

Pyridazines. XXXIV. Electron-impact Induced Fragmentation of Some *s*-Triazolo[4,3-*b*]pyridazines, Tetrazolo[1,5-*b*]pyridazines and Related Compounds

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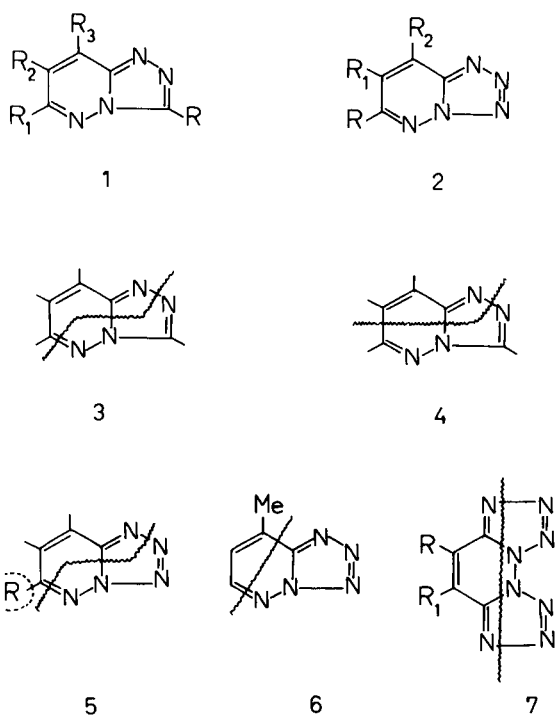
Mass spectra of several *s*-triazolo[4,3-*b*]pyridazines and tetrazolo[1,5-*b*]pyridazines were examined in order to establish their fragmentation patterns. Two distinct patterns could be observed upon electron impact of *s*-triazolo[4,3-*b*]pyridazines and tetrazolo[1,5-*b*]pyridazines. Azidotetrazolopyridazines show a loss of six nitrogens. This can be accounted for by a path proceeding *via* a molecular ion with a bis-tetrazolo structure.

The mass spectra of several azoloazines with bridgehead nitrogens, *i.e.*, imidazo[1,2-*a*]pyridines, imidazo[1,5-*a*]pyridines and imidazo[1,2-*a*]pyrimidines (1), and pyrazolo[2,3-*a*]pyridine (2) have been studied and their fragmentation patterns discussed. In the series of azolopyridazines mass spectra of imidazo[1,2-*b*]pyridazines were reported recently (3). Our continued interest in azolopyridazines prompted us to investigate the behaviour of *s*-triazolo[4,3-*b*]pyridazines, tetrazolo[1,5-*b*]pyridazines and some of the related systems, under electron impact.

A common feature of all mass spectra of *s*-triazolo[4,3-*b*]pyridazines (1) is that the molecular ion is the

most prominent peak, indicating a great stability of this system particularly when compared to tetrazolo[1,5-*b*]pyridazines (2), as discussed later. The abundance of molecular ions and fragments are given in Table I. The major fragments, however, are not common to all compounds investigated due to the substituents and their relative position which influence the fragmentation pattern. It appears that one fragmentation path of *s*-triazolo[4,3-*b*]pyridazine (1, R = R₁ = R₂ = R₃ = H) (Fig. 1) and its 6-methyl- (1, R = R₂ = R₃ = H, R₁ = Me) or 6-chloro analogs (1, R = R₂ = R₃ = H, R₁ = Cl) follows the pattern as indicated in 3. In all these cases, peaks corresponding to M-55 (-CHN₃) can be observed. The most intense peak at *m/e* 64 of the 6-chloro derivative and *m/e* 78 of 8-chloro-6-methyl- and 6-chloro-7,8-dimethyl derivatives correspond to subsequent loss of chlorine as evident from the absence of the peak for the natural isotopic abundance of chlorine. Furthermore, 6-methyl- (1, R = R₂ = R₃ = H, R₁ = Me), 6,7-dimethyl- (1, R = R₃ = H, R₁ = R₂ = Me), 6-hydroxy- (1, R = R₂ = R₃ = H, R₁ = OH) and 8-chloro-6-methyl analogs (1, R = R₂ = H, R₁ = Me, R₃ = Cl) undergo a second, sometimes preponderant fragmentation as indicated in 4. In particular with the first three compounds there are intense peaks corresponding to M-82 or M-84 (*m/e* 52 and *m/e* 66, respectively) whereas with the 8-chloro-6-methyl analog the M-82 (*m/e* 86) is of lesser intensity. There is no release of nitrogen as in the fragmentations encountered with the 1,2,4-triazoles (4,5), pyridazines (6-8), cinnolines (9) or 1,2,4-triazines (10).

A complex fragmentation occurs with 6-chloro-3,7-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (1, R₃ = H, R₁ = Cl, R = R₂ = Me). Here the most prominent species appears at *m/e* 78. An exact mass measurement of this species with a high resolution instrument revealed this to be C₅H₄N (determined 78.03458, calculated 78.03437). Further fragments of note appear with lesser intensity at



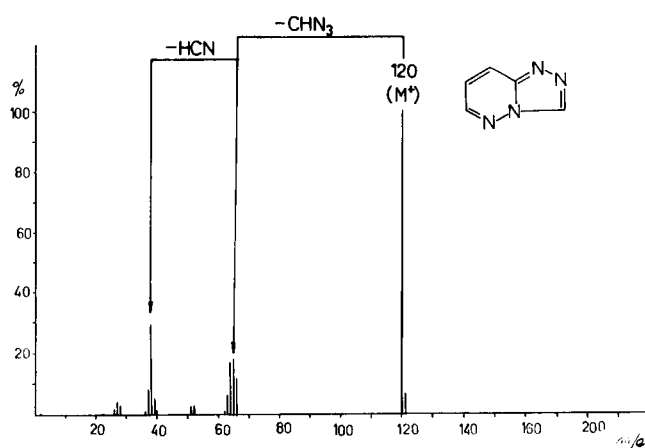
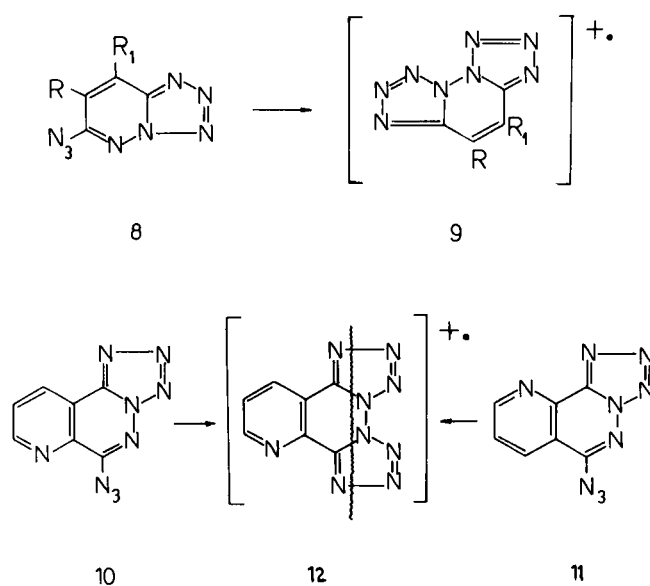


Figure 1

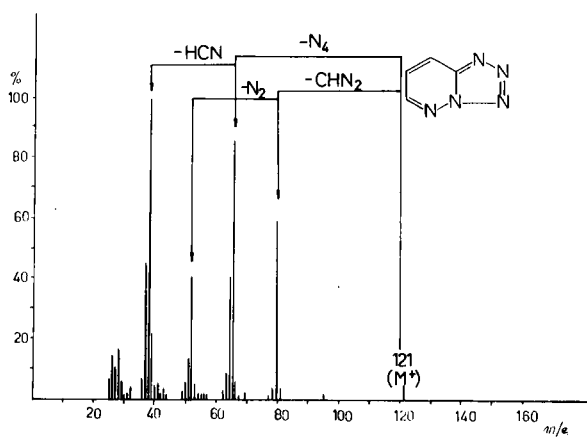


Figure 2

m/e 51 and 52 (species devoid of chlorine), as well as at 86 and 119. Whereas with the aid of high resolution the *m/e* 86 peak could be rationalized as being C₄H₄Cl (determined 85.9918, calculated 85.9923; species at *m/e* 86 and 88 are observed with a relative intensity ratio of 3:1), the same treatment did not permit clarification of the tantalizing *m/e* 119 (intensity 6%) peak.

In no case could loss of HCN, as observed with other azoloazines (1,3), be noticed. Loss of chlorine atom which is preferentially abstracted with aromatic halo-compounds (11,12) or halogenated pyridines (13), but not predominantly with halopyridazines (6,7,14) or imidazo[1,2-*b*]pyridazines (3), could be observed with the *s*-triazolo[4,3-*b*]pyridazines investigated. The expulsion of CO, which is a common and relatively important feature of many heterocyclic azinones, such as 2-pyridones (13, 15-17), 2-quinolones (18,19), 3-pyridazinones (6,14) or the corresponding phthalazinones (6), quinazolones (20), pteridones (21) and pyridopyrimidinones (22) could not be detected at all in the case of 6-hydroxy-*s*-triazolo[4,3-*b*]pyridazine (1, R = R₂ = R₃ = H, R₁ = OH). Based on the above observations one may conclude that the character and the position of substituents in the *s*-triazolo[4,3-*b*]pyridazine ring strongly affect the fragmentation pattern.

Tetrazolo[1,5-*b*]pyridazines (2) show some similarities to *s*-triazolo[4,3-*b*]pyridazines under electron impact, but the most prominent difference is their instability, under the conditions existing in the mass spectrometer since molecular ions are in fact of very low intensity. The abundance of molecular ions and fragments are given in Table II. Among the most abundant species in the mass spectrum of tetrazolo[1,5-*b*]pyridazine (2, R = R₁ = R₂ = H) (Fig. 2) is the M-56 peak (*m/e* 65) which corresponds to the loss of four nitrogens. This fragmentation proceeds most probably as indicated in 5 (full line) since another possibility of fragmentation is not compatible with the later described analogous processes of more complex tetrazolo compounds. The loss of four nitrogens (M-56) is also discernible in other tetrazolo[1,5-*b*]pyridazines, but the resulting fragments are of lower intensity. In no case could species, corresponding to the loss of only one nitrogen molecule be observed. 6-Chloro- (2, R₁ = R₂ = H, R = Cl), and 6-chloro-7-methyltetrazolo[1,5-*b*]pyridazine (2, R₂ = H, R = Cl, R₁ = Me) afforded as the major fragments those corresponding to loss of four nitrogens and one chlorine (M-91, *m/e* 64 and 78, respectively) (5, R = Cl, full and dotted line). The rest decomposes further and releases HCN as indicated by the subsequent loss of a *m/e* 27 fragment. In some cases, as with the 8-methyl analog (2, R = R₁ = H, R₂ = Me), fragmentation as indicated in 6 seems also to take place. There is also a loss of *m/e* 41 in the parent compound which would correspond

TABLE I

Mass Spectra of *s*-Triazolo[4,3-*b*]pyridazines (a)

Parent		6-Methyl-		6,7-Dimethyl-		6-Chloro-		8-Chloro-6-methyl-		6-Chloro-3,7-dimethyl-		6-Hydroxy-	
m/e	I (%)	m/e	I (%)	m/e	I (%)	m/e	I (%)	m/e	I (%)	m/e	I (%)	m/e	I (%)
121	7	135	8	149	10	156(M ⁺)	29	170(M ⁺)	33	184(M ⁺)	27	137	8
120(M ⁺)	100	134(M ⁺)	100	148(M ⁺)	100	155	6	169	8	183	10	136(M ⁺)	100
66	12	79	5	92	9	154(M ⁺)	88	168(M ⁺)	100	182(M ⁺)	100	80	14
65	18	53	9	78	7	101	4	88	4	119	6	53	30
64	17	52	45	67	7	99	11	87	9	86	7	52	50
63	7	51	9	66	55	65	6	86	12	78	80	51	11
39	6	39	9	65	15	64	100	79	6	77	8	38	8
38	30	38	6	54	8	63	19	78	93	76	7	37	7
37	9	27	8	53	14	52	8	77	11	64	6	29	6
				52	14	51	9	76	23	62	6	28	9
				51	20	38	13	75	14	52	14	27	10
				50	13	37	26	73	12	51	26	26	9
				41	8	36	6	72	7	50	7	51	9
				39	18	27	8	64	9	49	6	49	6
				38	6			63	10	42	8	42	8
				27	13			62	15	41	7	41	7
								52	17	39	13	39	13
								51	37	38	9	38	9
								50	20	36	7	36	7
								49	9	29	8	29	8
								39	11	28	18	28	18
								38	9	27	8	27	8
								37	20				
								27	21				
								26	9				

(a) In the Table are recorded all peaks having a relative abundance greater than 5%. Those less than 5% are included since they are significant in the discussion about the fragmentation pattern.

TABLE II

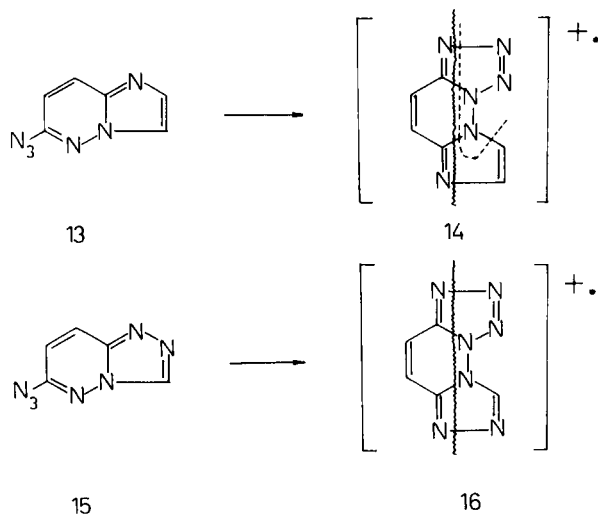
Mass Spectra of Tetrazolo[1,5-*b*]pyridazines and Related Compounds

Tetrazolo[1,5- <i>b</i>]pyridazines											
Parent		8-Methyl-		6-Deutero-8-methyl		6-Chloro-		6-Chloro-7-methyl-		6-Azido-	
<i>m/e</i>	I (%)	<i>m/e</i>	I (%)	<i>m/e</i>	I (%)	<i>m/e</i>	I (%)	<i>m/e</i>	I (%)	<i>m/e</i>	I (%)
121 (M ⁺)	6	135 (M ⁺)	8	136 (M ⁺)	10	157 (M ⁺)	0.3	171 (M ⁺)	0.5	162 (M ⁺)	2
80	59	79	9	94	7	155 (M ⁺)	1	169 (M ⁺)	2	79	7
66	6	64	13	80	6	101	4	86	9	78	100
65	85	53	19	79	8	99	11	79	7	77	29
64	41	52	100	65	14	65	6	78	100	76	6
63	9	51	23	64	6	64	100	77	10	53	9
52	41	50	17	54	18	63	12	76	9	52	25
51	14	39	20	53	100	52	9	75	7	51	54
50	6	38	9	52	40	51	8	73	6	50	9
39	22	37	12	51	23	38	15	63	6	49	6
38	100	28	27	50	17	37	27	62	8	39	7
37	45	27	14	39	20	36	9	52	18	38	12
36	7	26	14	38	12	28	20	51	41	37	15
29	6			37	12	27	6	50	21	28	100
28	27			29	20			49	12	27	11
27	12			28	30			39	10	26	12
26	15			27	18			38	11		
25	7			26	14			37	12		
								36	8		
								28	20		
								27	19		
								26	10		
6-Azido-7-methyl-	6-Azido-8-methyl-	6-Azidopyrido- [3,2- <i>d</i>]tetrazolo- [1,5- <i>b</i>]pyridazine	6-Azidopyrido- [2,3- <i>d</i>]tetrazolo- [1,5- <i>b</i>]pyridazine	6-Azidoimidazo- [1,2- <i>b</i>]pyridazine	6-Azido- <i>s</i> - triazolo[4,3- <i>b</i>]- Pyridazine	<i>m/e</i>	I (%)	<i>m/e</i>	I (%)	<i>m/e</i>	I (%)
176 (M ⁺)	1	176 (M ⁺)	1	213 (M ⁺)	1	213 (M ⁺)	1	161	9	161 (M ⁺)	48
93	7	92	41	141	6	141	6	160 (M ⁺)	100	135	6
92	55	77	10	131	9	131	8	134	12	79	7
91	7	67	7	130	10	130	8	132	9	78	100
78	6	66	20	129	100	129	100	106	15	77	30
77	16	65	100	104	25	104	19	105	8	53	11
76	7	64	24	103	10	103	11	104	61	52	35
67	11	63	16	102	27	102	24	80	9	51	55
66	44	62	10	77	26	78	6	79	13	50	6
65	100	52	60	76	26	77	25	78	82	38	11
64	58	51	32	75	18	76	28	77	27	37	14
63	37	50	21	73	13	75	19	76	6	28	27
62	23	41	70	62	6	63	6	64	15	27	20
53	22	39	41	53	7	62	7	63	6	26	16
52	98	38	60	52	10	61	6	53	24		
51	53	37	33	51	19	53	8	52	43		
49	21			50	27	52	10	51	39		
43	29			44	12	51	23	50	6		
42	16			43	6	50	26	39	7		
41	98			42	7	39	6	38	12		
				39	6	38	13	37	14		
				38	11	37	10	28	28		
				37	8			27	12		
								26	67		

(a) In the Table are recorded all peaks having a relative abundance greater than 5%. Those less than 5% are included since they are significant in the discussion about the fragmentation pattern.

to the expulsion of a CHN_2 unit, but in no other cases were such losses observed.

Isotope labelling has been a useful means of establishing the reaction paths induced by electron impact. Thus, deuterium substitution at position 6 of 8-methyltetrazolo[1,5-*b*]pyridazine afforded additional evidence for the above postulated fragmentations. With this 6-deutero analog (**2**, $\text{R}_1 = \text{H}$, $\text{R} = \text{D}$, $\text{R}_2 = \text{Me}$) there is an increase of one mass unit for the fragment M-56 as well as for the most intense peak at m/e 53.



Of particular interest are the mass spectra of 6-azido-tetrazolo[1,5-*b*]pyridazines and related compounds, since these systems are capable of valence isomerizations as recently shown (23-25). The most prominent feature of the mass spectrum of 6-azidotetrazolo[1,5-*b*]pyridazine (**2**, $\text{R}_1 = \text{R}_2 = \text{H}$, $\text{R} = \text{N}_3$) is the very abundant peak at M-84 (m/e 78) corresponding to the loss of six nitrogens (Fig. 3). Since it was shown previously that the investigated compound exists in the azidotetrazolo form, the observed fragmentation can only be accounted for by the bis-tetrazolo form as shown in **7**. The destabilization of a fused tetrazolo ring to form an azido group has been demonstrated in several azolopyridazines and explained by invoking the influence of the fused π -excessive azolo ring. Now, under electron impact such influence may be greatly diminished by forming the molecular ion and by cyclization of the azido group (**8**) to a fused tetrazolo ring (**9**).

With other investigated compounds, *i.e.*, the 8-methyl and 7-methyl analogs (**8**, $\text{R}_1 = \text{Me}$ or $\text{R} = \text{Me}$) and 6-azido-pyrido[3,2-*d*]tetrazolo[1,5-*b*]pyridazine (**10**) or 6-azido-pyrido[2,3-*d*]tetrazolo[1,5-*b*]pyridazine (**11**), the most prominent peaks at M-84 (at m/e 92 or m/e 129, respectively) also correspond to the loss of six nitrogens, indicating a fragmentation as shown in **7** and **12**. A subsequent process in all cases is the loss of a 27 mass unit corres-

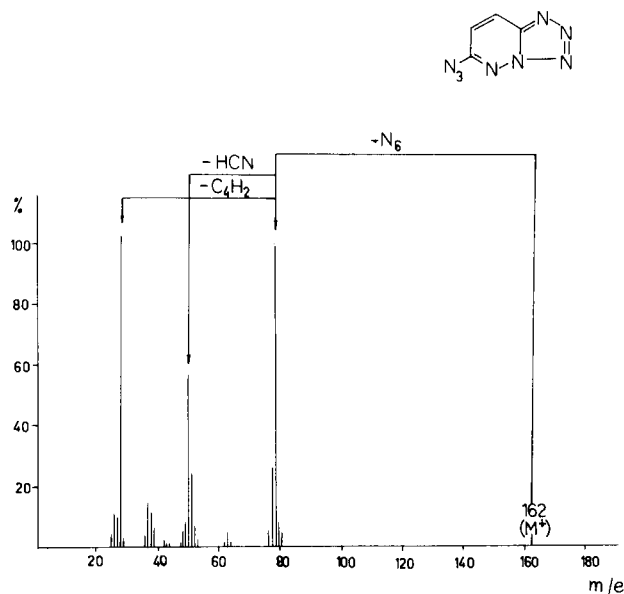


Figure 3

ponding to the abstraction of HCN. Thus, there are intense peaks at m/e 51 (6-azidotetrazolo[1,5-*b*]pyridazine), at m/e 65 (the isomeric 7-methyl and 8-methyl analogs) and at m/e 102 (both isomeric 6-azidopyridotetrazolo[1,5-*b*]pyridazines). This can be reasonably explained only by the availability of an α -hydrogen for transfer to the resulting cyano group for compounds of the type **7**. Since, with isomers **10** and **11** this process could be equally well envisaged to involve the pyridine part of the molecule, 2,3-dicyanopyridine and its analog, partially deuterated at position 4, were examined under electron impact. The mass spectrum of 2,3-dicyanopyridine (Fig. 5) is very similar to the mass spectra of both isomers **10** and **11** (Fig. 4) after abstraction of six nitrogens. Correlation of mass spectra of 2,3-dicyanopyridine and its 4-deutero analog showed that there is more loss of HCN than DCN. These results indicate that the main loss of the m/e 27 fragment results by loss of HCN involving the pyridine ring nitrogen and that the cyano group at position 3 and hydrogen (or deuterium) at position 4 are involved in this process to a minor extent only.

These results predicted that the intermediate formation of a tetrazolo ring in the molecular ion should also be anticipated for 6-azidoimidazo[1,2-*b*]pyridazine (**13**) and 6-azido-*s*-triazolo[4,3-*b*]pyridazine (**15**). This is actually evident in the case of compound **13** which exhibits a prominent peak resulting from loss of 56 mass units (m/e 104) which accounts for the release of four nitrogens (**14**, dotted line). However, in both cases, the most prominent peaks are at m/e 78 which would suggest a fragmentation as indicated in **14** and **16** (full line). The resulting species is further fragmented by loss of either 26 or 27

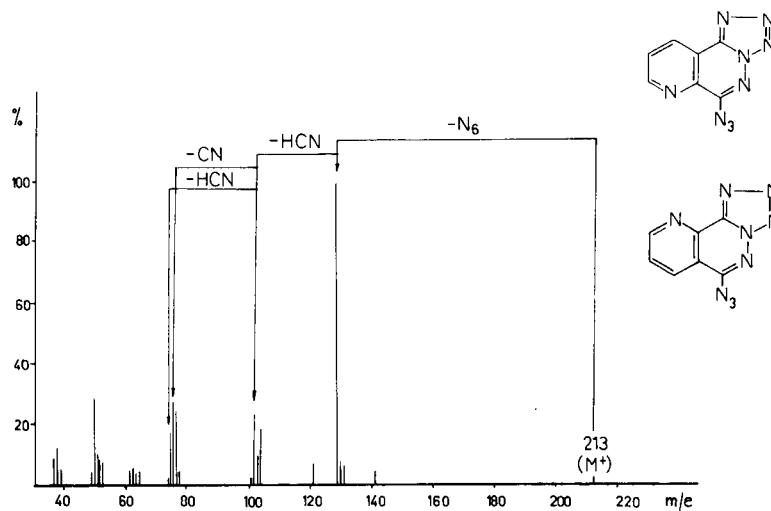


Figure 4

mass units giving rise to peaks at m/e 52 and 51. The main process is thus virtually consistent with the fragmentation pattern as indicated for compounds of the type **7** and **12**. Temperature variation in intervals from 85 to 115° of compound **15** did not produce any significant changes in the pattern of its mass spectrum.

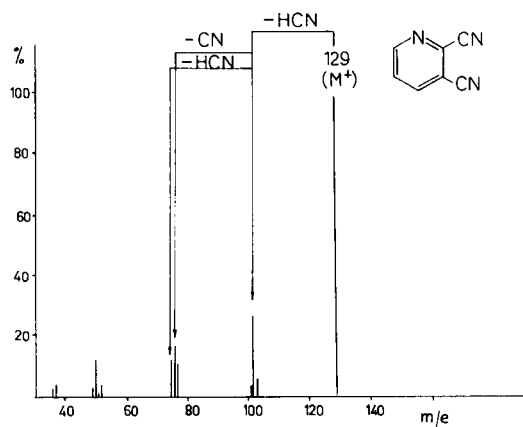


Figure 5

EXPERIMENTAL

All mass spectra were recorded at a resolution of approximately 1000 on a CEC 21-110C instrument using direct sample insertion into the ion source which was operating at temperatures in the range of 70 to 170°. The minimum temperature to obtain a spectrum was used in each case. Accurate mass measurements were carried out at a resolving power of 20,000. The ionization voltage was 70V and the emission current 100 μ A.

Most of the investigated compounds were described previously or were prepared according to the known procedures. These

compounds are the following: *s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_1 = R_2 = R_3 = H$) (**27**), 6-methyl-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_2 = R_3 = H$, $R_1 = Me$) (**28**), 6,7-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_3 = H$, $R_1 = R_2 = Me$) (**29**), 6-chloro-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_2 = R_3 = H$, $R_1 = Cl$) (**30**), 8-chloro-6-methyl-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_2 = H$, $R_3 = Cl$, $R_1 = Me$) (**28,31**), 6-chloro-3,7-dimethyl-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R_3 = H$, $R_1 = Cl$, $R = R_2 = Me$) (**29**), 6-hydroxy-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_2 = R_3 = H$, $R_1 = OH$) (**27,32**), tetrazolo[1,5-*b*]pyridazine (**2**, $R = R_1 = R_2 = H$) (**27,33**), 6-chlorotetrazolo[1,5-*b*]pyridazine (**2**, $R_1 = R_2 = H$, $R = Cl$) (**30,33**), 6-chloro-7-methyltetrazolo[1,5-*b*]pyridazine (**2**, $R_2 = H$, $R = Cl$, $R_1 = Me$) (**26**), 6-azidotetrazolo[1,5-*b*]pyridazine (**2**, $R_1 = R_2 = H$, $R = N_3$) and 6-azido-*s*-triazolo[4,3-*b*]pyridazine (**1**, $R = R_2 = R_3 = H$, $R_1 = N_3$) (**24**). The following compounds were described recently (**23**): 6-azido-7-methyltetrazolo[1,5-*b*]pyridazine (**8**, $R_1 = H$, $R = Me$), 6-azido-8-methyltetrazolo[1,5-*b*]pyridazine (**8**, $R = H$, $R_1 = Me$), 6-azidopyrido[3,2-*d*]tetrazolo[1,5-*b*]pyridazine (**10**) and 6-azidopyrido[2,3-*d*]tetrazolo[1,5-*b*]pyridazine (**11**). Similarly, 6-azidoimidazo[1,2-*b*]pyridazine (**13**) is a new compound (**34**).

8-Methyltetrazolo[1,5-*b*]pyridazine (**6**).

A solution of 6-chloro-8-methyltetrazolo[1,5-*b*]pyridazine (**26**) (0.83 g.) in 25 ml. of methanol was treated with palladiumized charcoal (0.2 g. of 5%) and ammonia (1 ml. of 25%). The mixture was stirred in an atmosphere of hydrogen at room temperature until the necessary uptake of hydrogen had occurred. The catalyst was collected by filtration, the solvent was evaporated to dryness and the residue was extracted with chloroform. The extracts were treated with charcoal and filtered into a fivefold quantity of ice cold petroleum ether. The separated product was collected (0.64 g.) and crystallized from chloroform and petroleum ether, m.p. 126-127°.

Anal. Calcd. for $C_5H_5N_5$: C, 44.44; H, 3.73; N, 51.83. Found: C, 44.72; H, 3.76; N, 52.03.

6-Deutero-8-methyltetrazolo[1,5-*b*]pyridazine (**2**, $R_1 = H$, $R = D$, $R_2 = Me$).

The catalyst was prepared as follows: palladium chloride (1 g.),

concentrated hydrochloric acid (2.4 ml.) and distilled water (6.1 ml.) were heated under reflux until palladium chloride had dissolved. Separately, active charcoal (12 g.) and nitric acid (50 ml. of 10%) were heated on a water bath for 3 hours. The charcoal was collected, washed thoroughly with distilled water and dried at 110°. The dried charcoal was treated with the prepared solution of palladium chloride, previously cooled and diluted with water (17.3 ml.). The mixture was then evaporated to dryness and dried at 110°. The prepared catalyst (0.3 g.) and methanol (20 ml.) were stirred in an atmosphere of deuterium until the consumption of deuterium had stopped.

6-Chloro-8-methyltetrazolo[1,5-b]pyridazine (26) (1 g.), methanol (20 ml.) and ammonia (2 ml. of 25%) were added and the mixture was stirred in an atmosphere of deuterium until the necessary uptake of deuterium had occurred. The catalyst was collected by filtration and the filtrate was evaporated to dryness. The residue was extracted with chloroform, treated with charcoal and filtered into a fivefold quantity of ice cold petroleum ether. The resulting suspension was allowed to stand in ice for some time and the product was collected and dried. The pure compound (0.72 g.) was obtained upon crystallization from chloroform and petroleum ether, m.p. 127-128.5°.

Anal. Calcd. for C₅H₄DN₅: C, 44.13; H,D, 4.44; N, 51.54. Found: C, 43.89; H,D, 4.41; N, 51.04.

REFERENCES

- (1) W. W. Paudler, J. E. Kuder and L. S. Helmick, *J. Org. Chem.*, **33**, 1379 (1968).
- (2) A. P. Krasnošček, R. H. Hmeljnickii, A. A. Poljakova and I. I. Grandberg, *Zh. Org. Khim.*, **3**, 1546 (1967).
- (3) M. Tišler and W. W. Paudler, *J. Heterocyclic Chem.*, **5**, 695 (1968).
- (4) P. R. Briggs, W. L. Parker and T. W. Shannon, *Chem. Commun.*, 727 (1968).
- (5) A. L. Jennings and J. E. Boggs, *J. Org. Chem.*, **29**, 2065 (1964).
- (6) J. H. Bowie, R. G. Cooks, P. F. Donaghue, J. A. Halleday and H. J. Rodda, *Aust. J. Chem.*, **20**, 2667 (1967).
- (7) S. J. Weininger and E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2050 (1961).
- (8) M. H. Benn and T. S. Sorensen, *Chem. Commun.*, 574 (1967).
- (9) J. R. Elkins and E. V. Brown, *J. Heterocyclic Chem.*, **5**, 639 (1968).
- (10) T. Sasaki, K. Minamoto, M. Nishikawa and T. Shima, *Tetrahedron*, **25**, 1021 (1969).
- (11) G. Spittler, "Massenspektrometrische Strukturanalyse organischer Verbindungen," Verlag Chemie, Weinheim, 1966.
- (12) H. Budzikiewicz, C. Djerassi and D. H. Williams: Mass Spectrometry of Organic Compounds, Holden-Day Inc., San Francisco, 1967.
- (13) G. H. Keller, L. Bauer and C. L. Bell, *J. Heterocyclic Chem.*, **5**, 647 (1968).
- (14) J. Heiss and K. P. Zeller, *Tetrahedron Letters*, 5969 (1968).
- (15) R. Lawrence and E. S. Waight, *J. Chem. Soc. (B)*, 1 (1968).
- (16) G. Spittler and M. Spittler-Friedmann, *Monatsh. Chem.*, **93**, 1395 (1962).
- (17) A. M. Duffield, C. Djerassi, G. Schroll and S. O. Lawesson, *Acta Chem. Scand.*, **20**, 361 (1966).
- (18) D. M. Clugston and D. B. MacLean, *Can. J. Chem.*, **44**, 781 (1966).
- (19) J. Moller and O. Buchardt, *Acta Chem. Scand.*, **21**, 1668 (1967).
- (20) T. J. Batterham, A. C. K. Triffett and J. A. Wunderlich, *J. Chem. Soc. (B)*, 892 (1967).
- (21) T. Goto, A. Tatematsu and S. Matsuura, *J. Org. Chem.*, **30**, 1844 (1965).
- (22) I. R. Gelling, W. J. Irwin and D. G. Wibberley, *J. Chem. Soc. (B)*, 513 (1969).
- (23) B. Stanovnik and M. Tišler, *Tetrahedron*, **25**, 3313 (1969).
- (24) A. Kovačič, B. Stanovnik and M. Tišler, *J. Heterocyclic Chem.*, **5**, 351 (1968).
- (25) B. Stanovnik, M. Tišler and P. Škufca, *J. Org. Chem.*, **33**, 2910 (1968).
- (26) S. Linholter and R. Rosenoern, *Acta Chem. Scand.*, **16**, 2389 (1962).
- (27) N. Takahayashi, *J. Pharm. Soc. Japan*, **76**, 765 (1965); *Chem. Abstr.*, **51**, 1192 (1957).
- (28) C. Bülow and K. Haas, *Ber.*, **43**, 1975 (1921).
- (29) M. Japelj, B. Stanovnik and M. Tišler, *Monatsh. Chem.*, **100**, 671 (1969).
- (30) N. Takahayashi, *J. Pharm. Soc. Japan*, **75**, 1242 (1955).
- (31) D. Libermann and R. Jacquier, *Bull. Soc. Chim. France*, 355 (1962).
- (32) A. Pollak, B. Stanovnik and M. Tišler, *J. Heterocyclic Chem.*, **5**, 513 (1968).
- (33) T. Itai and S. Kamiya, *Chem. Pharm. Bull. (Tokyo)*, **11**, 348 (1963); *Chem. Abstr.*, **59**, 8734 (1963).
- (34) B. Stanovnik, M. Tišler, M. Cegljar and V. Bah, *J. Org. Chem.*, in press.

Received December 15, 1969

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