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ELECTRON IMPACT STUDY ON SIMPLE PYRIMIDINES—III[1]

FURTHER EXAMPLES ON THE FRAGMENTATION OF 2-AMINOPYRIMIDINES

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Abstract—Mass spectra of ten 2-aminopyrimidines have been determined and typical fragmentation patterns characteristic of the nature and position of additional substituents discussed. 2-Amino-4-phenyl-6-methylpyrimidine and its 5-bromo compound afford mass spectra exhibiting a pronounced $(M-1)^+$ ion. Loss of ketene assumes a great importance in the spectra of 2-acetylaminopyrimidines. A halogen atom at C-4 (or 6) is more easily removed from the molecular ion of 2-aminopyrimidines than the one at C-5. Fragmentations of 2-piperidino- and 2-morpholino-pyrimidines were interpreted. Major ions arise from cleavage of the piperidine or morpholine portion of the molecule. In addition, in the spectra of these compounds elimination of the nitrogen containing substituent with and without migration of one hydrogen assumes an importance.

RECENTLY studies on the electron impact induced fragmentation have been applied to a variety of heterocycles and aided the structural elucidation of natural products containing heterocycles.[2,3] In the pyrimidine field the mass spectral behaviour of the pyrimidine components of nucleic acid[4] and barbituric acid derivatives[5] have been reported. In Part I of this series[6] mass spectral behaviour of six 2-aminopyrimidines was discussed and it has been revealed that the amino group is lost as hydrogen cyanide through the imino form and in most cases can direct fragmentations but if there are other functions in the molecule, fragmentation triggered by these additional functional groups operates in an appreciable manner. In view of the biological importance of 2-aminopyrimidines additional knowledge of their fragmentation patterns is very desirable. The ten 2-aminopyrimidines examined include 2-acetylamino-, 2-piperidino- and 2-morpholinopyrimidines. The electron impact induced fragmentations of each are discussed in this communication. 5-Halogenopyrimidines were prepared by the action of N-halogenosuccinimide on appropriate 2-aminopyrimidines.[7] N,N,5-d_3-2-Amino-4-phenyl-6-methylpyrimidine required for the present study was prepared from deuterated benzoyl acetone.

EXPERIMENTAL

Mass spectra were determined with a Hitachi RMU 6D mass spectrometer fitted with an all-glass inlet system at an ionization voltage of 80 eV. The sample was introduced through a heated inlet

[1] Part II. T. Nishiwaki, *Chem. & Pharm. Bull.* under consideration.
[2] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of mass spectra of organic compounds* Chapter 11. Holden-Day, San Francisco (1964).
[3] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Structure elucidation of natural products by mass spectrometry* Vol. 1. Holden-Day, San Francisco (1964).
[4] J. Rice, G. Dudek and M. Barber, *J. Amer. Chem. Soc.* **87**, 4569 (1965).
[5] A. Costopanagiotis and H. Budzikiewicz, *Monatsh. Chem.* **96**, 1800 (1965).
[6] T. Nishiwaki, *Tetrahedron* **22**, 3117 (1966).
[7] T. Nishiwaki, *Chem. & Pharm. Bull.* **10**, 1029 (1962); *Tetrahedron* **22**, 2401 (1966).

TABLE 1. MASS SPECTRA OF 2-AMINOPYRIMIDINES

Compound														
IV	*m/e*	28	39	42	43	50	51	52	63	71	74	75	76	77
	I(%)	4	7	4	7	4	10	3	3	4	4	7	4	11
	m/e	81	88	89	92	100	101	102	103	104	114	115	116	117
	I(%)	3	3	4	3	3	7	3	3	5	3	15	6	3
	m/e	118	119	127	128	140	141	142	143	157	180	182	183	184
	I(%)	3	3	9	5	5	5	15	22	5	5	7	12	98
	m/e	185	194	196	262	263	264	265	266					
	I(%)	12	3	3	34	100	47	98	13					
IX	*m/e*	15	17	18	27	28	39	40	41	42	43	53	54	55
	I(%)	6	6	26	4	8	10	5	4	10	30	3	4	4
	m/e	66	67	81	82	83	95	96	107	108	123	124	137	165
	I(%)	6	12	4	6	7	7	39	3	4	100	7	2	37
	m/e	166												
	I(%)	4												
X	*m/e*	15	18	28	39	40	42	43	50	51	52	54	63	66
	I(%)	4	3	6	6	3	6	26	3	7	3	2	3	3
	m/e	67	76	77	78	89	102	103	104	115	116	128	129	142
	I(%)	7	5	12	3	3	7	4	5	4	5	7	4	3
	m/e	143	144	157	158	169	170	183	184	185	186	199	227	228
	I(%)	8	4	3	3	2	2	5	98	100	12	2	72	11
XX	*m/e*	15	18	27	28	29	32	39	40	41	42	43	53	54
	I(%)	5	17	13	38	8	5	23	7	23	32	5	10	7
	m/e	55	56	65	66	67	68	80	81	82	83	84	85	93
	I(%)	17	7	5	11	43	5	5	10	7	9	73	5	15
	m/e	107	108	109	122	123	124	135	136	137	148	149	150	162
	I(%)	21	66	13	10	16	4	30	52	9	54	15	12	94
	m/e	163	176	177	190	191	192							
	I(%)	16	39	4	44	100	13							
XXI	*m/e*	15	18	27	28	29	39	40	41	42	43	51	52	53
	I(%)	5	13	15	20	9	22	6	25	41	4	5	5	11
	m/e	54	55	56	65	66	67	68	69	73	78	79	80	81
	I(%)	7	20	9	5	13	34	5	3	5	3	2	5	5
	m/e	82	83	84	85	107	141	142	143	144	156	157	158	159
	I(%)	5	5	86	5	10	16	50	13	16	9	16	6	5
	m/e	169	170	171	172	182	183	184	185	186	196	197	198	199
	I(%)	25	41	14	13	37	9	23	3	3	80	12	27	4
	m/e	210	211	212	224	225	226	227	228					
	I(%)	40	5	12	44	100	27	34	4					
XXII	*m/e*	27	28	29	39	40	41	42	52	53	54	55	56	65
	I(%)	6	10	3	12	4	7	18	3	6	4	9	3	3
	m/e	66	67	68	80	81	82	86	93	94	107	108	109	122
	I(%)	8	31	3	4	8	2	4	16	3	17	100	8	4
	m/e	135	136	137	148	149	150	162	163	164	178	192	193	194
	I(%)	7	49	6	43	7	12	89	27	6	6	18	48	6

system. Only those peaks with an intensity equal to or greater than 2% of the base peak are recorded in the reproduced spectra. The following compounds are considered in the present study: 2-amino-4-phenyl-6-methylpyrimidine (I); 2-amino-4-phenyl-5-bromo-6-methylpyrimidine (IV); 2-amino-5-chloro-4,6-dimethylpyrimidine (V); 2-acetamino-4,6-dimethylpyrimidine (IX); 2-acetamino-4-phenyl-6-methylpyrimidine (X); 2-amino-4,6-dichloropyrimidine (XII); 2-amino-5-bromo-4,6-dichloropyrimidine (XIII); 2-piperidino-4,6-dimethylpyrimidine (XX); 2-piperidino-5-chloro-4,6-dimethylpyrimidine (XXI); 2-morpholino-4,6-dimethylpyrimidine (XXII).

N,N,5-d_3-2-*Amino-4-phenyl-6-methylpyrimidine.* Benzoyl acetone (0·50 g) in abs ether (4 ml) was added to the DCl-D_3PO_4 soln (D_2O 4 ml and PCl_5 1·0 g)[8] and stirred for 2 hr at room temp. The ethereal soln was separated, the solvent removed, the residue dissolved in abs ether (4 ml) and again stirred with DCl-D_3PO_4 (D_2O 4 ml and PCl_5 1·0 g) for 4 hr. The ethereal layer was separated, the ether removed, and the residue (0·42 g) was fused with guanidine carbonate (0·40 g) for 1·5 hr at 150° which was obtained by dissolving commercial guanidine carbonate (1·0 g) in D_2O (3 ml) and evaporating the solvent *in vacuo*. The solid was filtered and crystallized twice from abs EtOH to give the compound (0·13 g), m.p. 178–179°.

The spectra of N,N-d_2- and N,N,5-d_3-2-amino-4-phenyl-6-methylpyrimidine were taken by Shannon's procedure.[9]

RESULTS AND DISCUSSION

Burr *et al.*[10] have noted that biphenyl undergoes little fragmentations and the principal product is $C_6H_4^+$ with concomitant formation of $C_6H_6^+$ ion, while Natalis *et al.*[11] and Eland *et al.*[12] have shown that the main fragment ions observed in the spectrum of biphenyl correspond to the loss of one or two hydrogen atoms or to the loss of C_2H_2, C_3H_3 and C_4H_4 groups from the molecular ion. Structural similarity

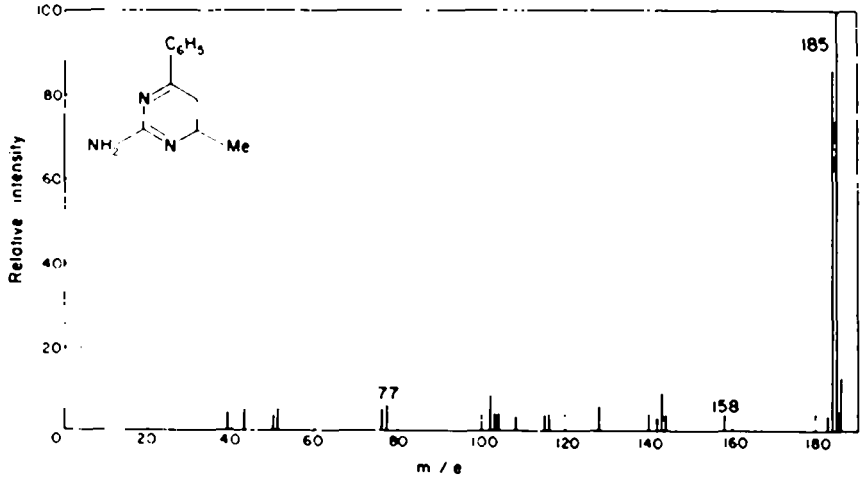


FIG. 1. Mass spectrum of 2-amino-4-phenyl-6-methylpyrimidine

of 4-phenylpyrimidines to biphenyl has led to the investigation of the mass spectrum of 2-amino-4-phenyl-6-methylpyrimidine (I). The molecular ion (*m/e* 185) of I, which is the base peak and amounts to 32% of the total ion current, loses a hydrogen, giving rise to a very intense ion at *m/e* 184. This is an unexpected feature from the

[8] J. Seibl and T. Gäumann, *Helv. Chim. Acta* **46**, 2857 (1963).
[9] J. Shannon, *Austral. J. Chem.* **16**, 683 (1963).
[10] J. Burr, J. Scarborough and R. Shudde, *J. Phys. Chem.* **64**, 1359 (1960).
[11] P. Natalis and J. Franklin, *J. Phys. Chem.* **69**, 2935 (1965).
[12] J. Eland and C. Danby, *J. Chem. Soc.* 5935 (1965).

TABLE 2. DEUTERIUM CONTENTS OF N,N,5-d_3 AND N,N-d_2 COMPOUNDS OF I

m/e	Deuterated species (%) N,N,5-d_3-compound	N,N-d_2-compound
184	—	18
185	8	39
186	13	33
187	33	10
188	37	—
189	8	—
190	1	—

behaviour of, for example, 2-amino-4,6-dimethylpyrimidine.[6] Although incomplete deuteration somewhat complicates the result, the fact that the spectrum of N,N,5-d_3-2-amino-4-phenyl-6-methylpyrimidine also displays a very prominent $(M-1)^+$ ion (*m/e* 187) (Table 2) signifies that formation of this $(M-1)^+$ ion involves loss of a phenyl hydrogen. The $(M-1)^+$ peak has been frequently observed in the spectra of phenyl-substituted compounds.[13,14] This $(M-1)^+$ ion will not involve loss of a hydrogen from the methyl in view of the behaviour of 2-ethylpyridine[15] and 2-amino-4,6-dimethylpyrimidine.[6] This behaviour is still maintained in the spectra of its 5-bromo- and 2-acetylamino-compounds (*vide infra*).

As might be expected from the behaviour of other 2-aminopyrimidines,[6] the molecular ion of I undergoes loss of hydrogen cyanide (Scheme 1). Although the intensity of the ion (*m/e* 158) (*m/e* 159 in N,N-d_2-compound) thus produced is negligible (R.I. 3%), occurrence of this process is supported by the observation of a metastable ion at *m/e* 135 (calc. for 185 → 158, 134·9) and deuteration. The most obvious structure for the $(M-27)^+$ ion arised from the molecular ion of I will be the open-chain ion-radical (II-a) but by analogy to the previous assumption on the fragmentation of 2-amino-4,6-dimethylpyrimidine the molecular ion of 3-phenyl-5-methylpyrazole (III-a) will be an another possible representation. The mass spectrum of 3-phenyl-5-methylpyrazole was determined and is presented in Table 3. But it was almost impossible to compare the spectra of I and 3-phenyl-5-methylpyrazole in detail because of the low intensity of all peaks up to *m/e* 158. It can only be seen that the latter is also very stable under electron bombardment, the molecular ion amounting to 37% of the total ions. It should be noted that loss of a hydrogen from the molecular ion is also appreciable in the spectrum of the latter.

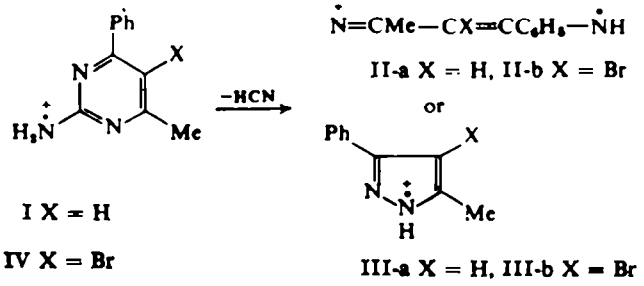
Although of low abundance, there are ions with *m/e* 77 and 76, which will be $C_6H_5^+$ and $C_6H_4^+$ ions and may arise by the scission of the phenyl-pyrimidine linkage

TABLE 3. MASS SPECTRUM OF 3-PHENYL-5-METHYLPYRAZOLE

m/e	39	42	50	51	63	77	78	79	89	90	102	103
I (%)	3	3	3	7	4	10	3	3	4	4	3	3
m/e	104	115	117	127	128	129	130	143	157	158	159	
I (%)	3	4	5	5	10	7	7	6	21	100	11	

[13] J. Bowie, D. H. Williams, S. Lawesson and G. Schroll, *J. Org. Chem.* **31**, 1384 (1966).
[14] A. Bose, I. Kugaievsky, P. Funke and K. Das, *Tetrahedron Letters* 3065 (1965).
[15] K. Biemann, *Mass spectrometry. Organic chemical applications* p. 134. McGraw-Hill (1962).

Scheme 1



of I, II-a (or III-a), or other possible intermediates. Formation from the $(M-15)^+$ ion may be partly responsible for the *m/e* 77 species, since a metastable ion was recognized at *m/e* 34·5 (calc. for 170 → 77, 34·9). An ion *m/e* 108 was observed and the pyrimidine portion formed by this cleavage may account for this ion species. Two peaks, though small in intensity, should be noted. An ion *m/e* 143 shifted to *m/e* 145 in N,N-d_2-compound, while shift to *m/e* 146 was recognized in N,N,5-d_3-compound. These results suggest that this ion will be formed by loss of acetonitrile from the $(M-1)^+$ ion. An ion *m/e* 102 which did not shift in N,N-d_2-compound but shifted to *m/e* 103 in N,N,5-d_3-compound, showing the retention of the C-5-hydrogen, will be formulated as the molecular ion of phenyl acetylene.

In order to compare with the spectrum of 2-amino-4-phenyl-6-methylpyrimidine the behaviour of its 5-bromo-compound (IV) was examined. Loss of a hydrogen from the molecular ion (*m/e* 263 and 265) of IV is still a significant process and yields two prominent ions (*m/e* 262 and 264) with height of 34 and 47%, respectively, to the base peak. IV exhibits a very pronounced loss of a bromine atom and produces a peak at *m/e* 184. Metastable ions were recognized for this process at *m/e* 129 (calc. for 263 → 184, 128·7) and *m/e* 128 (calc. for 265 → 184, 127·7).

There is a prominent ion at *m/e* 143. The ratio of the isotopic ion-intensities at *m/e* 144 and 145 to the ion-intensity at *m/e* 143 were 0·110 and 0·005, respectively. These values are reasonably close to the calculated ratios (0·1060 and 0·0051) for the atomic combinations $C_9H_7N_2$. Thus it is assumed that this *m/e* 143 ion is produced by loss of acetonitrile from the $(M-Br)^+$ ion.

The molecular ion of IV will suffer loss of hydrogen cyanide and produce two isotope peaks at *m/e* 236 and 238 formulated by either II-b or III-b (Scheme 1). Hydrogen cyanide may also be ejected from the $(M-Br)^+$ ion to result in the formation of an *m/e* 157. But small or negligible abundance of these expected peaks illustrates the relatively unfavourable nature of such sequences, and in fact metastable ions characteristic for these pathways were not well recognized.

In a previous paper[6] fragmentations of two 2-amino-5-halogenopyrimidines were discussed. An additional example is now provided. The molecular ion of 2-amino-5-chloro-4,6-dimethylpyrimidine (V), which appears at *m/e* 157 and 159 with the intensity of 3:1, undergoes loss of hydrogen cyanide (Scheme 2) and gives two prominent isotope peaks at *m/e* 130 and 132, consistent with the behaviour of 2-amino-4,6-dimethylpyrimidine. Metastable ions at *m/e* 108 (calc. for 157 → 130, 107·6) and *m/e* 109·5 (calc. for 159 → 132, 109·5) can support this process. Again either VI or

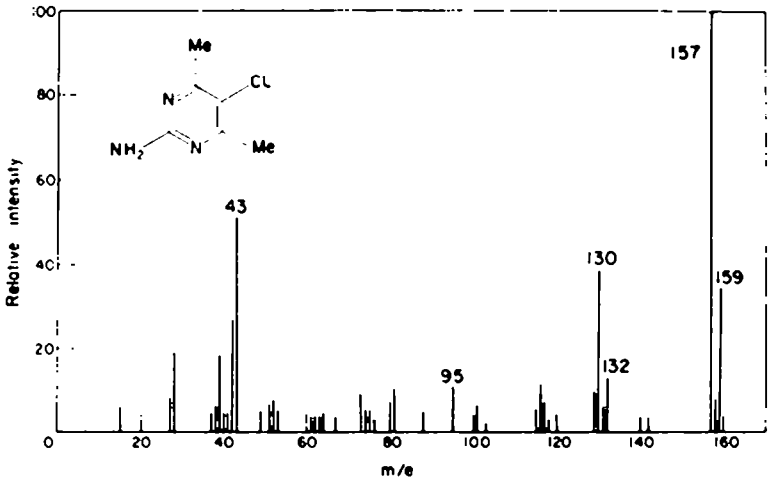
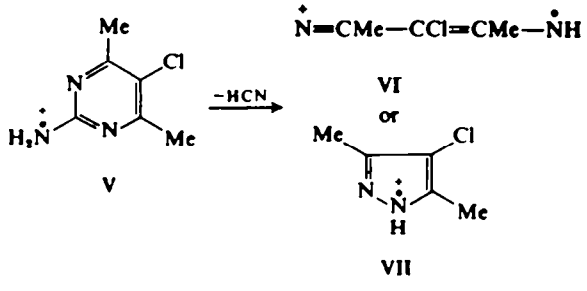


FIG. 2. Mass spectrum of 2-amino-5-chloro-4,6-dimethylpyrimidine.

VII may represent this ion species. As was the case with 2-amino-4,6-dimethylpyrimidine each of these two isotope peaks will lose a hydrogen atom. In fact small ions with *m/e* 129 and 131 were observed, with a metastable ion at *m/e* 128 (calc. for 130 → 129, 128·0). Elimination of a chlorine atom from the $(M-27)^+$ ion is a comparatively significant process, resulting in the formation of an ion *m/e* 95, as is evidenced by metastable ions *m/e* 68·5 (calc. for 132 → 95, 68·4) and *m/e* 69·5 (calc. for 130 → 95, 69·4). The *m/e* 95 ion probably suffers loss of mass units 15 to give an ion *m/e* 80. The fact that the ion *m/e* 80 was found in small abundance in the

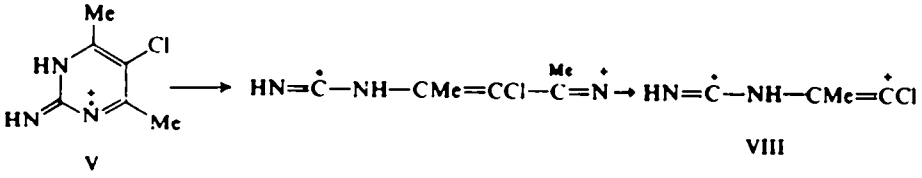
Scheme 2



spectrum of 2-amino-4,6-dimethylpyrimidine may rationalize the formulation of this ion as $\overset{+}{N}$=CMe—C≡C—$\dot{N}$H. The $(M-Cl)^+$ ion (*m/e* 122) is of negligible abundance, which shows the preference of the loss of hydrogen cyanide from the molecular ion over the loss of C-5 chlorine. Loss of N_2H from the $(M-27)^+$ ion will be a probable occurrence, since there were recognized two chlorine-containing peaks *m/e* 101 and 103 with intensity ratio 3:1.

Alternatively, initial ionization at the ring nitrogen atom, even if mechanistically less favourable, brings about loss of acetonitrile from the molecular ion of V and two peaks corresponding to this process were observed at *m/e* 116 and 118 with the intensity ratio of 3:1 (Scheme 3). VIII may be a plausible representation for this.

Scheme 3

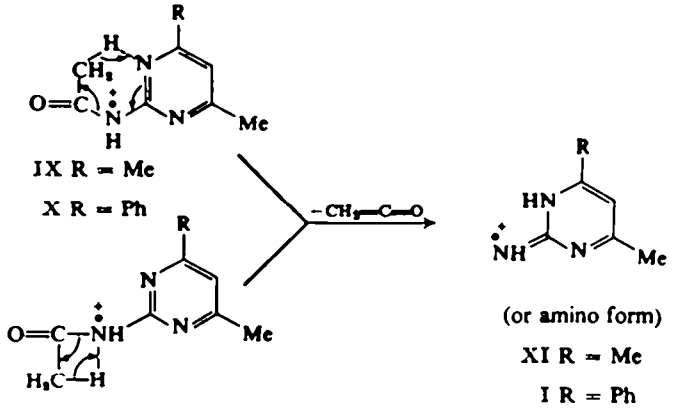


V VIII

This $(M-41)^+$ ion subsequently ejects a chlorine and produces an ion *m/e* 81, showing the preference of the loss of acetonitrile over the loss of the C-5–halogen.

To help the discussion on the mechanism of the fragmentation of 2-amino-pyrimidines the spectra of their acetylated compounds, namely, 2-acetamino-4,6-dimethylpyrimidine (IX) and 2-acetamino-4-phenyl-6-methylpyrimidine (X) were determined. Each of their molecular ions is prominent. An important feature in each of the spectra is elimination of a molecule of ketene with migration of a hydrogen to produce an ion *m/e* 123 or *m/e* 185, which is observed as the base peak. Their formation can be accounted for by invoking the six- or four-membered cyclic transition state and they will be represented as XI and I (Scheme 4). Metastable transition was recognized at *m/e* 92 (calc. for 165 → 123, 91·6) for IX and at *m/e* 151 (calc. for 227 → 185, 150·7) for X, respectively. Such a rearrangement process has been known to be operative in the fragmentation of N-acetyl alkyl amines.[16] It can be seen that

Scheme 4



IX R = Me

X R = Ph

(or amino form)

XI R = Me

I R = Ph

loss of a hydrogen from the $(M-42)^+$ ion is also prominent in the spectrum of X and the benzene hydrogen may be responsible. The $(M-42)^+$ ions XI and I undergo loss of hydrogen cyanide to give ions at *m/e* 96 and *m/e* 158, respectively, as demonstrated by appropriate metastable ions. In general, however, it is not necessary to invoke new principles for the explanation of the lower mass region than the $(M-42)^+$ ion with the exception of $(M-57)^+$ and $(M-58)^+$ ions (*vide infra*).

Behaviour of 2-amino-5-halogenopyrimidines under electron impact has become clear from the foregoing discussion, but 2-amino-4-halogenopyrimidines are expected to behave in a different way reflecting the difference of electron availability at C-4

[16] Chapter 4 of Ref. 2.

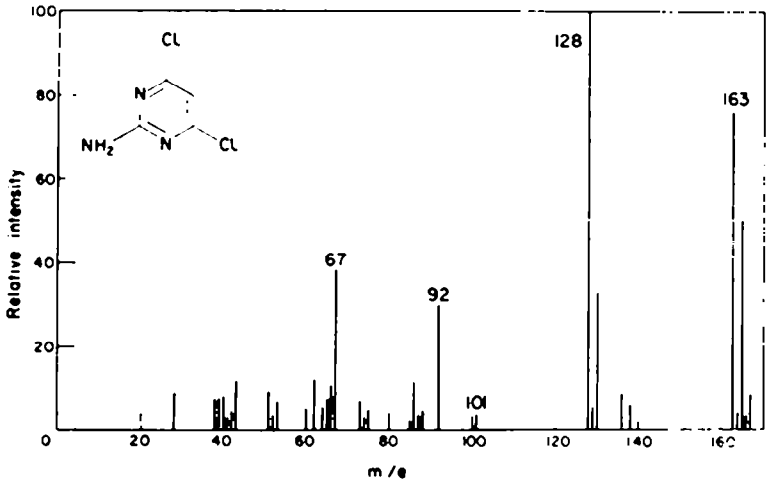


FIG. 3. Mass spectrum of 2-amino-4,6-dichloropyrimidine.

and C-5. The spectra of 2-amino-4,6-dichloropyrimidine (XII) and its 5-bromo-compound (XIII) were determined. The molecular ion of XII appears at *m/e* 163, 165, and 167 with the intensity ratio of 9:6:1. Loss of hydrogen cyanide from the molecular ion still assumes an importance, chlorine-containing small peaks being produced at *m/e* 136, 138 and 140, which may be formulated as XIV-a or XV-a (Scheme 5). In fact metastable ions were recognized at *m/e* 113 (calc. for 163 → 136, 113·5), 115 (calc. for 165 → 138, 115·4) and 117 (calc. for 167 → 140, 117·4). The $(M-27)^+$ ion further eliminates one or two chlorine atoms, yielding negligible peaks at *m/e* 101 and 103 and a small peak at *m/e* 66. These ions may be represented as XVI-a and XVII-a. Negligible abundance of *m/e* 101 and 103 ions suggests that the one-step elimination of chlorine atoms prevails over the stepwise elimination.

Initial loss of a chlorine atom may compete with the process in which hydrogen cyanide is initially eliminated. Thus the molecular ion of XII ejects one chlorine

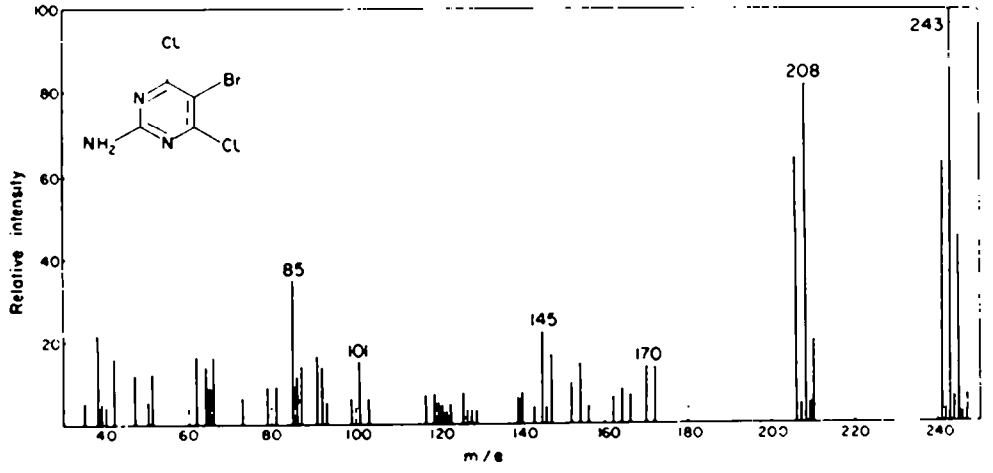
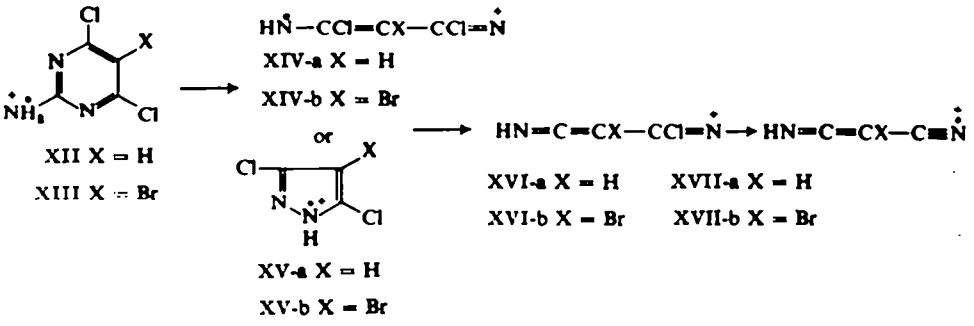


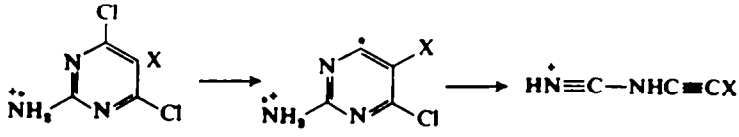
FIG. 4. Mass spectrum of 2-amino-5-bromo-4,6-dichloropyrimidine.

Scheme 5



atom, giving rise to prominent ions *m/e* 128 and 130 with the intensity ratio of 3:1 (XVIII-a). As the ion *m/e* 128 is the base peak, initial loss of a chlorine atom is likely to be a more favourable process. This $(M-Cl)^+$ ion further loses a chlorocyan molecule resulting in the formation of a prominent *m/e* 67 peak (XIX-a) (Scheme 6). An ion *m/e* 92 is prominent in the spectrum of XIII and this has been ascribed to a combined loss of a hydrogen and two chlorine atoms. There are several possible pathways for the elimination of the HCl_2 group, but it is uncertain which way prevails.

Scheme 6

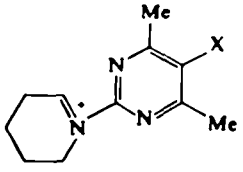


The spectrum of XIII differs in one point from the behaviour of XII. As there is one bromine atom in addition to two chlorine atoms, the molecular ion can be observed at *m/e* 241, 243, 245 and 247 with the intensity ratio of 18:30:14:2. As might be expected, loss of a chlorine atom from the molecular ion is a major process, producing ions at *m/e* 206, 208 and 210 (XVIII-b), which further lose chlorocyan, giving rise to ions at *m/e* 145 and 147 (XIX-b) (Scheme 6). But loss of hydrogen cyanide was not observed neither from the molecular ion (Scheme 5) nor from the $(M-Cl)^+$ ion. Again in this spectrum the $(M-HCl_2)^+$ ion is likely to be produced, since there were two bromine-containing peaks at *m/e* 170 and 172.

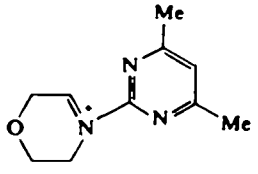
As representative of 2-tertiary aminopyrimidines the spectra of XX, XXI and XXII have been determined, which show that a combination of the fragmentation modes for pyrimidine and piperidine or morpholine operates. Especially these spectra show many intense peaks at the higher mass region, which arise from the fragmentations of the piperidine or morpholine portion of the molecule probably reflecting favourable charge retention on the extra nuclear amino nitrogen. As is supposed from the behaviour of piperidine itself[17,18] the molecular ion of XX and XXI suffers loss of

[17] A. Duffield, H. Budzikiewicz, D. H. Williams and C. Djerassi, *J. Am. Chem. Soc.* **87**, 810 (1965).
[18] L. Daash, *J. Phys. Chem.* **69**, 3196 (1965).

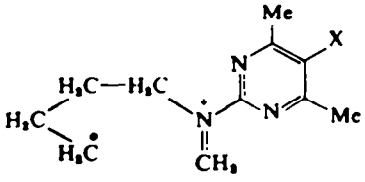
an α-hydrogen to yield a very prominent $(M-1)^+$ ion (XXXIII-a, b). This is also the case with XXII, the $(M-1)^+$ ion (XXXI) being very intense. There are many prominent ions (*m/e* 176, 163, 162, 150, 149 and 136) in the spectrum of XX, which will arise with intermediacy of XXIV-a and can be represented as XXV-a, XXVI-a, XXVII-a, XXIII-a, XXIX-a and XXX-a. Corresponding ions XXV-b, XXVI-b, XXVII-b, XXIX-b and XXX-b are observed in the spectrum of XXI, but an expected ion XXVIII-b does not show the intensity ratio of 3:1 and a possible explanation for this is that two contributory ions XXVIII-b and $((XXIX\text{-}b)\text{-}1)^{17}$ will bring about the intensification of an *m/e* 184 ion.



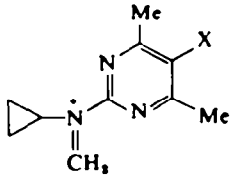
XXIII-a X = H
XXIII-b X = Cl



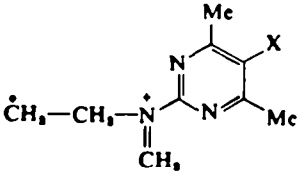
XXXI



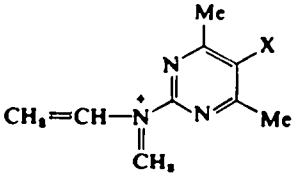
XXIV-a X = H
XXIV-b X = Cl



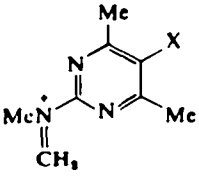
XXV-a X = H
XXV-b X = Cl



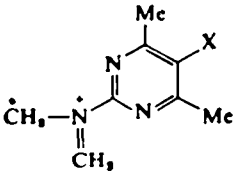
XXVI-a X = H
XXVI-b X = Cl



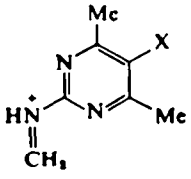
XXVII-a X = H
XXVII-b X = Cl



XXVIII-a X = H
XXVIII-b X = Cl



XXIX-a X = H
XXIX-b X = Cl

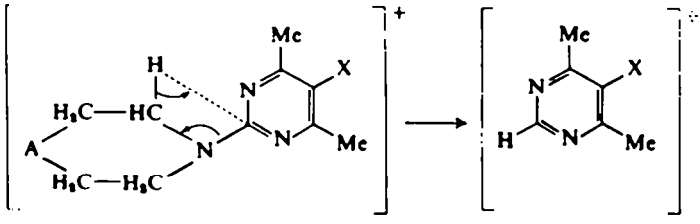


XXX-a X = H
XXX-b X = Cl

The spectra of XX, XXI and XXII displays an interesting feature unexpected from the behaviour of 2-amino-4,6-dimethylpyrimidine. Each of the molecular ions of them loses a piperidine or morpholine portion of the molecule with concomitant migration of a hydrogen and produces a prominent ion, which can be best formulated

as XXXII-a,b. A metastable ion was recognized at *m/e* 61 (calc. for 191 → 108, 61·1: XX) or at *m/e* 60 (calc. for 193 → 108, 60·4: XXII). Metastable ions corresponding to this process were not recognized for XXI, but as the ions *m/e* 142 and 144 can be observed with the intensity ratio of 3:1, occurrence of this process is certain. Although no deuterium labeling was carried out to substantiate the transfer of a hydrogen, the ion XXXII-a, b can be visualized through a four-membered cyclic transition state (Scheme 7). This process is responsible for the base peak for XXII illustrating the facile nature of this fragmentation. There is a very intense peak at

Scheme 7



XX A = CH_2 X = H
XXI A = CH_2 X = Cl
XXII A = O X = H

XXXII-a X = H
XXXII-b X = Cl

m/e 84 in the spectra of XX and XXI. Ratios of the isotopic intensities at *m/e* 85 and 86 to the ion-intensity at *m/e* 84 were 0·062 and 0·001, respectively, in the spectrum of XX, and 0·061 and 0·001, respectively, for XXI. These values, although greater than the calculated ratio (0·0595 and 0·0015) for the atomic combinations $C_5H_{10}N$, are more consistent with them than the calculated ratios (0·0668 and 0·0019) for the atomic combinations C_6H_{12}. Therefore it is reasonable to assume that this ion can be produced by the scission of the (piperidine)-C_2 linkage without migration of a hydrogen and the charge remains with the piperidine portion. Such schemes are likely to operate in the spectra of IX and X. An $(M-58)^+$ ion as well as an $(M-57)^+$ ion, though negligible in intensity, may be produced by loss of the acetamino group with and without migration of a hydrogen.

In summary it has been revealed that the mass spectra of pyrimidines can be interpreted in terms of the interplay of the substituents present in the molecule.