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HETARYLNITRENES—II

AZIDO/TETRAZOLOAZINE TAUTOMERISATION, AND EVIDENCE FOR NITRENE FORMATION IN THE GAS-PHASE[1]

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Abstract—Azide-tetrazole tautomerism in tetrazoloazines has been examined by IR, NMR and mass spectrometry. Tetrazolo[1·5-*a*]pyrimidines (IV) with electron donating groups in position 5 showed no pronounced tendency to tautomerize to azides. An electron withdrawing group (Cl) in position 5, by contrast, favours the azido-form (Ve) which is a metastable solid at room temperature, rearranging to the tetrazole (IVe) at the m.p.; the azide is formed again when the tetrazole melts. In the tetrazolo[1·5-*c*] pyrimidine/4-azidopyrimidine series (VI–VII) the exactly opposite effect has been observed; electron donating groups in positions 5 and 7 stabilize the azido-form (VII), while in position 8 they favour the tetrazole form.[5] Contrary to general belief, "2,4-diazidopyrimidines" exist in the 5-azido-tetrazolo [1·5-*a*]pyrimidine form (IVf) with the isomeric 5-azido-tetrazolo[1·5-*c*]pyrimidine form (VIf) as a likely minor constituent. The diazido-form (Vf) is metastable at room temperature, rearranging to the tetrazoles at the m.p. Liquid SO_2 was found to be a suitable solvent for preserving individual tautomers in solution. Tetrazolopyrazine (XI) isomerizes partly to the azido-form (XII) in chloroform and trifluoacetic acid, while tetrazolo[1·5-*b*]pyridazine (XIII) and tetrazolo[1·5-*a*]pyridine (I) are completely stable in the tetrazole forms in solution and at 140°. The mass spectra of the labile tetrazoles indicate that the first step in gas-phase pyrolysis is azide-tautomerization with subsequent nitrene formation. Preparation of several tetrazolo-diazines is described.

THE thermal ring contraction of tetrazoloazines[2] and tetrazolodiazines[3] has been reported. The possibility that concerted reaction of the tetrazoles takes place in some cases[3] without intervention of nitrenes raised questions of the structures of such compounds in the gas-phase, and of the influence of substituents on the ease of tautomerization, e.g. I ⇋ II → III. The first question has been examined by mass spectrometry, the second by NMR and IR spectroscopy.

RESULTS AND DISCUSSION

NMR spectral data for the solvent dependent[4, 5] tetrazole-azide isomerism in tetrazolo[1·5-*a*]pyrimidines/2-azidopyrimidines (IV ⇋ V) and tetrazole [1·5-*c*]pyrimidines/4-azidopyrimidines (VI ⇋ VII) are given in Table 1. Full IR spectra are given in the Experimental. The work of Temple *et al.*[4, 5] forms the background for the NMR assignments. These authors have established that labile tetrazoles exist mainly in the tetrazole form in dimethyl sulphoxide (DMSO), and in the azido-form in trifluoroacetic acid (TFA), whereas mixtures may be found in chloroform. The heat

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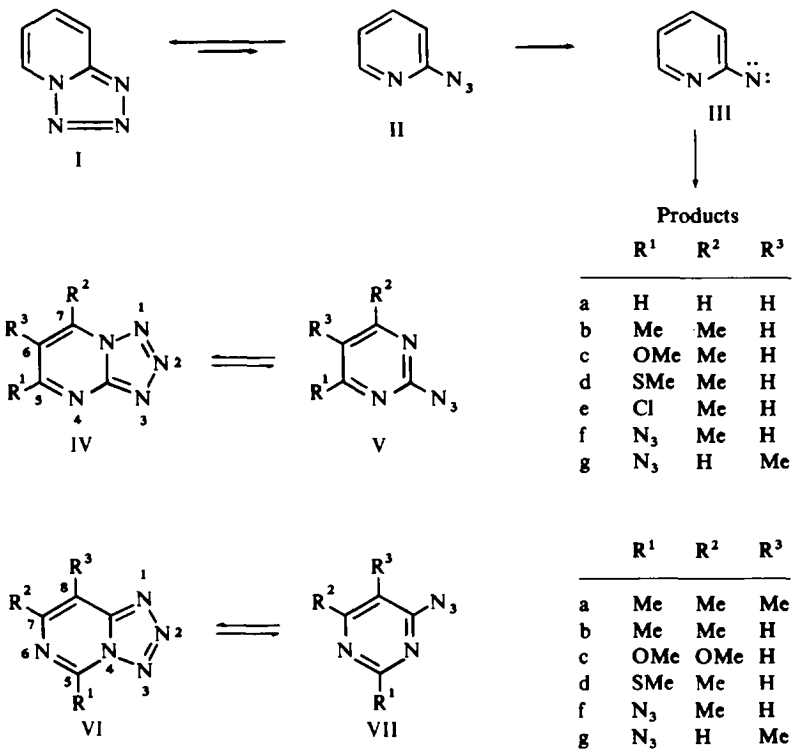


Products

	R^1	R^2	R^3
a	H	H	H
b	Me	Me	H
c	OMe	Me	H
d	SMe	Me	H
e	Cl	Me	H
f	N_3	Me	H
g	N_3	H	Me

	R^1	R^2	R^3
a	Me	Me	Me
b	Me	Me	H
c	OMe	OMe	H
d	SMe	Me	H
f	N_3	Me	H
g	N_3	H	Me

of isomerization of tetrazolo[1·5-*a*]pyrmidine (IVa) in DMSO was 5·1 ± 0·1 kcal/mole and *ca* 2 kcal/mole more for IVb.[5] It appears that the heat of isomerization is generally less than 12 kcal/mole,[4] and therefore, azide tautomerization may very well be the first step in pyrolysis[2, 3] of the tetrazoles.

It has been stated[7] that all known examples of heterocyclic azides for which the isomeric fused-ring tetrazoles were unknown could be explained by the effect of electron withdrawal, the underlying idea being that a tetrazole ring is electronegative, while an azido-group is electropositive.[8] As can be seen from Table 1, the tetrazolo [1·5-*a*]pyrimidines (IV)* conform to this statement.

With electron-donating groups in positions 5,7 these compounds showed moderate N_3-bands in the IR, increasing with temperature, but showed no pronounced tendency to ring opening, even in TFA where they required 30 min heating at 65° to fully isomerize. They were only partially isomerized in $CDCl_3$ at 60°. By contrast, the 5-chloro-compound (IVe) was quickly converted to the azide (Ve), both in $CDCl_3$

* That the compounds (IV) have the structures shown, and not the isomeric structures (i.e. R^1 and R^2 interchanged by tetrazole ⇌ tetrazole isomerization), follows from the magnitude of the CH_3-H coupling constants (Table 1). These are always about 1 cps, as expected for allylic coupling. The 5-CH_3 group in (IVb) does not couple with the ring-H.[4] A similar situation exists in compound (XV), Table 2. The chemical shifts of CH_3 in (IVc–f) are also in agreement with the value for the 7-CH_3 group in (IVb).[4] In no case has an isomer such as (VIII) been found. Such an isomerization is known, however, in the tetrazolopyrimidines (IX) ⇌ (X).[16]

and in TFA, with $t_{\frac{1}{2}} \leqslant 5$ min. It tautomerized partly even in DMSO, but not in liquid SO_2 at $-20°$. Generally, liquid SO_2 was found to be superior to DMSO in preserving labile tautomers. This is probably more a temperature effect than a solvent effect.

The azido-form of IVe, i.e. Ve, was obtained in the crystalline state by evaporation of solutions in $CHCl_3$ or TFA. The compound is metastable at room temperature for at least several weeks, but after standing for $\frac{1}{2}$ year, during which time the temperature may have been as high as 35–40°, it had completely rearranged to the stable tetrazole form (IVe). The azide melts briefly at 58–60° then resolidifies to give the tetrazole (IVe), which melts at 108–110°. After cooling, IVe melts again at 108–110° without preliminary melting at 58–60°. However, when cooled rapidly by throwing the melt in liquid N_2, it then melts and resolidifies again at 58–60°. Thus the azide at its m.p., is converted to the tetrazole and this on melting is again converted to the azide:

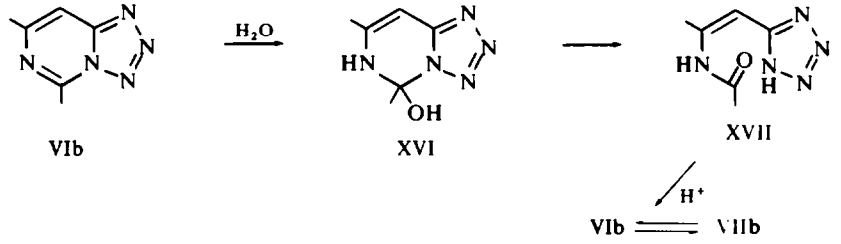
$$\text{IVe} \underset{58\text{–}60°}{\overset{108\text{–}110°}{\rightleftharpoons}} \text{Ve}$$

The IR spectrum of crystalline Ve in KBr showed strong azide bands at 2130, 2155 cm^{-1}, which are absent in crystalline IVe. Both forms gave identical IR spectra in $CHCl_3$ solution. The azide was stable in liquid SO_2 at $-20°$ (Table 1), but converted slowly to the tetrazole at $-15°$. The tetrazole dissolved very slowly in ether with formation of the azide which, unlike the tetrazole, is very soluble in ether and chloroform and cannot be recrystallized from these solvents. The azide was obtained also when the tetrazole was sublimed at $90°/10^{-3}$ mm through a tube at 300° and the vapours condensed in a liquid nitrogen Dewar. Therefore the compound exists as the azide in the gas-phase at 300°. This appears to be the first case where the tautomeric azide and tetrazole have both been isolated as stable solids (see also below). Evaporation of TFA solutions of the methoxy- or methylthio-compounds (IVc, d) and addition of water (to remove the last traces of TFA) did not at once give any crystalline material, but the starting materials crystallized from the aqueous solutions as very pure, long prismatic needles.

The exact opposite effect of electron-donating groups is observed in the tetrazolo [1·5-*c*]pyrimidines (VIa–d, Table 1). Here, electron-donating groups in positions 5,7 favour the azido forms (VII). This result is in accord with the finding[9] that 7-amino derivatives of this system exist as tetrazoles only in the solid state, but contrasts the report of Temple *et al.*[5] that electron donating groups (in position 8) favour the *tetrazole* isomer. This appears to be an exception to Boyer's above-mentioned statement.[7] The dimethoxy-4-azidopyrimidine (VIIc) exists exclusively as the azide, both in the liquid and solid state, and it has so far not been possible to convert it to a tetrazole (VIc). The corresponding methylthio-compound (VId) exists as 50% azide (VIId) even in DMSO, 18% in SO_2, and is easily converted to azide by heating a suspension in Nujol above the melting point (67°) (Experimental). Curiously, there is an opposite trend in the methyl-substituted compounds (VIa, b) which are both stable in the tetrazole forms even in $CDCl_3$ (Table 1). The infrared, which is more sensitive to azide detection than NMR, showed only weak N_3-bands in $CHCl_3$ solutions of (VIa–b). Heating of Nujol suspensions above 100° caused development of weak to medium azide bands, the trisubstituted (VIa) being most stable as tetrazole. This is similar to the case of tetrazolo[1·5-*c*]pyrimidine itself, which exists predominantly as the tetrazole.[5] VIa, c and d, unlike[5] the parent compound, were completely stable to

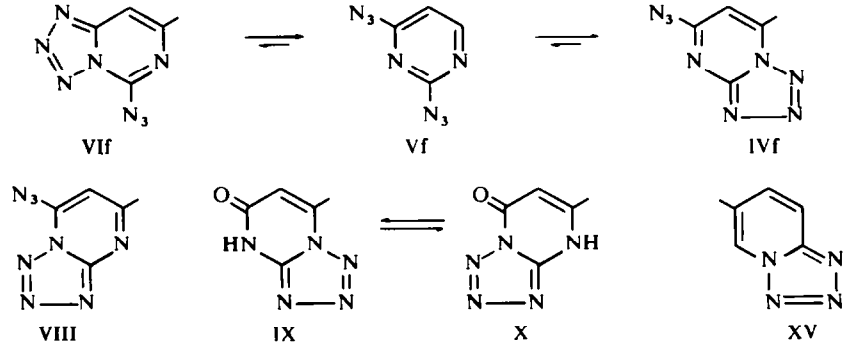
boiling water, while VIb could not be prepared in the presence of warm water, presumably due to covalent hydration.[5, 10]

Compound VIb, after standing for 1½ years at room temperature, transformed into a higher melting solid corresponding to addition of water, and containing only about 25% of the original material (which was easily removed by means of its far greater solubility in benzene). The IR spectrum of the new compound showed bands which can be interpreted as amide bands, but no OH-band. The most reasonable structure which fits the IR, NMR and mass spectra (Experimental) is XVII; notably, the mass spectrum showed a strong peak due to loss of 42 (ketene?).



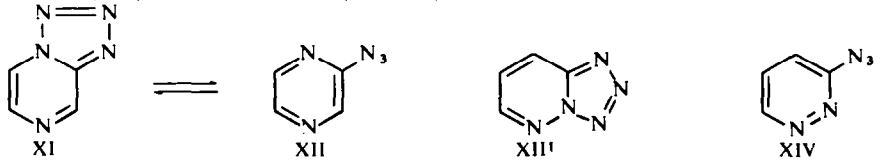
Treatment of the new compound (XVII) with acid (TFA) regenerated VIb as shown by the NMR spectrum. Evaporation of the TFA solution gave initially an oil, being the azide VIIb, containing about one equivalent of TFA (NMR in $CDCl_3$: τ 3·18 (*q*, 1H), 7·16 (*s*, 3H), 7·32 (*d*, 3H). Repeated addition of water and evaporation gave the tetrazole form VIb, m.p. 84–85°, NMR ($CDCl_3$) as in Table 1. The unsubstituted VI is known[5] to add water to the 5,6-bond (as in XVI), though ring opening was not reported. However, a similar hydration of the isomeric tetrazole IVb is known[4] to take place in alkaline solution, giving the sodium salt of a compound isomeric with XVII, and with an NMR spectrum very similar to that of XVII. In that case also the original tetrazole IVb was regenerated on acidification.[4]

It has generally been held that 2,4-diazidopyrimidines (e.g. Vf) exist in the diazido-form.[11–14] However, the aromatic azido group being electron donating and in this respect midway between OMe and Me,[8] the results presented above lead to the conclusion that in a compound like Vf the 2-azido group should destabilize the tetrazolo[1·5-*c*]pyrimidine form (VIf), but the 4-azido group should stabilize the tetrazolo[1·5-*a*]pyrimidine form (IVf).



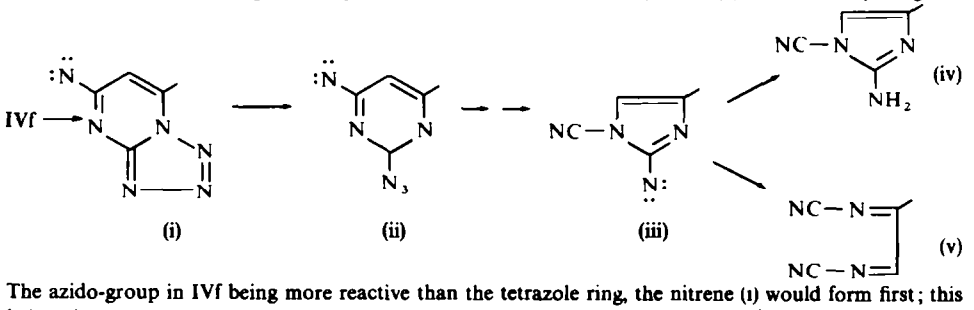
Indeed, the compound is found to exist in the monotetrazolo form (IVf) in the solid state, containing *ca* 10% of another tetrazole which must be VIf. That the major tetrazole is IVf follows from the NMR data (Table 1) which are almost identical with those for the methoxy compound (IVe). Since the minor tetrazole has an allylic CH_3—H coupling similar to that in other tetrazolo[1·5-*c*]pyrimidines, it is assumed to have the structure VIf rather than the only remaining possibility, VIII, which should show a CH_3-singlet[4] (compare IVb). Compound IVf exhibits a strong azide band in the IR, along with tetrazole bands. In $CHCl_3$ solution the tetrazole bands diminish strongly, and azide bands increase. Correspondingly a new tautomer, the diazide (Vf) is observed in the NMR spectrum. The tetrazole mixture is stable and free of diazide in SO_2, and is slowly converted to the diazide in TFA (Table 1). The pure diazide (Vf) can be obtained as a crystalline solid at room temperature by evaporating the TFA solution and adding water. Like the chloro-compound (Ve, *vide supra*) it melts at 40–42°, resolidifies at 45–50°, converting to the tetrazole mixture which itself melts at 127–128° with re-conversion to Vf. The same type of behaviour is observed with the isomeric 5-azido-6-methyltetrazolo[1·5-*a*]pyrimidine (IVg). The IR spectra of the crystalline diazides (Experimental) are devoid of tetrazole bands; and the NMR spectra of solutions in SO_2 show that the isomers are pure. Since all three tautomers (IV, V, VIf–g) can be obtained in one solution there can be no doubt that two different tetrazolo-forms exist.* The reported m.ps, and the solvents used in recrystallization[11–14] (aqueous ethanol) clearly indicate that previous investigators have handled the tetrazole forms.

Tetrazolopyrazine (XI) developed a moderately strong azide band in the IR in $CHCl_3$ solution, and a weak one by heating a Nujol suspension above the melting point. The NMR spectrum of the chloroform solution showed the presence of a small amount of azide (not mentioned in the original report[17] on this compound) which was mainly obscured by the resonance lines of the tetrazole tautomer. 55% of the azido form (XII) resulted in TFA (Table 2).



XI XII XII' XIV

* The thermal behaviour of the azidotetrazoles (IVf–g) is in agreement with the assigned structures. Gas-phase pyrolysis of IVf gives two products to which the structures (iv) and (v) are tentatively assigned.



(i) (ii) (iii) (iv) (v)

The azido-group in IVf being more reactive than the tetrazole ring, the nitrene (i) would form first; this being electron withdrawing it would require the azido-form (ii) which by normal[3] ring contraction and further fragmentation gives the new nitrene (iii). The known types of reactions[15] of 5-membered hetaryl-nitrenes would then give the products (iv) and (v).

TABLE 1. NMR SPECTRA OF TETRAZOLO/AZIDOPYRIMIDINES[a,b]

Compound	Solvent	Tetrazole tautomer			Azide tautomer			Ratio
		ring-H (*q*)	X-CH_3 (*s*)	CH_3 (*d*)	ring-H	X-CH_3 (*s*)	CH_3	Azide:Tetrazole
IVb–Vb	TFA[c]				2·62		7·23 (*d*, 0·5)	1:0
	$CDCl_3$[c]	2·92	7·22 (*s*)	7·00 (1·1)	3·15		7·53 (*d*, 0·5)	1:3
	DMSO-d_6[c]	2·62	7·31 (*s*)	7·11 (1·0)				0:1
	SO_2	2·78 (1·1)	7·24 (*s*)	7·04 (1·1)				0:1
IVc–Vc	TFA	2·90 (1·0)	5·65	6·90 (1·0)	3·22 (*q*, 0·8)	5·65	7·35 (*d*, 0·80)	1:25 → 1:0 (65°; ½ h)
	$CDCl_3$	3·40 (1·01)	5·85	7·08 (1·01)	3·65 (*q*)	6·02	7·60 (*d*, 0·70)	1:10[d]
	DMSO-d_6	3·00	5·92	7·18				0:1[d]
	SO_2	3·26 (1·1)	5·85	7·08 (1·1)				0:1
IVd–Vd	TFA	2·55 (1·0)	7·15	6·95 (1·0)	2·80 (*q*)	7·20	7·40 (*d*, 0·75)	3:1 → 1:0 (65°; ½ h)
	$CDCl_3$	3·14 (1·0)	7·28	7·10 (1·01)	3·20 (*q*)	7·43	7·59 (*d*, 0·4)	1:4[d]
	DMSO-d_6	2·60	7·34	7·20				0:1[d]
	SO_2	2·95 (1·1)	7·30	7·15 (1·1)				1:0
IVe–Ve	TFA	2·40		6·85 (1·1)	2·43		7·18 (*d*, 0·5)	1:0; $t_{\frac{1}{2}} \leqslant 5$ min
	$CDCl_3$	2·85		6·95 (1·1)	3·00		7·48 (*d*, 0·2)	11:1
	DMSO-d_6	2·28 (1·1)		7·04 (1·1)	2·57		7·52	1:6·5
	SO_2	2·65 (1·1)		6·97 (1·1)	2·88		7·52 (*d*, 0·5)	both stable[e]
IVf–Vf	TFA	2·93 (1·05)		6·90 (1·05)	3·18 (*q*, 0·8)		7·32 (*d*, 0·8)	0:1 → 1:0 (65°; ½ h)
	$CDCl_3$	3·40 (1·1)		7·03 (1·1)	3·58 (*q*)		7·55 (*d*, 0·6)	1·3:1 (1·8:1 at 50°[e])
	SO_2	3·25 (1·05)		7·06 (1·05)	3·50 (*q*)		7·58 (*d*, 0·5)	both stable[e, f]
IVg–Vg	TFA	0·94 (1·2)		7·54 (1·2)	1·75 (0·8)		7·70 (*d*, 0·8)	0:1 → 1:0 (65°; ½ h)[g]
	$CDCl_3$	1·25 (1·2)		7·66 (1·2)	1·75 (0·8)		7·88 (0·8)	0:1 → 8:1 ($t_{\frac{1}{2}}$ < 5 min)
	SO_2	1·12 (1·3)		7·65 (1·3)	1·80 (0·8)		7·86 (0·8)	both stable[e, h]

(VIf)[i]	$CDCl_3$				7·10 (1·1)					
	SO_2				7·13 (~1·1)					
(VIg)[j]	SO_2				7·18 (1·3)					
VIa–VIIa	TFA								7·14, 7·30, 7·70	1:0
	$CDCl_3$			6·90 (*s*)	7·15 (*s*)	7·37 (*s*)				0:1
	$DMSO-d_6$			7·00 (*s*)	7·45 (*s*)	7·45 (*s*)				0:1
	SO_2			6·96 (*s*)	7·40 (*s*)	7·40 (*s*)				0:1
VIb–VIIb	TFA						3·00		7·10, 7·28 (*d*, 0·7)	1:0
	$CDCl_3$	2·37 (*q*)		6·85 (*s*)	7·33 (1·0)					0:1
	$DMSO-d_6$	2·13 (*q*)		7·04 (*s*)	7·47 (1·0)					0:1
	SO_2	2·42 (*q*)		7·00 (*s*)	7·45 (1·0)					
VIc–VIIc	$CDCl_3$						4·13	5·98		1:0
	$DMSO-d_6$						3·95	6·05		1:0
VId–VIId	TFA						3·28	7·18 (*q*)	7·35 (*d*, 0·4)	1:0
	$CDCl_3$	2·56	7·17		7·33 (0·9)		3·65	7·43 (*q*)	7·60 (*d*, 0·4)	5:1
	$DMSO-d_6$	2·17	7·20		7·40 (0·9)		3·36	7·47 (*q*)	7·62 (*d*, 0·4)	1:1
	SO_2	2·48	7·18		7·32 (0·9)		3·57	7·46 (*q*)	7·53 (*d*)	1:5·5

[a] TMS as internal standard; *s*, singlet; *d*, doublet; *q*, quartet; coupling constants in parentheses.
[b] TFA, $CDCl_3$ and $DMSO-d_6$ at 37°; SO_2 at −20°.
[c] Previously reported.[4]
[d] No change in 12 h at 60°.
[e] Azides tautomerize slowly to tetrazoles at −15°.
[f] See also (VIf).
[g] Each stable in frozen solution.
[h] See also (VIg).
[i] As 10% constituent in (IVf).
[j] As 5% constituent in IVg).

The tetrazolopyridazine (XIII) did not show any azide bands in the IR in $CHCl_3$, nor on heating above 140°. The NMR spectra of solutions in $CDCl_3$, DMSO-d_6, and TFA were all identical (Table 2) except for solvent shifts, giving no evidence for tautomerization to the azide (XIV). It has been reported[18] that tetrazolopyridazine is preferentially stabilized in the tetrazole form even when a second 5-membered ring is fused onto the 6,1-pyridazine bond. However, decreasing the electron density of the ring by making the N-oxides causes both 3- and 6-azidopyridazine-1-oxides to shift to the azido forms.[19]

The tetrazolo[1·5-*a*]pyridines (I) are known to be stable in the tetrazole forms, but nitro groups cause them to ring-open to azides.[7] I and Me derivatives thereof showed no azide bands in the IR, in solution or at 140°, nor were any azide tautomers detectable by NMR in $CDCl_3$ or TFA solution. The spectra of 6-methyltetrazolo[1·5-*a*] pyridine (XV) are given in Table 2 as a representative example. Even in the super-acid HF-SbF_5-SO_2 XV gave essentially the same spectrum as in other solvents. The N-H proton due to protonation was observable at −60° as a broad peak at −3 τ. However, there were also present minor resonance lines shifted downfield from the main compound. These may be due to the presence of two differently protonated tetrazoles, or to a small amount of protonated azide; they cannot be due to unprotonated azide, since the shifts are to lower field (*cf* the general trends in Table 1). The other tetrazoles described above also gave protonated species in HF-SbF_5, with the N-H protons observable, but the spectra were usually not well resolved. At least two species were always present. It appears that localized (on the NMR time scale) protons due to protonation of tetrazoloazines have not previously been observed. Azide tautomerization in TFA is presumably due to protonation.[4, 5] Since azide (Vb) gives only one signal for the Me groups (Table 1) there must be rapid exchange of the proton.

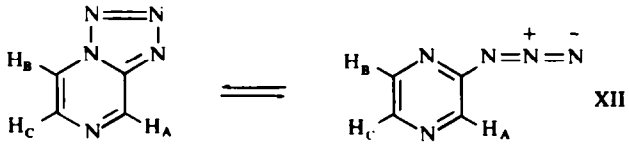
Mass spectra

The mass spectra of the tetrazoles described above suggest that gas-phase pyrolysis[2, 3] is essentially that of an azide (e.g. II), i.e. N_2 loss to give a nitrene (e.g. III) rather than a concerted[3] reaction. In all cases the tetrazoloazines and azidoazines (I, IV–V, VI–VII, XI, XIII) showed the following fragmentation pattern:

$$M^{+\cdot} \xrightarrow{m^*} (M\text{-}N_2)^{+\cdot} \xrightarrow{m^*} (M - N_2 - HCN)^{+\cdot}$$

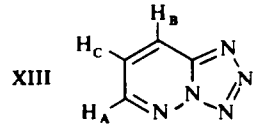
where m* denotes a meta-stable peak for the transition (see Experimental for full mass spectra). In the thermally stable tetrazolo[1·5-*c*]pyrimidines (VIa–b) and tetrazolopyridines (I) the ($M–N_2$) peak was very intense and usually the base-peak of the spectrum. In contrast to this, those compounds which exist as azides at room or elevated temperature (IVb–g, VIc–d) showed only small ($M–N_2$) peaks, and in addition showed apparent (M-26) peaks. The latter were shown to be due to the thermal process [($M - N_2$) + 2H], since the (M-26) peaks could still be seen after pumping away the azides/tetrazoles, leaving typical amine spectra. Thus the (M-26) peaks are due to thermal fragmentation to nitrenes, which by H-capture give amines. This thermal reaction occurred even with a direct insertion probe at 100°. The same phenomenon has been observed with phenyl azides.[20] It has been shown by ^{15}N-labelling that tetrazolopyridines (I) undergo thermal reactions *via* nitrenes (i.e. not concerted), and although they are stable in the tetrazole form at 140° (*vide supra*) and give ($M–N_2$) as base peaks on mass spectrometry, they also give small (M-26) peaks

TABLE 2. NMR SPECTRA OF (XI-XII, XIII, AND XV)



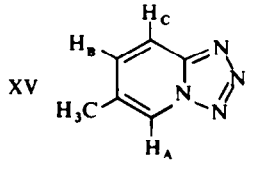
XI XII

Solvent	H_A	H_B	H_C	H_A	H_B	H_C	Ratio tetrazole:azide
$CDCl_3$[a]	0·37 *d*	1·20 *dd*	1·68 *d*	*b*	*b*	1·85	9:1
DMSO[a]	0·15 *d*	0·60 *dd*	1·65 *d*				1:0
TFA[c]	0·22 *d*	0·65 *dd*	1·28 *d*	1·54 *dd*	0·79 *dd*	1·42 *dd*	1:1·2



XIII

	H_A	H_B	H_C	
$CDCl_3$[d]	1·15 *dd*	1·42 *dd*	2·25 *dd*	1:0
DMSO[d]	1·00 *dd*	1·80 *dd*	2·19 *dd*	1:0
TFA[d]	0·94 *dd*	1·13 *dd*	1·97 *dd*	1:0



XV

					Other Isomer				
	H_A	H_B	H_C	CH_3	H_A	H_B	H_C	CH_3	
$CDCl_3$[e]	1·33 sextet	2·00 *dd*	2·43 *dd*	7·47 *d*					
TFA[f]	0·91 sextet	1·65 *d*[g]	1·71 d[g]	7·25 *d*					
SO_2[h]	2·00 sextet	2·67 *dd*	2·93 *dd*	8·18 *d*					
HF-SbF_5[h,i]	1·20 m	1·75 *d*	2·00 *d*	7·64	0·85	1·50	1·77	7·50	10:1

[a] J_{BC} = 4·7 cps; J_{AB} = 1·6; $J_{AC} \leqslant$ 0·5 cps.

[b] obscured.

[c] Tetrazole: J_{BC} = 5·0; J_{AB} = 1·6; J_{AC} < 0·5 cps; azide: J_{BC} = 3·2; J_{AB} = 1·2; J_{AC} = 0·5 cps.

[d] J_{BC} = 9; J_{AC} = 4·5; J_{AB} = 2 cps.

[e] J_{A-CH_3} = 1·2; J_{BC} = 9·2; $J_{AC} \simeq$ 1·4; $J_{AB} \simeq$ 0·09; $J_{B-CH_3} \leqslant$ 0·4 cps.

[f] J_{A-CH_3} = 1·1; J_{BC} = 9; $J_{AC} \simeq$ 1·4; $J_{AB} \leqslant$ 1 cps.

[g] Due to great proximity inner lines overlap, and outer lines are strongly reduced.

[h] External TMS as reference; subtraction of 0·42 from these τ-values gives the approximate shifts relative to internal TMS.

[i] In SO_2 at −60°. N—H at −3 τ.

(16–18% of base), demonstrating that tautomerization to azide II does occur. Significantly, the isomeric 1H-triazolopyridines,[21] which cannot tautomerize to azides, do not give any (M-26) peaks, but spectra otherwise similar to (I).[22] Huisgen *et al.*[23] recently succeeded in intercepting 2-azidopyridine (II) in a 1,3-dipolar cycloaddition reaction at 190°.

Tetrazolopyrazine (XI) resembled tetrazolopyridine (I) in that it gave an abundant ($M-N_2$) peak, but also a small (M-26) peak which persisted at 12 eV. The mass spectrum of tetrazolopyridazine (XIII) is consistent with the thermal behaviour,[3] showing only a small (M-28) peak, the base peak being ($M-N_2-N_2$) = C_4H_3N, which persisted at 12 eV and probably is due (in part) to thermal reaction.

TABLE 3. MASS SPECTRA OF COMPOUNDS IVf AND IVg

		(IVf)					(IVg)	
	m/e	Direct, 70 eV	110° 12 eV	Heated, 125° 70 eV	Heated, 150° 70 eV	150° 15 eV	Direct, 70 eV	110° 12 eV
M^+	176	10	100	17	24	62	44	100
$M-N_2+2$	150	—		0·2	0·6		0·5	
$M-N_2$	148	0·3		0·4	0·5		4	
$M-2N_2+2$	122	—		0·6	2·2		0·3	
$M-2N_2$	120	0·6		2·6	15		0·6	
	94	3·3		2·6	6		0·3	
	93	—		2·6	6		0·4	
	78	2		2	2·2		2	
	77	2		2	2·2		2	
	67	100	100	100	100	100	100	34
	53	40		20	22		17·5	
	41	10		12	22		6	
	40	18		16	20		14	
	39	22		18	24		15	
	38	12		10	13		7	
HCN	27	16		14	17·5		9	

EXPERIMENTAL

NMR spectra were recorded on a Perkin–Elmer R 10 or a Varian A-60 spectrometer, using TMS as internal standard except where otherwise stated. The temp was 37° except where otherwise stated (SO_2 at −20°). IR spectra were recorded on a Unicam SP 200G instrument. Mass spectra were recorded on an A.E.I. MS 902 mass spectrometer with all-glass or direct inlet, or an A.E.I. MS 10C2 mass spectrometer as stated. Mass spectra are given as M^+ (*m/e* for molecular ion) followed by abundance in % of the base peak. M.ps are uncorrected.

(i) *Tetrazolo*[1·5-a]*pyrimidine* (IVa)

A mixture of 2·0 g (0·0165 mole) 2-chloropyrimidine, 2·3 g (0·0354 mole) sodium azide, and 21·7 ml 10% EtOH containing 0·0165 mole HCl was refluxed for 3 hr, kept at 40° for 8 hr, then refluxed for 1 hr, active carbon was added, the mixture filtered hot and allowed to crystallize at −10° giving 1·25 g tetrazole (59%), m.p. 119–120°. Recrystallization from EtOH gave colourless crystals, m.p. 119·5–120°, undepressed on admixture with a sample prepared by Shirakawa's method.[24] The IR spectra of the two samples were also identical, ν ($CHCl_3$, cm^{-1}): 2165 w, 2130 s, 1615 s, 1400 s, 1320 s, 1070 s. (In Nujol): 3100 s, 1620 s, 1530 s, 1510 s, 1490 s, 1465 m, 1395 s, 1370 s, 1335 s, 1265 s, 1160 s, 1100 s, 985 s, 925 s, 800 s, 785 s; mass spectrum: M^+ 121 (100), M-26 (10), M-28 (8), 66 (10), 65 (30), 64 (26), 53 (25), 52 (8), 51 (5).

(ii) 5,7-*Dimethyltetrazolo*[1·5-*a*]*pyrimidine* (IVb)

The NMR spectrum of this compound in $CDCl_3$, DMSO and TFA has been discussed previously.[4] The first IR spectrum of a soln in $CHCl_3$ at 22° showed no N_3 band. It developed in the course of 30 min during which time the cell warmed to 30°. Further heating to 45° caused the N_3 band to increase further. On this basis the following bands are assigned to the azide tautomer: 2145 s, 2125 s, 1595 s, 1340 s, 1070–60 s cm^{-1}. From the spectrum in Nujol the following bands are assigned to the tetrazole tautomer: 3070 s, 1640–25 s (several bands), 1530, 1460, 1380, 1350, 1325, 1245, 1200, 1100, 995, 780 cm^{-1}. Mass spectrum: M^+ 159 (100), M-26 (10), M-28 (10), M-29 (12), M-43 (32), M-55 (7), M-57 (9), 80 (33), 79 (11), 67 (33), 66 (45).

(iii) 4-*Methoxy-6-methyl-2-methylmercaptopyrimidine*

The method was adopted from Johns.[25] 47·0 g (0·27 mole) 6-Chloro-4-methyl-2-methylmercaptopyrimidine in ether was added dropwise to a stirred mixture of 100 ml MeOH and 27 g NaOMe (0·50 mole) in a flask fitted with a reflux condenser. After addition, the mixture was refluxed with stirring for 30 min, the solvents removed *in vacuo*, ice-water was added, the mixture extracted with ether, the ether phase washed with water, dried (Na_2SO_4, active carbon), and evaporated to give 45·5 g (0·27 mole; 100%) 6-methoxy derivative as a yellow liquid. It was pure according to the mass spectrum (M^+ 170) with no trace of a dimethoxy- or a chloro-derivative.

(iv) 7-*Methyltetrazolo*[1·5-a]*pyrimidin*-5(4H)-*one* (IX)

This was prepared by Brady and Herbst[26] in 40% yield by refluxing 5-aminotetrazole, ethyl acetoacetate, and piperidine in EtOH for 48 hr. The same procedure was used here except that a boiling stick was added. After 48 hr the boiling stick with adhering crystals was removed (45% yield) and reflux continued with a new stick for another 3 days which afforded an additional 10% yield of large, colourless, rhombohedra, m.p. 247–248° (lit.[26] 247–248°), not changed after recrystallization. Chilling of the mother liquor afforded a further 5% yield. Evaporation of the filtrate gave a 20% recovery of 5-aminotetrazole.

The *compound*, described as the 5-hydroxy derivative[26] exists in the keto-form (*cf.* Temple *et al.*[16]) as evidenced by a strong carbonyl band near 1690 cm^{-1}. It is almost insoluble in all ordinary solvents at ordinary temperature, but dissolves in aq. NaOH, DMF and DMSO on warming.

(v) 5-*Chloro-7-methyltetrazolo*[1·5-a]*pyrimidine* (IVe)

This was prepared from IX as described by Kano and Makisumi.[27] It had m.p. 108–110° from benzene–light petroleum and mol wt by mass spectrometry 169 and 171, and existed in the tetrazole form (see the Discussion and Table 1). Evaporation of a soln in TFA gave an oil which, on addition of water, deposited the pure azide Ve, m.p. 58–60°, resolidifying to IVe, as shown by the IR spectra (*vide infra*) and the NMR spectra (Table 1). Evaporation of solns in $CHCl_3$ or ether of IVe gave Ve containing 10% IVe as shown by the NMR spectra of SO_2 solns (Table 1), melting partly at 58–60°. Throwing the melt of IVe into liquid N_2 gave Ve, m.p. 58–60°. Subliming IVe at 90°/10^{-3} mm through a tube at 300° and condensing the vapours in liquid N_2 gave Ve, m.p. 58–60°.

IR spectra of IVe; in KBr: 3100 (m), 1620 (s) several bands, 1540 (s) several bands, 1430 (s), 1375 (m), 1350 s, 1315 s, 1162 s, 1120 s, 1100 s, 1050 s, 990 s, 910 s, 880 s, 790 s, 775 s cm^{-1}. In $CHCl_3$: 3000 s, 2155 s, 2130 s, 1620 m, several bands 1570–1520 s, 1360 s, 1310 m, 1200 s, 1130 m.

IR spectra of Ve: in KBr: 3060 m, 2155 s, 2130 s, 1620 m, several bands 1570–1520 s, 1360 s, 1310 s, 1230 s, 1195 s, 1135 s, 960 m, 890 s, 850 s, 770 s, 730 s; in $CHCl_3$: the spectrum was identical with that of IVe in $CHCl_3$; mass spectrum: M^+ 171 (32), M-H_2 (93), M-N_2 (10, m* 120), 141 (22, m* 117·7), M-N_2-27 (1·8), 114 (4·8), M-N_2Cl (62·5), M-N_2-Cl-27 (23, m* 59), M-N_2-Cl-28 (100).

(vi) 5-*Methoxy-7-methyltetrazolo*[1·5-a]*pyrimidine* (IVc)

(a) 8·50 g (0·05 mole) 4-methoxy-6-methyl-2-methylmercaptopyrimidine (see iii) was heated with sodium azide and EtOH-HCl[28] (0·10 mole HN_3) for 3 days and, after cooling, the white solid was collected and recrystallized from benzene to give 0·33 g, m.p. 163–164° (lit.[24] 163–165°). 7·8 g starting material was recovered from the filtrate.

(b) The *compound* was also prepared from IVe in the same way as the 5-ethoxy-derivative was prepared,[27] yield, 68%; m.p. 164–165° from aqueous MeOH. The two samples had identical IR, NMR, and mass spectra. (Calc mass: 165·0651; Found: 165·0652). The IR spectra in $CHCl_3$ and Nujol were very similar to those of IVb. The soln was initially transparent in the azide region but a band at 2135 cm^{-1} developed rapidly, increasing in intensity with time and with temp, both in $CHCl_3$ and in CCl_4. Bands at 1600 and

1350 cm^{-1} increased at the same time. In Nujol: 3050 s, 1645 s, 1540 s (several bands), 1470 s (several bands), 1390 s, 1375 s, 1350 s, 1340 s, 1220 s, 1160 s, 1100 s, 1037 s, 997 m, 984 m, 940 s, 878 s, 790 s, 774 s, 655 s; mass spectrum: M^+ 165 (89), M-26 (6), M-27 (4), M-28 (7, m* 113·8), M-28-15 (28), M-55 (8·5), M-43-28 (100), 82 (5·5), 81 (11), 80 (6), 70 (30), 67 (38), 66 (33).

Evaporation of a soln in TFA and addition of water gave no precipitate initially, but the starting material crystallized in long colourless prismatic needles, m.p. 164–165° in 24 hr at room temp.

(vii) 7-*Methyl-5-methylmercaptotetrazolo*[1·5-a]*pyrimidine* (IVd)

The reported procedure[27] was simplified as follows: A soln of 8·00 g of IVe (see v) and 8·00 g thiourea in 320 ml EtOH was refluxed for 35 min, evaporated to dryness, and the residue methylated directly by shaking with 100 ml N NaOH and 10 ml MeI for 40 min. The solid product was collected, washed thoroughly with water, and recrystallized from EtOH to yield 5·25 g (61·5%) product, m.p. 151–152° (lit.[27] 151–152°; 30% yield). The initial IR spectrum ($CHCl_3$) showed a very weak N_3 band which increased to strong in 30 min at 30°; ν 2132, 2150 (sh); other azide bands: 1580 s, 1370 s, 1295 s, 1100 s; tetrazole bands (Nujol and $CHCl_3$): 3050 m, 1635 vs, 1442 vs, 1370 m–s, 1310 s, 1245 s, 1105 s, 1005 s, 1030 m–s, 990 s, 908 s, 975 s, 770 s; mass spectrum: M^+ 181 (100), M-26 (4), M-43 (15), M-55 (24), M-61 (8), 113 (23), 110 (30), 108 (7·5), 107 (9), 106 (17), 86 (25).

Evaporation of a soln in TFA and addition of water resulted only in the crystallization of the starting material in 24 hr as long prismatic, faintly yellow needles, m.p. 152°.

(viii) 5-*Azido-7-methyltetrazolo*[1·5-a]*pyrimidine* (IVf)

(a) Prepared from IVe and sodium azide as reported,[12] it had m.p. 126–127° (aq. MeOH) (lit.[11] 126–126·5°; lit.[12] 127–128° (aq. EtOH)).

(b) 2,6-dihydrazino-4-methylpyrimidine (1·00 g; see xiii below) in 6 ml 30% AcOH was treated with 0·925 g dry $NaNO_2$ at room temp with stirring. The product was filtered after 30 min, washed with water, and dried in a dessicator; yield 1·10 g (96%), m.p. 124–126°. Two recrystallizations from aq. EtOH raised the m.p. to 126–127° (decomposing slightly).

The compound existed in the tetrazole form with 10% of another tetrazole present (*cf* Table 1). Evaporation of a soln in TFA and addition of water, or throwing the melt of IVf into liquid N_2, gave Vf whose NMR spectrum in liquid SO_2 (Table 1) showed that it was the pure azide, free of tetrazole. Evaporation of a chloroform soln of IVf gave the diazide containing 50% tetrazole. The diazide melted at 40–42°, resolidifying at 45–50°, giving the tetrazole mixture which melted again at 126–128°.

IR spectra of the tetrazole form (IVf) in Nujol: 3060 m, 2230 w, 2210 w, 2190 m, 2150 s, 2120 w, 2075 w, 1630 vs, 1600 sh, 1550 m, 1520 vs, 1450 s (several bands), 1410 s, 1395 s, 1380 s, 1350 s, 1340 s, 1230 s, 1165 m, 1120 m, 1040 m, 990 s, 880 s, 775 s; in $CHCl_3$: 2190 m, 2140 s, 2125 s, 2090 w, 1635 s, 1590 m, 1540 s, 1445 s, 1390 m, 1380 m, 1365 m, 1350 s, 1240 s, 1050 s, 930 m.

The IR spectrum of the azido form (Vf) in $CHCl_3$ was identical with that of IVf, and the spectrum in KBr was similar to that in $CHCl_3$ and to that of Vg (*vide infra*).

Mass spectra are listed in Table 3 (MS 902, direct and heated inlet).

(ix) 5-*Azido-6-methyltetrazolo*[1·5-a]*pyrimidine* (IVg)

This was prepared from 2,4-dichloro-5-methylpyridine and sodium azide according to the directions of Ref 11 for preparation of IVf, yield 77%, colourless needles, m.p. 104–105° (aq. EtOH), dec 105°; exploding on rapid heating over 250°. The product was the monoazido-tetrazole (IVg) containing 9% of another tetrazole (Table 1). The azido form (Vg) was obtained as colourless prisms in the same way as in viii, m.p. with rearrangement at 80°.

IR of the tetrazole (IVg) in KBr: 3050 w, 2285 m, 2210 s, 2150 s, 1670 sh, 1635 s, 1520 s, 1450 s, 1415 vs, 1350 s, 1320 s, 1290 s, 1250 s, 1140 s, 1010 s, 985 s, 925 m, 985 s, 830 m, 770 s, 745 m, 720 m; in $CHCl_3$: 3000 m, 2145 s, 1590 m, 1565 s, 1540 m, 1520 m, 1405 s, 1375 m, 1330 m, 1300 m, 1210 vs, 1040 w, 1010 w, 925 w.

IR of Vg in KBr: 2250 sh, 2150 vs, 2130 vs, 1640 w, 1590 m, 1550 s, 1520 m, 1450 w, 1405 s, 1375 m, 1320 m, 1310 m, 1290 s, 1235 s, 1220 s, 965 s, 780 s, 675 s; in $CHCl_3$: the spectrum was identical with that of the tetrazole, (IVg) in $CHCl_3$.

(x) 5,7-*Dimethyltetrazolo*[1·5-c]*pyrimidine* (VIb)

Ethyl acetoacetate and acetamidine hydrochloride were converted into 2,4-dimethylpyrimidin-6-ol[29]

and further into the 6-chloro derivative.[30] According to VPC the crude chloride was of better than 99% purity, and it was used as such in the following step. A mixture of 6·58 g (0·0477 mole) 2,4-dimethyl-6-chloropyrimidine, 30 ml 95% EtOH, and 8 ml hydrazine hydrate (99%) was refluxed for 2 hr, cooled and filtered to give the hydrochloride of the 6-hydrazino derivative. Treatment with K_2CO_3,[31] extraction with EtOH, and evaporation of the soln afforded 6·7 g (96%) of the free hydrazine, subl. >160°, m.p. (sealed tube) 182–184° (lit.[32] 192–193°). (Calc for $C_6H_{10}N_4$: C, 52·15; H, 7·30; N, 40·55; Found: C, 52·54; H, 7·40; N, 40·61%; IR ($CHCl_3$, cm^{-1}) 1600 s, 1650 sh, 1575 sh, 3400, 3350, 3250 (broad); in Nujol: 3270, 3170 cm^{-1}).

1·5 g of this crude hydrazine in 5 ml 30% AcOH was treated with 0·75 g dry $NaNO_2$ at room temp, allowed to stand for 1 hr, cooled to 0°, and filtered to give 1·15 g (78%) of the tetrazole. Recrystallization from benzene–light petroleum gave colourless needles, m.p. 84–85° (corr), M^+ 149 (100); M-28 (43) m*; (M-28)-1 (54), m*; (M-28)-27 (35), m*. (Calc for $C_6H_7N_5$: C, 48·31; H, 4·73; N, 46·96; Found: C, 48·82; H, 4·85; N, 46·70%).

IR ($CHCl_3$, cm^{-1}): strong tetrazole bands at 1550 and 1640; in Nujol: only tetrazole bands, 3070 s, 1640–10 vs, 1550 vs, 1500–1490 vs, *ca* 1450, 1400, 1375, 1310, 1250, and numerous bands at lower frequency. Heating of the Nujol suspension above the m.p. (*ca* 100°) caused development of a medium-sized azide band at 2120. At the same time new bands at 1585 and 1360 appeared. The IR spectrum of the soln in $CHCl_3$ showed initially very weak azide bands at 2120, 2150. No apparent change occurred in 20 min while warming to 30°. Heating to 50° caused a marked increase of the azide bands at 2120–2150, 1585 and 1360; *cf* also Temple *et al.*[5]

This *compound* was not obtainable from the chloropyrimidine and sodium azide as in the following preparation (xi). An unidentified product, presumably due to hydration,[5] was obtained.

After 1½ years VIb was found to have transformed into a new *compound* (XVII?), obtained from benzene as colourless needles, m.p. 154–155° (dec) which was almost insoluble in benzene, chloroform or water, but dissolved readily in EtOH, alkali or acid; NMR (SO_2, −20°) 4·22 (q, H), 7·52 (d, J = 1·2, 3H), 7·74 (s, 3H) and −1·0 (broad, H or 2H). The spectrum in TFA was identical with that of VIb in TFA (Table 1); IR (KBr): 3200–3000 s (broad, NH), 2900 s, 1700 s, 1640 s (amide I; tetrazole), 1515 s (amide II), 1410 s, 1370 m, 1335 s, 1280 s, 1195 m, 1110 s, 1085 m, 1055 s, 980 m, 855 m, 759 s, 665 s cm^{-1}; mass spectrum (CEC, source, 200°, probe 120°): M^+ 167 (100), M-H_2O (2·3), M-28 (14), M-42 (81, m* 93·5), M-42-28 (35), M-42-29 (32, m* 73·5), *m/e* 97 → 96 (m* 95).

(xi) 5,7,8-*Trimethyltetrazolo*[1·5-*c*]*pyrimidine* (VIa)

From ethyl α-methylacetoacetate (14·4 g, 0·10 mole) was obtained 2·22 g (0·0161 mole) of the 4-hydroxypyrimidine (16·1%) which was further transformed into the chloride in the same way as in the preceding preparation (x). The crude chloride was treated with sodium azide (0·2 mole) and 10% EtOH–HCl (0·1 mole) under reflux for 24 hr. The warm soln was filtered through active carbon, evaporated to dryness, the residue extracted with abs EtOH, the extract filtered, concentrated to partial crystallization, heated to boiling, and allowed to crystallize at room temp, giving 0·70 g (26·7%) of the title compound, m.p. 96–97°. M⁺ 163 (76); M-28 (61), m*; M-29 (40), m*; (M-28)-15 (16), m*; (M-28)-26 (34), m*; (M-28)-27 (18); (M-28-26)-27 (100), m*. (Calc for $C_7H_9N_5$: C, 51·52; H, 5·65; N, 42·92; Found: C, 51·90; H, 5·84; N, 43·16%). The *compound* existed exclusively as the tetrazole in the solid state; IR (N): 1620–1600 (several very strong bands), 1550, 1510–1500, 1440, 1380, 1360, 1295, 1180, 1150, 1100, 995, 815, 770; no absorption above 3000 cm^{-1}. (Thus the peak near 3100 cm^{-1} in other spectra is due to the pyrimidine-H). A weak azide band appeared on heating above 100° (2140 cm^{-1}). IR ($CHCl_3$): weak band at 2145 cm^{-1} at 22°, increasing to about double intensity at 60°; no other change was apparent. The *compound* was completely stable to boiling water.

(xii) 4-*Azido*-2,6-*dimethoxypyrimidine* (VIIc)

(a) A mixture of 8·73 g (0·05 mole) 4-chloro-2,6-dimethoxy-pyrimidine, 6·5 g (0·10 mole) sodium azide, and 66 ml 10% EtOH containing 0·05 mole HCl was refluxed for 10 hr, cooled to 0°, and filtered to give 5·28 g product which liquefied at room temp. VPC analysis (5% Carbowax 20 M on Aeropak, 125° → 2°/min, 60 ml He/min) showed that it was a 1:1·4 mixture of the starting material and an azide, m.p. 37—38°, λ_{max} 273 mμ (the chloride has λ_{max} 259 mμ (C_6H_{12}); both had a second band at 220 mμ). IR ($CHCl_3$, N, or LF) showed a very strong azide band at 2120 cm^{-1}; also 1600 vvs, 1490, 1480, 1420, 1360, 1125, 1110, 1055, 985, 830 cm^{-1} (all strong). The compound did not add water (contrast Albert[10] and Temple[5]) and there is

no evidence for the presence of a tetrazole tautomer. The NMR spectrum showed a single tautomer in $CDCl_3$ and DMSO (Table 1). The latter solvent is known to stabilize the tetrazolo form[5]; mass spectrum: (MS 10C2, 75°): M^+ 181 (76), M-28+2 (16), M-28 (6), M-28-15 (100); M-28+2 remained after pumping the azide away and is presumably due to the amine. When all-glass heated inlet at 200° was used, only the amine spectrum appeared.

(b) The chloride (2·50 g) was treated as above but refluxed for 48 hr after which time some chloride, which had sublimed into the condenser, was combined with the reaction mixture and reflux continued for 48 hr with a fresh portion of sodium azide (1·8 g). After cooling, 2·16 g (83·5%) of nearly pure azide was obtained, m.p. 41–42° after recrystallization from aq. MeOH (lit.[33] m.p. 41–42° (aq. MeOH)); IR and NMR spectra as above.

(xiii) *4-Hydrazino-6-methyl-2-methylmercaptopyrimidine* (XVIII) *and 2,4-dihydrazino-6-methylpyrimidine* (XIX)

A mixture of 45·5 g (0·27 mole) 4-methoxy-6-methyl-2-methylmercaptopyrimidine (see iii above), 250 ml EtOH, and 17·5 g 85% hydrazine hydrate (0·30 mole) was refluxed for 72 hr, evaporated to half volume, cooled to −10°, filtered, and the ppt washed with light petroleum to yield 3·6 g (8·7%) XIX, m.p. 200–202°. Recrystallization from EtOH raised the m.p. to 210–212° (lit.[34] 213°); M^+ 154. (Calc for $C_5H_{10}N_6$: C, 38·95; H, 6·54; N, 54·51; Found: C, 38·65; H, 6·20; N, 54·81%). Evaporation of the filtrate from XIX and addition of light petroleum caused precipitation of 10·4 g (22·3%) XVIII, m.p. 135–136° from EtOH–light petroleum. One further recrystallization gave m.p. 140–142° (lit.[32] 142–143°); M^+ 170. (Calc for $C_6H_{10}N_4S$: C, 42·3; H, 5·88; N, 32·95; S, 18·82; Found: C, 42·02; H, 6·14; N, 33·16; S, 18·64%). Evaporation of the filtrate from XVIII gave 31·4 g (69%) starting material.

(xiv) *7-Methyl-5-methylmercaptotetrazolo*[1·5-c]*pyrimidine* (VId)

To 2·52 g (0·0148 mole) XVIII (see xiii) in 7·5 ml 30% AcOH was added 1·12 g (0·0177 mole) dry $NaNO_2$ at room temp. After standing for 1 hr, the solid was collected, washed with water and dried *in vacuo* to yield 2·7 g (100%) crude tetrazole, m.p. 65–66°. Recrystallization from benzene–light petroleum (active carbon) gave colourless crystals (88%), m.p. 66·5–67° without dec; M^+ 181. (Calc for $C_6H_7N_5S$: C, 39·8; H, 3·86; N, 38·6; S, 17·7; Found: C, 40·09; N, 38·77; S, 17·8%).

The *compound* existed almost exclusively as the tetrazole in the solid state, and partly as azide in soln or at elevated temp. IR (N): weak bands at 2120, 2150 cm^{-1}; strong tetrazole bands at 1600, 1570, 1540–20, 1460 (SCH_3), 1380–70, 1325 (SCH_2), 1315, 1025, 835 cm^{-1}. Gradual heating of the nujol suspension to 100° caused development of strong azide bands at 2120, 2150, 1570, 1540, 1380, 1340 cm^{-1}, whereas tetrazole bands at 1600, 1520, 1460–40, 1370 cm^{-1} decreased markedly. The initial spectrum reappeared on cooling. In $CHCl_3$ and CCl_4: strong azide bands at 2120, 2150, 1580, 1350, 1285, 1200, 945, 920 cm^{-1}, and medium S-Me bands at 1440, 1320 cm^{-1}; NMR (Table 1) indicated a 1:5 mixture of tetrazole and azide in $CDCl_3$, and a nearly 1:1 mixture even in DMSO; mass spectrum (MS 10C2, 50°): M^+ 181 (85), M-28+2 (22), M-28 (15), M-28-15 (64), 126 (13), 120 (6·5), 113 (83), 111 (40), 96 (53), 95 (37), 94 (55), 79 (44), 76 (100). *m/e* 155 (M-28+2) remained after pumping the azide/tetrazole away.

(xv) *Tetrazolo*[1·5-a]*pyrazine* (XI)

Chloropyrazine (0·1 mole) was refluxed with sodium azide (0·2 mole) and 10% EtOH-HCl (0·1 mole HCl) for 24 hr, evaporated to dryness, and the dark material recrystallized from benzene, yield: 50%, m.p. 90–91° (lit.[17] 90·8–91·5°, prepared from fluoropyrazine and sodium azide). UV and NMR data (Table 2) were in agreement with reported[17] values, except that azide tautomerization (Table 2) has not previously been noticed; IR spectrum (Nujol): 3080 m, 3030 w, 3000 m, 1520 s, 1480–1460 vs, 1450 s, 1440 m, 1405 m, 1345 s, 1090 s, 1030–1020 s, 910 s. Weak azide bands appeared at 2140 and 2120 cm^{-1} on heating above the m.p. (100°). In $CHCl_3$ soln moderate azide bands developed at 2140, 2120 cm^{-1} in ½ hr at 30°; mass spectrum (MS 9, direct): at 70 eV: M^+ 121 (73), 95 (6·3), 93 (63), 79 (8·3), 66 (100), 53 (25), 52 (10·5), 51 (8·3), 39 (73), 27 (12·6); at 12 eV: M^+ 121 (100), 95 (4), 93 (60), 66 (12).

(xvi) *Tetrazolo*[1·5-b]*pyridazine* (XIII)

This was prepared as described by Itai and Kamiya[19] m.p. (benzene or sublimation) 110–111°; IR spectrum ($CHCl_3$ or Nujol): 3080 m, 3040 m, 1620 s, 1540 s, 1490 s, 1375 s, 1350 s, 1330 s, 1270 s, 1225 s, 1130 s, 1080 s, 1010 s, 985 m, 915 m, 810 s, 765 cm^{-1}. No azide bands appeared in $CHCl_3$ at 35°, or in Nujol on heating to 140°; mass spectrum (MS 9, direct) at 70 eV: M^+ 121 (19), 95 (1·1), 94 (2·8), 93 (2·8), 65 (100),

64 (34), 39 (17), 38 (92), 37 (32), 27 (8·5); at 12 eV: M^+ 121 (30), 95 (3·7), 94 (9·5), 93 (9·5), 65 (100). (Calc mass for $C_4H_3N_3$ (*m/e* 93): 93·03770; Found: 93·03746. Calc mass for C_4H_3N (*m/e* 65): 65·02655; Found: 65·02640).

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