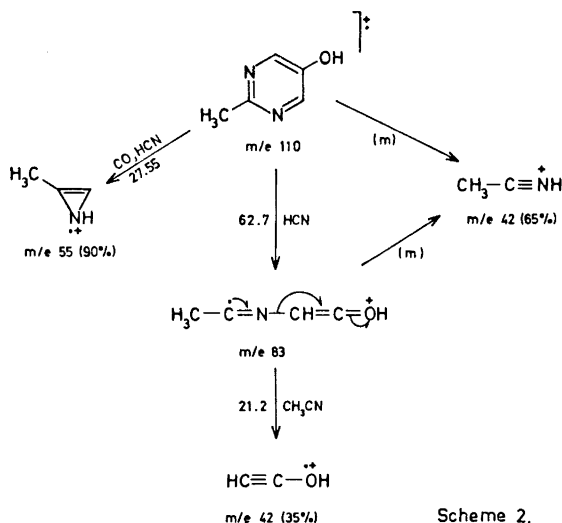
The fragmentation pattern shows high temperature dependence. At a source temperature of 165° the molecular ion abundance is 95 % of the base peak at m/e 42, at 255° the figure is 35 %. Minor changes in the m/e 83 are also apparent. The composition of m/e 42 remains unchanged within the temperature range studied. Other derivatives also showed some dependence on the source temperature.
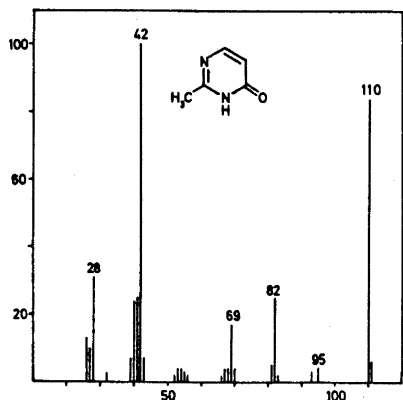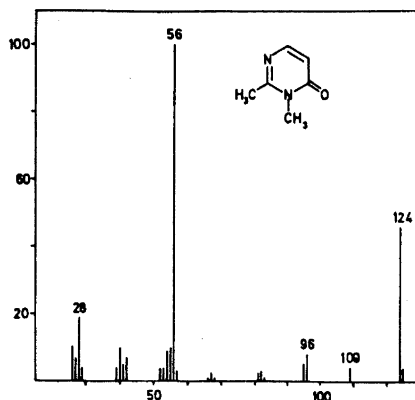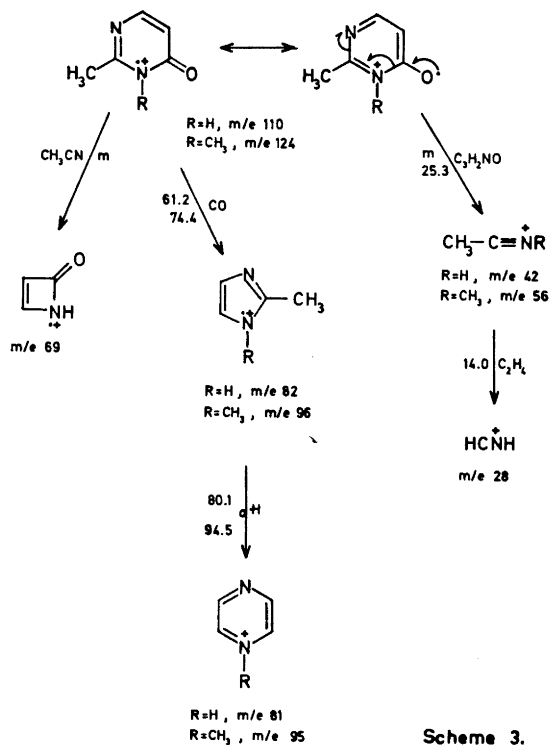
Fig. 3.

Fig. 4.

The 4-hydroxy derivative (XII) (Fig. 3) fragments differently from the 5-isomer above. HCN expulsion is no longer important. Instead loss of CO and CH$_3$CN are the major pathways. The prominent peak at m/e 42 (C$_2$H$_4$N) is formed both from (M − CO) and from the molecular ion.

The N-methyl derivative (XVIII) (Fig. 4) behaves in an analogous fashion.

Scheme 3.

It would appear that the difference in the fragmentation pattern of the two isomeric hydroxy compounds is in part caused by the existence of XII in the lactam form while II is aromatic.
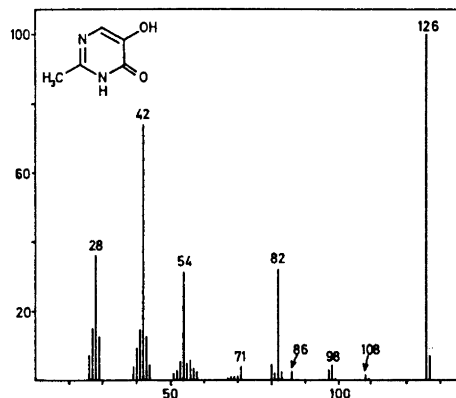

Fig. 5.

The presence of two hydroxyl groups in the 4,5-positions (Fig. 5) complicates the fragmentation pattern. Expulsion of H_2CNO followed by loss of CO seems to be the most important pathway. Both processes are confirmed by metastable peaks. The latter fragment further decomposes (metastable) to m/e 28 (H_2NC) by loss of acetylene. Contributions from the species CO, N_2, and C_2H_4 to the m/e 28 peak are negligible. Deuteration of the two acidic protons showed that both these were lost in the first step of the above processes.
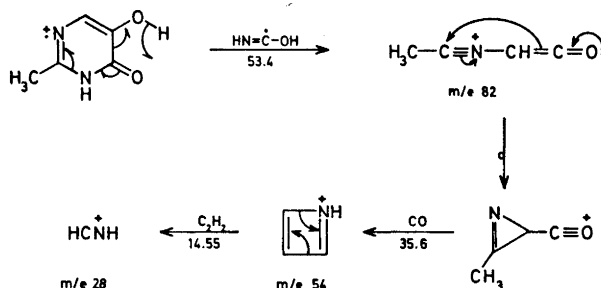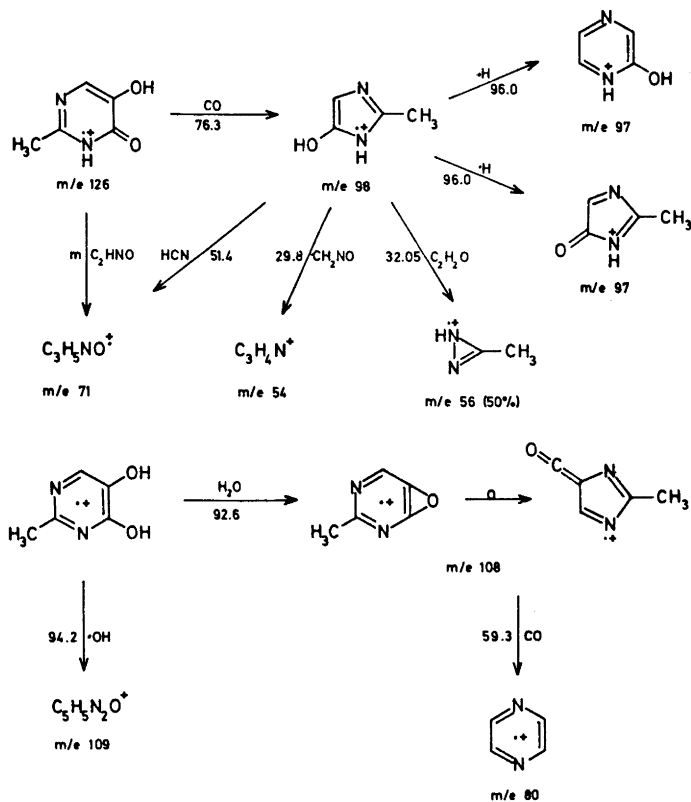

Scheme 4.

m/e 86 arises by expulsion of CH_2CN from the molecular ion. Both deuteriums are retained in the fragment. Scheme 5 suggests its formation.

A weak signal due to loss of a hydroxyl radical (m/e 109) from the molecular ion is present in the spectrum. Loss of water is followed by expulsion of CO to the fragment m/e 80 ($C_4H_4N_2$). Both deuteriums are lost in the process. The (M − CO) fragment is the precursor for a number of fragments as shown by appropriate metastable peaks.
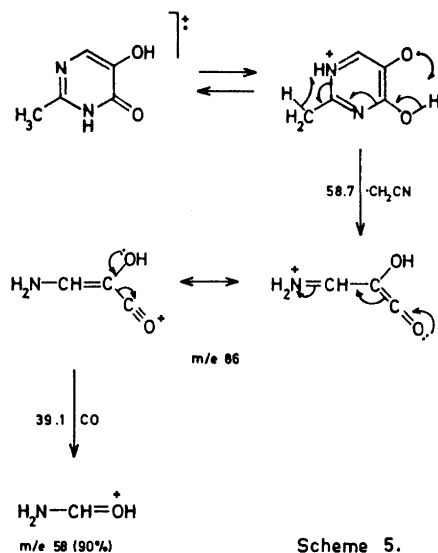
Scheme 5.

Scheme 6.

In the deuterated compound m/e 71 (C_3H_5NO) is shifted to m/e 72 which means that DCN is lost from (M − CO). The prominent peak at m/e 42 is a doublet consisting of 83 % C_2H_4N and 17 % C_2H_2O. The metastable peaks suggest formation from both the molecular ion and from the weak m/e 83, probably by analogous processes to those described for the 5-hydroxy derivative (II).

The O-methyl derivative (IV) (Fig. 6) shows an abundant (M − H) peak. Similar γ-cleavages to the pyrimidine ring have been observed for 6-methoxy and 6-ethoxy derivatives.[5] The 5-ethoxy derivative (III) shows no γ-cleavage. It is therefore reasonable to assume that this fragmentation mode is dependent on electron stabilization from the lone pair on the annular nitrogen, and therefore will occur in derivatives substituted *ortho* to the annular nitrogen. Thus both 2-alkyl [9] and 2-alkylthiopyridines [10,11] show γ-cleavage. Other characteristic fragments are due to loss of CO and formaldehyde from the (M − H) species, and the formyl radical and formaldehyde from the molecular ion. The prominent peaks at m/e 42 and m/e 53 are due to C_2H_4N and C_3H_3N, respectively.
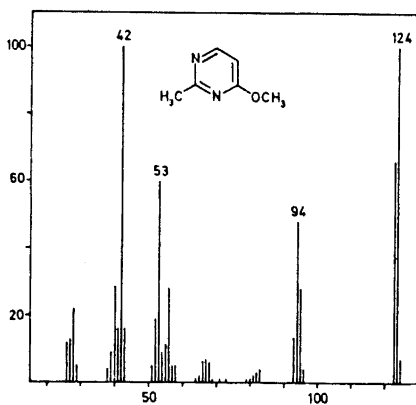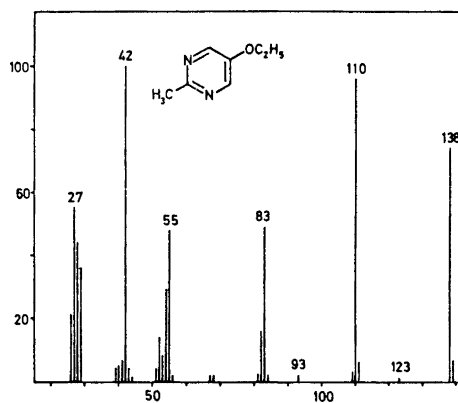

Fig. 6.

Fig. 7.

It is interesting to note that the intense peak at m/e 53 is due to the loss of CH_3CN from m/e 94 while expulsion of HCN is unimportant. In 2-methylpyrimidine (I) the opposite behaviour is observed. In addition a relatively intense metastable peak is present in the ordinary spectrum for the transition m/e 94→m/e 42, while the corresponding process in the spectrum of I is only detectable by metastable defocusing. It is therefore reasonable to believe that the structure of the m/e 94 ion, when generated by loss of formaldehyde from the molecular ion in IV, is different from the structure of the molecular ion in I. The methio derivative (VI) behaves in an analogous fashion.

A possible structure for the m/e 94 ion is suggested in Scheme 7.

The simple 5-ethoxy derivative (III) (Fig. 7) is characterized by expulsion of ethylene (m/e 110). Further fragmentation of the (M − C_2H_4) fragment is the same as that of the 5-hydroxy derivative (II) except for some quantitative differences. Such differences in the breakdown pattern may be due to dif-

Scheme 7.
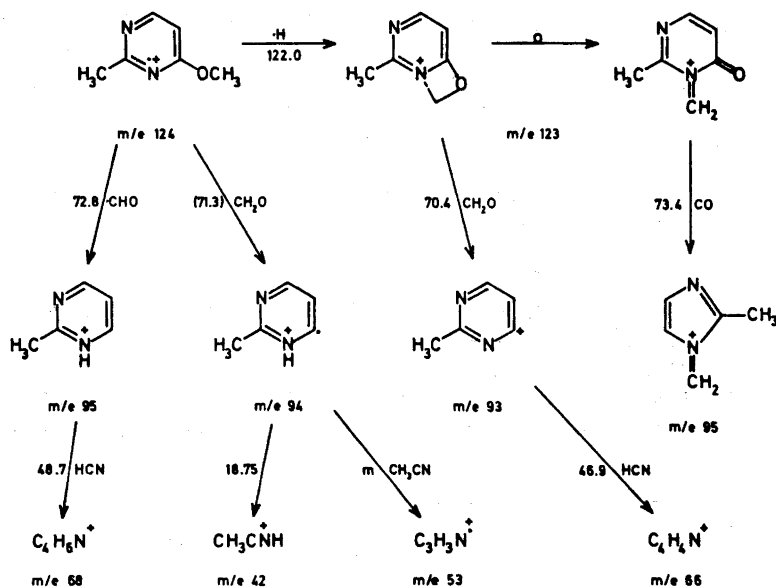
ferent energy distribution of the ions generated *via* fragmentation compared with that generated by direct ionization.[12] The peaks at m/e 27 (C_2H_3) and m/e 29 (C_2H_5) arise from the ethyl group.
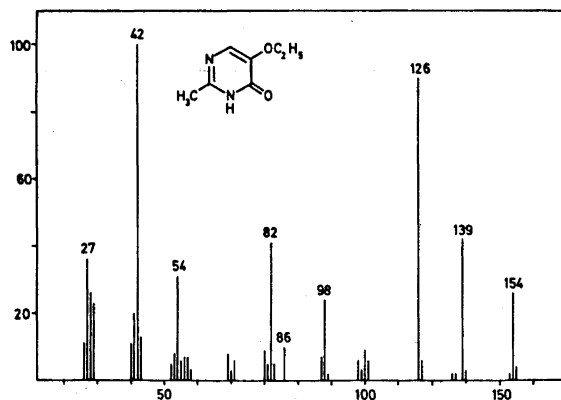

Fig. 8.

An interesting feature in the spectrum of the 5-ethoxy lactam (XIV) (Fig. 8) is the high abundance of the (M − 15) fragment. This fragment is barely present in the simple 5-ethoxy derivative (III). Its formation is best

explained by participation of the neighbouring oxygen in the expulsion of the methyl radical as indicated below. This mode of fragmentation is even more pronounced if the molecule can only exist as a lactam such as in the
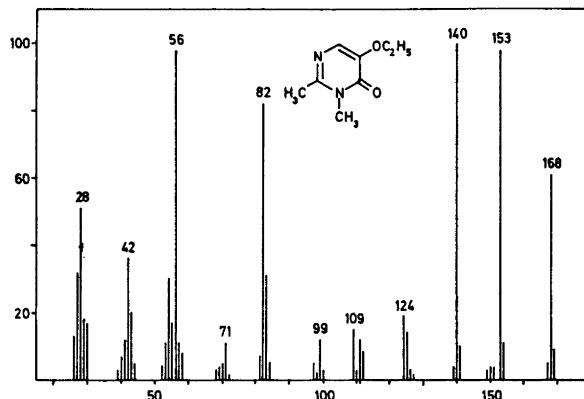

Fig. 9.

N-methyl derivative (XIX) (Fig. 9). The presence of $(M-CH_3)$ in the thiolactam derivative (XVII) (Fig. 14), as discussed below, and the absence of a corresponding fragment in the 4-chloro derivative (X) (Fig. 20) is consistent with the postulated mechanism. A similar mechanism has been proposed for the loss of a methyl group in the spectrum of o-ethoxy benzamide.[13]


R=H, m/e 154
R=CH₃, m/e 168

R=H, m/e 139
R=CH₃, m/e 153
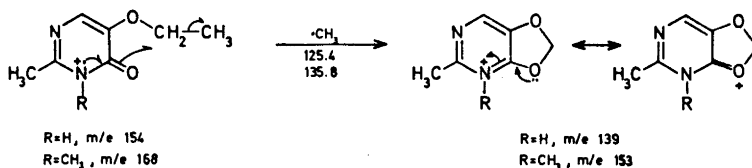
Scheme 8.

A strong peak in the spectrum of XIV (Fig. 8) is at m/e 126 $(M-28)$ due to loss of C_2H_4. This fragment is structurally similar to the dihydroxy compound (XIII) and fragments as such (Fig. 5). The low abundant peaks of m/e 111 and m/e 110 arise by loss of an acetyl radical or acetaldehyde from the molecular ion.

The N-methyl derivative (Fig. 9) furnishes the base peak $(m/e$ 140) by loss of ethylene from the molecular ion. The m/e 140 fragment goes on to expel the $CH_3-N=COH$ radical giving the m/e 82 fragment analogous to the formation of the same fragment from the dihydroxy derivative (XIII). The use of the metastable defocusing technique showed weak transitions to the strong peak at m/e 56 (C_3H_6N), the N-methyl homologue of protonated acetonitrile, from m/e 153, 140, 124, and 111. Its formation and structure is probably analogous to the formation of protonated acetonitrile from the 4-hydroxy compounds. The peaks at m/e 125 and m/e 124 correspond to loss of an acetyl

radical and acetaldehyde as found for XIV. The m/e 42 peak is composed of C_2H_2O (45 %) and C_2H_4N (55 %). Scheme 9 shows the most important processes.

Scheme 9.
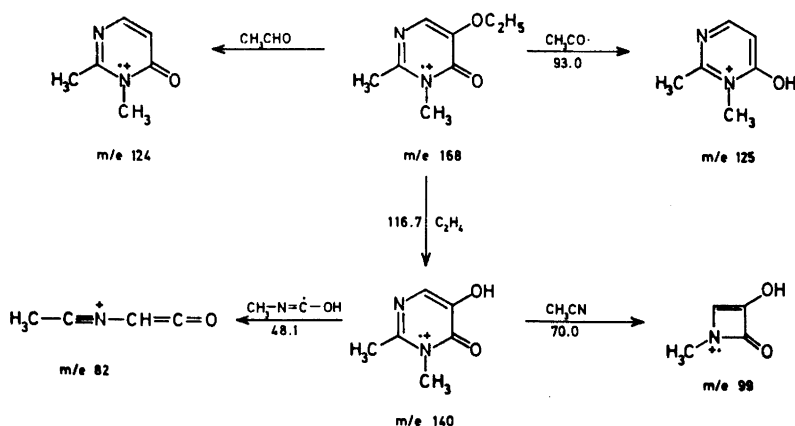
The spectrum of the 4-methoxy-5-ethoxy derivative (V) (Fig. 10) is different from that of the isomeric N-methyl derivative (XIX) discussed above. Besides the expulsion of ethylene (m/e 140) the compound shows loss of methyl
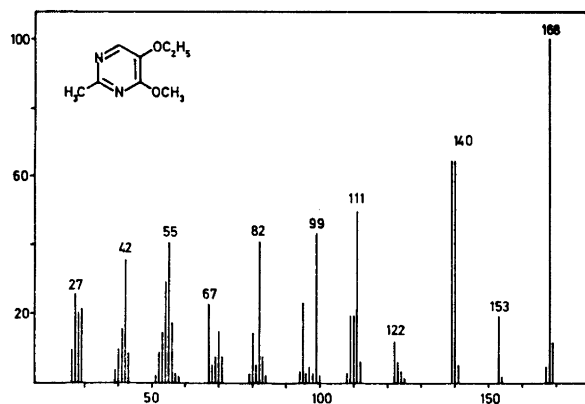

Fig. 10.

(m/e 153) and ethyl (m/e 139) radicals from the molecular ion. It may be assumed by analogy to o-methoxyanisole [14] that this is due to loss of either oxygen substituent with formation of quinonoid structures (a, b; Scheme 10). The behaviour at low electron voltages, however, strongly suggests that expulsion of a methyl radical is a rearrangement process rather than a simple bond cleavage.

A method based on the quasi-equilibrium theory [15] may be applied to the problem for distinguishing between rearrangement reactions and apparently simple bond cleavages. [16] Assuming the formation of (a) and (b) to be simple bond cleavages one would expect the corresponding frequency factors to be of the same order of magnitude. Consequently the higher abundance of (M − 29) over (M − 15) suggests a lower energy of activation for the formation of the former. By lowering the electron energy, however, the ratio (M − 29): (M − 15) decreased rapidly and became less than 0.5 at 14 eV (Fig. 11). Loss of a methyl radical, therefore, has a lower frequency factor. This is also consistent with the observation of an intense metastable peak for this process [17]
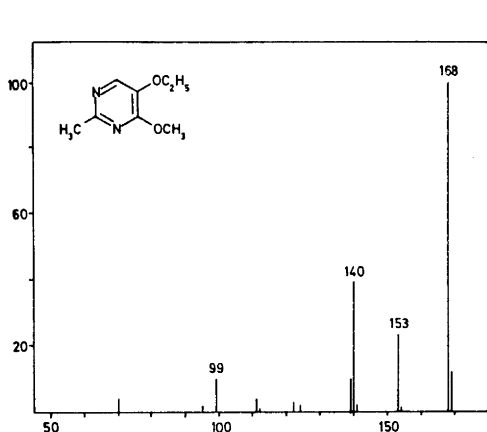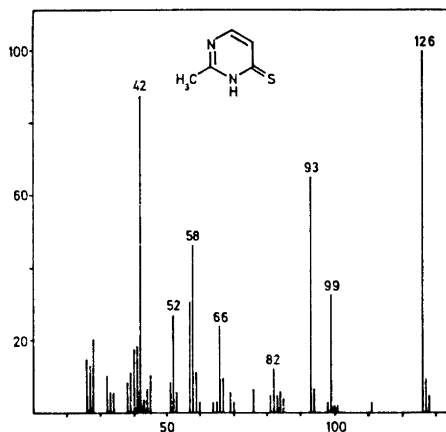

Fig. 11.
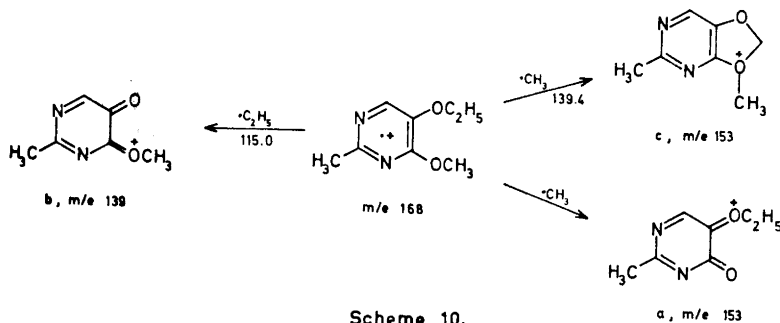

Fig. 12.

as compared with the very small metastable peak associated with loss of the ethyl group. The deuterated thioether (VIII), showed the same behaviour. Therefore a five-membered ring (c) is proposed for the (M − 15) species. The quinonoid structure (a) cannot be definitely excluded, but its contribution to the (M − 15) fragment is considered to be of minor importance.

Scheme 10.

The fragmentations of the thio derivatives differ in some respects from those of the oxygen analogues. In the simplest derivative, the thiolactam (XV) (Fig. 12), the most prominent fragment is caused by loss of SH from the molecular ion (m/e 93). HCN expulsion (m/e 99) is important in contrast to the corresponding lactam (XII). ($M - CH_3CN$) is hardly seen. Expulsion of CS, which is important in the case of 2-mercaptopyridine,[11] gives rise only to a weak signal at m/e 82.

Scheme 11.
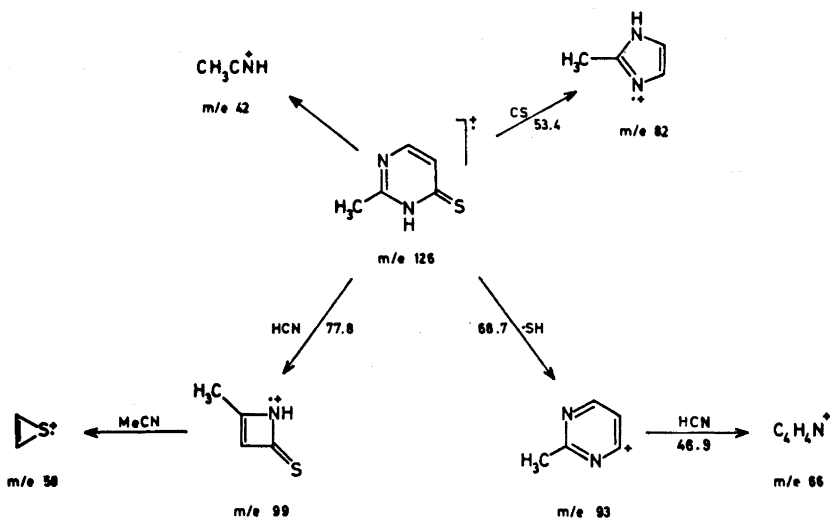
The 5-hydroxy analogue (XVI) (Fig. 13) again shows loss of SH (m/e 109) followed by HCN to give the most intense fragment in the spectrum at m/e 82. In the oxygen analogue (XIII) the same fragment appeared to be formed in a one-step process. In this case a two-step process is involved and no met-

Scheme 12.
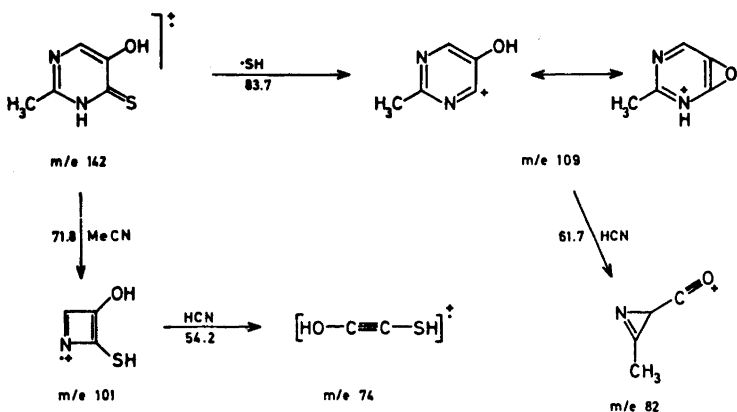
astable was found for the direct loss of H₂SCN from the molecular ion. The metastable peaks for further breakdown of the m/e 82 fragment have the same shapes and relative intensities as in the corresponding oxygen compound (XIII) which suggest similarities in ion structure. Initial loss of HCN is of no importance. Instead CH_3CN is expelled from the molecular ion to give m/e 101 which further loses HCN (m/e 74).

The 5-ethoxy compound (XVII) (Fig. 14), like the oxygen analogue (XIV) (Fig. 8), gives rise to a (M − 15) fragment (m/e 155) but with a lower relative intensity. As in XIV the base peak is due to expulsion of ethylene (m/e 142). This fragment probably has the same structure as the 5-hydroxy compound (XVI) and fragments as such (Fig. 13). Minor peaks due to initial losses of SH, CH_3CN, and CH_3CHO are also present at m/e 137, 129, and 126, respectively. Loss of HCN and SH from m/e 126 is responsible for the peaks at m/e 99 and m/e 93.
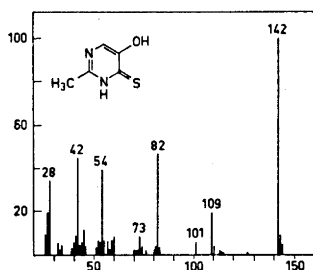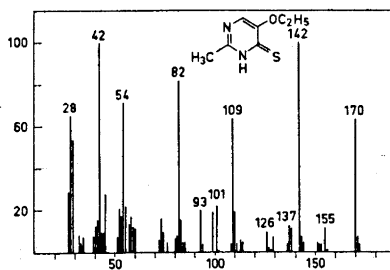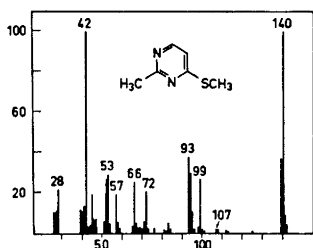

Fig. 13.

Fig. 14.

Fig. 15.
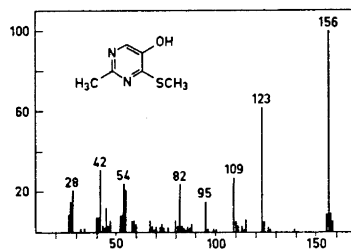
Fig. 16.

In the 4-methio ether (VI) (Fig. 15) loss of SH and S is of little importance. Loss of CH_3CN with formation of the fragment m/e 99 is important. The peaks at m/e 95, 94, and 93 arise by expulsion of CHS, CH_2S, and CH_3S from the molecular ion as reported for 2-alkylthiopyridines.[10],[11] As in the case of the oxygen analogue (IV) γ-cleavage is important with the expulsion of a hydrogen radical.

The 5-hydroxy derivative (VII) (Fig. 16), in contrast to VI, has loss of SH radical as most important process. The (M − SH) fragment decomposes further by loss of CO. The loss of the 4-substituent gives rise to the same fragmentation sequence as observed from (M − SH) in the parent thione (XVI). The expected γ-cleavage is non-important.

Scheme 13.
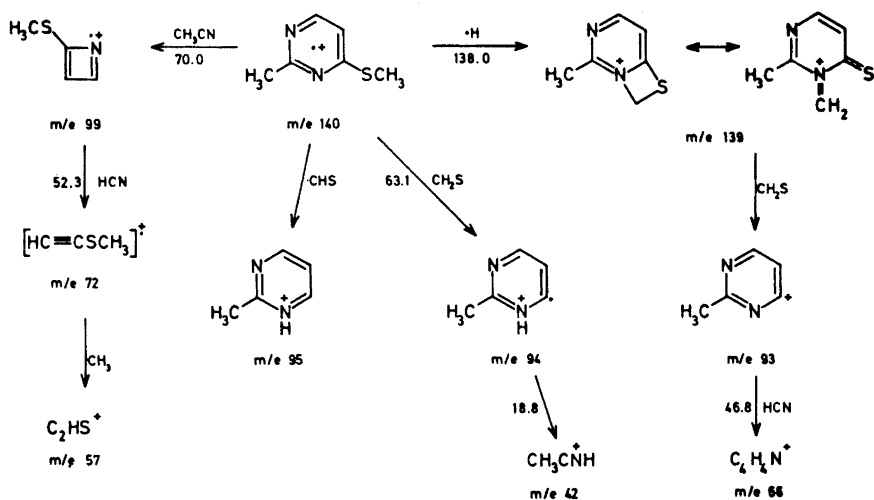
The S-methyl-O-ethyl derivative (VIII) (Fig. 17) like the oxygen analogue (V), exhibits intense fragments due to loss of methyl (m/e 169) and ethyl (m/e 155) groups from the molecular ion (m/e 184). A similar behaviour at low electron voltages suggests a rearrangement reaction with loss of a methyl

Scheme 14.
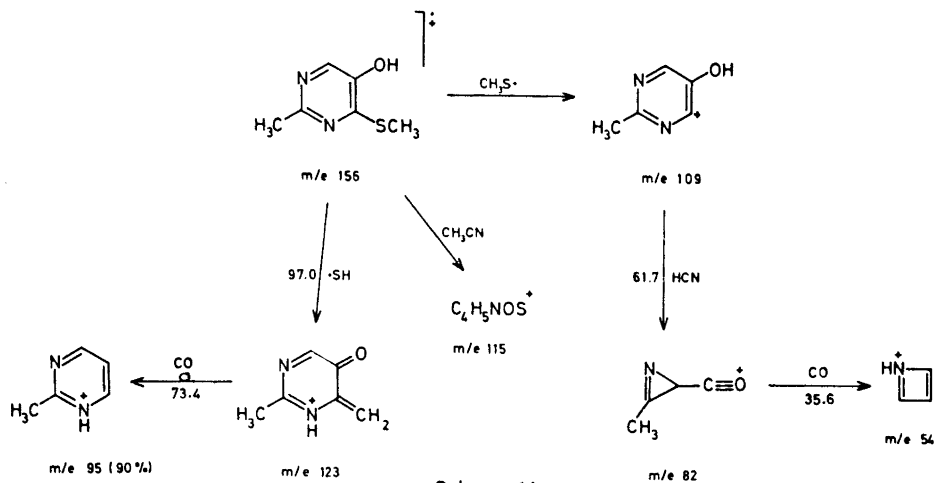
group as found for V. By deuteration of the S-methyl group it was found that 80 % of the (M − CH₃) peak is due to loss of ·CH₃ and that the remaining 20 % is due to loss of ·CD₂H as shown by high resolution. No direct expulsion of

·CD$_3$ could be detected. The structures for the fragments (M − 29) and (M − 15) are supposed to be similar to the postulated structures (b) and (c) from compound V. That other mechanisms may also be involved is indicated by the loss of ·CD$_2$H and by the finding that 25 % of the ethyl group lost contained
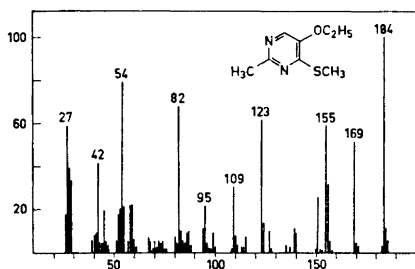
Fig. 17.
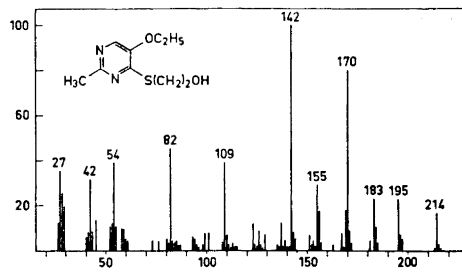
Fig. 18.

one deuterium atom. Ethylene elimination gives rise to the *m/e* 156 fragment which further fragments as the 5-hydroxy compound (VII). Loss of SH and acetaldehyde from the molecular ion gives rise to less abundant peaks at *m/e* 151 and *m/e* 140, respectively.

The *β*-hydroxyethioether (XI) (Fig. 18) expels C$_2$H$_4$O by a McLafferty rearrangement to the corresponding thiolactam (*m/e* 170) which fragments further as XVII (Fig. 14). Loss of water, which is probably a thermal process, is responsible for the *m/e* 196 peak. Further expulsion of a hydrogen radical seems to be a favourable process explained by formation of a thiazolo structure (*m/e* 195). The corresponding dihydrothiazolo system may be proposed for the (M − OH) fragment. *γ*-Cleavage with expulsion of the CH$_2$OH radical explains the *m/e* 183 peak.
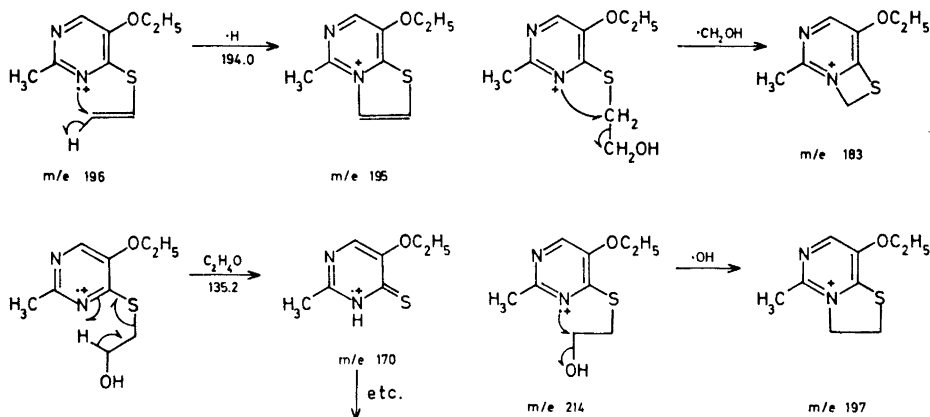
Scheme 15.

Chlorine expulsion (m/e 93) is the dominating pathway for the chloro derivative (IX) (Fig. 19). In the 5-ethoxy analogue (X) (Fig. 20) ethylene is initially lost (m/e 144) followed by chlorine (m/e 109). The m/e 93 fragment further breaks down by loss of HCN (m/e 66) or CH_3CN (m/e 52). The otherwise abundant peak at m/e 42 is of only moderate intensity in the spectra of the chloro compounds.
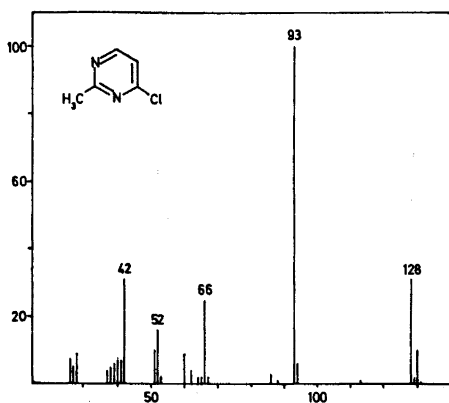
Fig. 19.
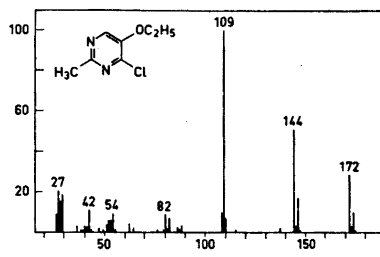
Fig. 20.

Table 1. UV absorption.
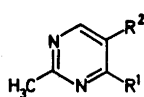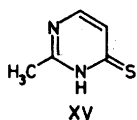
II		R² = OH
III	} R¹ = H	R² = OEt
VI		R² = H
VII	} R¹ = SMe	R² = OH
VIII		R² = OEt

Comp.	0.1 N HCl				0.1 N NaOH			
	λ_{max}	$\varepsilon \times 10^{-3}$	λ_{max}	$\varepsilon \times 10^{-3}$	λ_{max}	$\varepsilon \times 10^{-3}$	λ_{max}	$\varepsilon \times 10^{-3}$
XV			305	14.3	219	8.5	299	12.3
II	223	10.1	292	5.9	237	12.2	311	3.8
III	227	9.4	294	4.0	217	10.4	279	3.6
VI	224	6.9	299	17.3	251	7.8	283	10.4
VII	238	8.3	314	15.3	235	10.6	327	9.3
VIII	240	8.2	313	16.9	225 245	9.1 5.4	299	10.9

Table 2. NMR Spectra in TFA.

II		R² = OH
	} R¹ = H	
III		R² = OEt
VI		R² = H
VII	} R¹ = SMe	R² = OH
VIII		R² = OEt
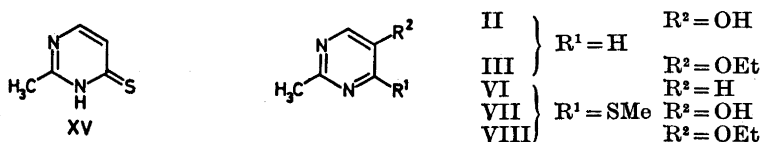
The shifts are given in τ.

Comp.	2	4	5	6
XV	7.12	–	2.58	2.28
II	7.02	1.10	–	1.10
III	6.95	1.07	α 5.58 β 8.40	1.07
VI	7.08	7.20	2.40	1.77
VII	7.14	7.22	–	2.12
VIII	7.14	7.24 ᵃ	α 5.68 β 8.37	2.27

ᵃ Shown by deuteration.

EXPERIMENTAL

The mass spectra were recorded on an AEI MS 902 mass spectrometer. The source temperature was kept at 200°, the electron energy at 70 eV and trap current at 100 μA. The compounds I, III, V, VI, VIII – X were introduced through the "all glass heated inlet system" with the inlet system at 130°. All the other compounds were introduced directly into the source. High resolution measurements were performed by peak matching with a resolving power of 15 000.

The NMR spectra for the new compounds synthesized for this MS investigation were recorded on a Varian A-60A instrument and the UV spectra on a Jasco model J − 10 spectropolarimeter.

The UV spectra recorded in acid and basic media are given in Table 1. The long-wave absorption band in acid medium undergoes a blue shift when changing to basic medium. The 5-hydroxy compounds, however, show a red shift due to the phenolate ion formed in basic medium.

The NMR spectra were recorded in TFA solution (Table 2). The chemical shifts of the 2-methyl and the S-methyl protons appear close together. For compound VIII it was shown by deuteration of the S-methyl group, by methylation of the corresponding thione (XVII) using deuteriomethyl iodide in the usual way, that the lower field signal is due to the 2-methyl protons. It seems reasonable to assume that the 5-substituents in this series will hardly affect the relative chemical shifts for the protons of the two methyl groups. Therefore the 2-methyl protons have been assigned to the lower field signal also for the compounds VI and VII.

The following compounds were available or were synthesized by reported procedures: I, IX, XII;[18] IV;[19] V, X, XI, XVI, XVII, XIX;[20] XIII;[21] XIV;[22] XVIII.[23]

The new compounds synthesized are described below:

5-Hydroxy-2-methylpyrimidine (II). To a solution of 5-hydroxy-2-methylpyrimid-4-thione [20] (0.4 g, 2.4 mmol) in water (10 ml) and aq. ammonia (3 ml) was added Raney-nickel [24] (1.5 g). The mixture was heated under reflux for 1 h, filtered hot, the filtrate

and aqueous washing combined, the resultant solution heated with charcoal, and the decolourized solution evaporated to dryness. The solid residue was crystallized from ethyl acetate in white needles; yield 0.08 g (31 %), m.p. 171 – 171.5°. (Found: C 54.82; H 5.3. Calc. for $C_5H_6N_2O$: C 54.52; H 5.5.)

5-Ethoxy-2-methylpyrimidine (III). The title compound was prepared as above from the corresponding thione (XVII). The filtrate after the reaction was made further alkaline with dilute NaOH, the desired product extracted into ether, the ether extracts evaporated and the residue distilled, b.p. 79 – 80°/10 mmHg. The colourless distillate crystallized in white plates; yield 31 %, m.p. 34.5 – 35°. (Found: C 60.55; H 7.05; N 20.41. Calc. for $C_7H_{10}N_2O$: C 60.85; H 7.30; N 20.28.)

4-Methio-2-methylpyrimidine (VI). Methyl iodide (200 mg, 1.3 mmol) was added to a solution of 2-methylpyrimid-4-thione (126 mg, 1 mmol) in 2 N KOH (5 ml). The solution became turbid after stirring for a few minutes at room temperature. The insoluble material formed was extracted into ether, the ether extracts evaporated and the residue distilled to give a nearly colourless liquid, b.p. 94 – 96°/15 mmHg. The yield in this reaction is nearly quantitative. (Found: C 51.10; H 5.69; N 20.11. Calc. for $C_6H_8N_2S$: C 51.40; H 5.75; N 19,98.)

5-Ethoxy-4-methio-2-methylpyrimidine (VIII). The title compound was prepared as above from the corresponding 4-thione (XVII) and purified by sublimation at 35°/15 mmHg; white needles, m.p. 58 – 58.5°. (Found: C 51.94; H 6.38; N 15.23. Calc. for $C_8H_{12}N_2OS$: C 52.14; H 6.56; N 15.20.)

5-Hydroxy-4-methio-2-methylpyrimidine (VII). The title compound was prepared as above from the corresponding thione (XVI). The pH of the solution was brought to 4 and the solution concentrated when the desired substance was precipitated. Recrystallization from water gave white needles, m.p. 191 – 192°. (Found: C 46.35; H 5.33; N 17.90. Calc. for $C_6H_8N_2OS$: C 46.13; H 5.16; N 17.94.)

2-Methylpyrimid-4-thione (XV). A stirred solution of 2-methylpyrimid-4-one [18] (1.1 g, 0.01 mol) and phosphorus pentasulphide (2.2 g, 0.01 mol) in dry pyridine (35 ml) was heated for 5 min at 70°. Longer heating reduced the yield. The cold, dark red solution was poured into water (150 ml), the resultant mixture evaporated to dryness and the desired substance extracted into boiling ethyl acetate and the solution evaporated. The residual solid crystallized as yellow needles from ethyl acetate or water and was further purified by sublimation at 115°/0.5 mmHg; yield variable (35 – 65 %), m.p. 148 – 149°. (Found: C 47.53; H 4.69; N 22.27. Calc. for $C_5H_6N_2S$: C 47.59; H 4.79; N 22.20.)

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