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HETARYLNITRENES—I

RING CONTRACTION AND FRAGMENTATION IN NITRENODIAZINES

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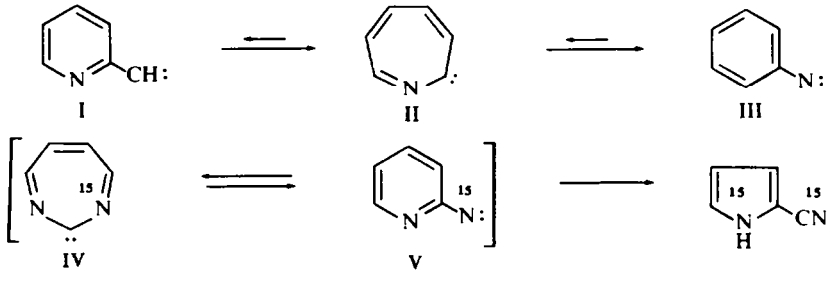
Abstract—Gas-phase thermolysis of tetrazolo[1.5-*a*]pyrimidines gives 1-cyanopyrazoles by ring contraction and 2-aminopyrimidines by H-abstraction. Tetrazolo[1.5-*c*]pyrimidines give 1-cyanoimidazoles; 1-cyanoimidazole similarly results from pyrolysis of tetrazolo[1.5-*c*]pyrazine. Tetrazolo[1.5-*b*]pyridazine lose two molecules of N_2 to form C_4H_3N, which isomerizes to cyanoallene, tetrolonitrile, propargyl cyanide and 2-cyanocyclopropene.

It is concluded that 2-pyrimidylnitrene and 3-pyridazinylnitrene do not interconvert on the $C_4H_3N_3$ energy surface *via* ring expansion.

INTRODUCTION

IN RECENT communications we have demonstrated isomerization of 2-pyridylcarbene to phenylnitrene (III)[1] on the C_6H_5N energy surface, and N-scrambling in the conversion of 2-pyridylnitrene (IV) to cyanopyrroles[2] on the $C_5H_4N_2$ surface. In both cases we proposed mechanisms which involved ring expansion† (to azatropylidene



I II III IV V

II and diazatropylidene V respectively). The work also showed that the products did not arise by concerted processes in the precursors (e.g. tetrazolo[1·5-*a*]pyridines). We have now extended this work into the nitrenodiazine field, and report here conclusions from the gas-phase pyrolysis of tetrazolo- and azidodiazines.

Pyrolysis of Tetrazolodiazines

The purpose of this work was to examine the intramolecular transformations of the nitrenodiazines VI, VII, VIII and IX, in which the nitrene N is offered various possibilities for insertion into a number of ring systems. Thermal decomposition of the tetrazole ring system was used as a routine method of nitrene generation. Pyrolysis

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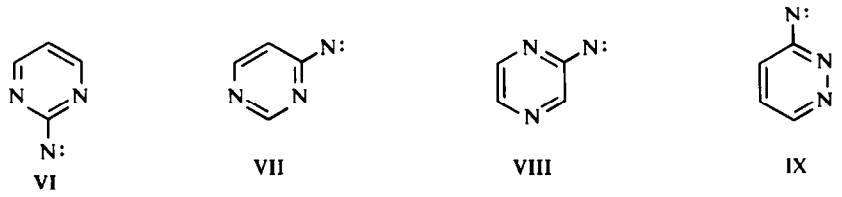
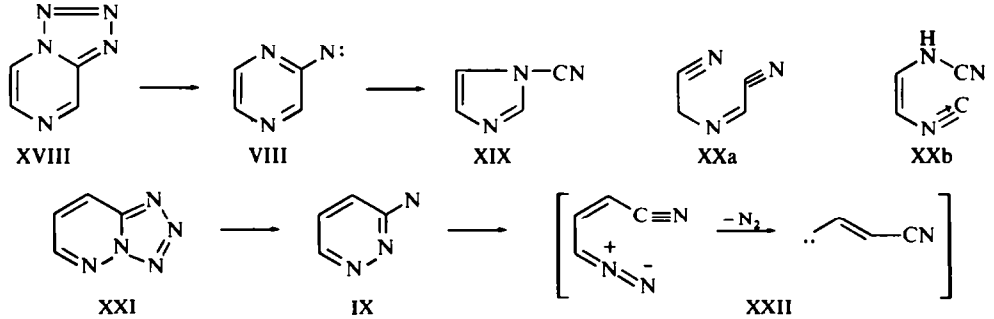
† Ring expansion represents the most elementary hypothesis which will serve; more sophisticated theories might serve equally well, but require further experimental evidence.

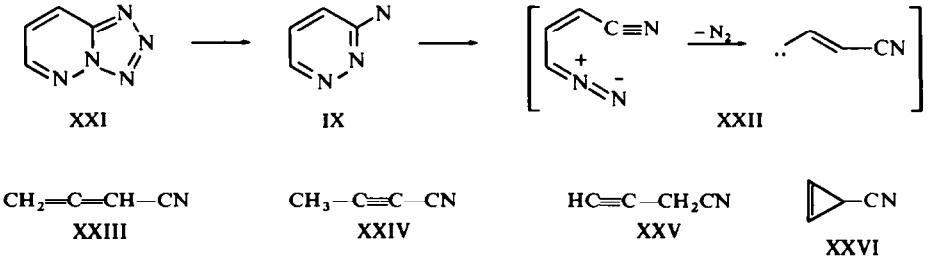


VI VII VIII IX

of tetrazolo[1·5-*a*] pyrimidines (X) gave 1-cyanopyrazoles (XII) and 2-aminopyrimidines (XIII), accompanied in one case by loss of the CN group with formation of pyrazole (XIV) and HCN (Table 1). The isomeric tetrazolo[1·5-*c*]pyrimidines (XV) gave 1-cyanoimidazoles (XVII) in high yield, but without the formation of any accompanying 4-aminopyrimidine (Table 2). The dimethoxyderivative XV*c*, which exists exclusively as the azide (XVI*c*) at room temperature,[3] underwent typical[4] azide-type pyrolysis, with extensive carbonization and low yield of ring contraction products.

Tetrazolopyrazine (XVIII) gave, at 380°/0·10 mm, a 65% yield of 1-cyanoimidazole (XIX) together with two other compounds (Experimental) which appear to arise from the nitrene VIII, possibly by ring cleavage to XX*a* (*cf* Ref 2) and/or XX*b*. Both gave the same mass spectrum as XIX, although the major component (25%) was a red glassy polymer (γ_{CN} = 2210 cm^{-1}, γ_{NC} – 2140 cm^{-1}).

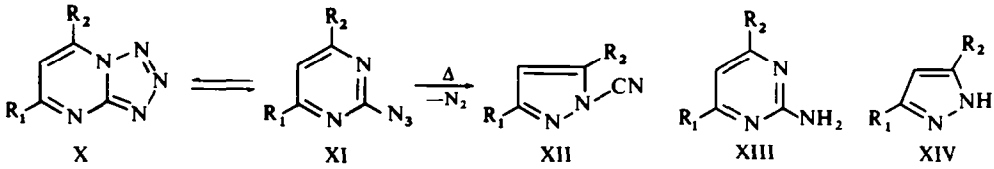




XXIII XXIV XXV XXVI

Tetrazolo[1·5-*b*]pyridazine (XXI) gave, at 380°/0·02–0·03 mm, a mixture of cyanoallene (XXIII), tetrolonitrile (XXIV), propargyl cyanide (XXV) and 2-cyanocyclopropene (XXVI). The last two were identified only by NMR and IR spectra of the crude pyrolysate, since they rearranged to XXIII and XXIV on attempted isolation by GLC. There was some evidence that 2-cyanocyclopropene also rearranged to 1-cyanocyclopropene on GLC (Experimental). There was no primary reaction product from the nitrene IX (e.g. XII, R_1 = R_2 = H) detected in the pyrolysate even at 305°/0·01 mm where only 33% conversion of XXI occurred. At the lower temperature the yields of XXIV and XXV fell relative to those of XXIII and XXVI, possibly indicating that they arise by isomerization of these compounds.

TABLE 1. PYROLYSIS OF TETRAZOLO[1.5-*a*]PYRIMIDINES[a]



X XI XII XIII XIV

	R_1	R_2	T°/Pmm	Product Yield (%)[d] XII	XIII	XIV
Xa	H	H	400/0·10	14·3	17·5	1·0
			600/0·10	33	7	8
Xb	Me	Me	320/0·05–0·10	15·3	58	—
			400/0·05	21	34	—
Xc	MeO	Me	380/0·02	trace[b]	40	—
			600/0·10	6	43	—
Xd	MeS	Me	380/0·10	0	17[c]	—
Xe	Cl	Me	380/0·01	2	15	—

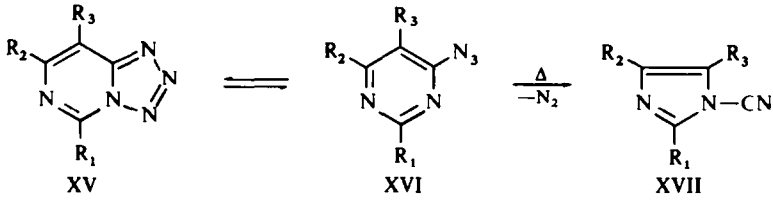
[a] All compounds were volatilized into the furnace at 100°, and product analysis was by GLC on column C (Experimental) at 125° → 2°/min, He 60 ml/min.

[b] Detected only by ν_{CN} in the IR spectrum of the crude product.

[c] Only volatile product; also obtained as sole product emerging from GLC after injection of Xd with the injection port at 270°.

[d] Extensive charring was observed in all cases, 80% in the case of Xe.

TABLE 2. PYROLYSIS OF TETRAZOLO[1.5-*c*]PYRIMIDINES



XV XVI XVII

	R_1	R_2	R_3	T°/Pmm	Sample Introduction (°C)	% Yield XVII	T_R (min)[a]
XVa	Me	Me	H	340/0·03	75	95	8
b	Me	Me	Me	320/0·01–0·02	80	100	12
c[b,c]	MeO	MeO	H	340/0·10[c]	50	12	25
d[d]	MeS	Me	H	380/0·01–0·02	60	88[e]	30

[a] Retention time on Column C (Experimental); 120° → 2°/min, He 60 ml/min.

[b] Exists exclusively in the azido form XVIc.[3]

[c] Pyrolyzed with extensive charring.

[d] Melts at 66·5–67° with partial tautomerization to XVId.

[e] Injection of XVd into the GLC port at 300° gave 100% yield.

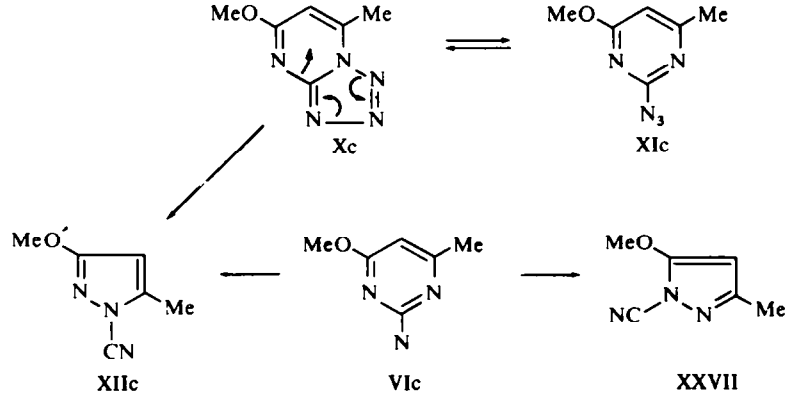
The cyanoazoles reported in Tables 1 and 2 are, with the exception of XIX,[5] new, and structural assignments were made by NMR, IR and mass spectral data. The NMR and IR data are presented in Table 3; compounds XIIa, XIIb, VIIIa and XIX were also synthesized from the appropriate diazole and cyanogen bromide. It may be

seen that the chemical shifts are determined largely by the electronegative effect of the CN group, as in the case of the cyanocyclopentadienes,[6] although substituents can substantially counterbalance this. The νCN bands are all very strong and at 2250–2260 cm^{-1} are rather higher than for conjugated nitriles[6,7] (e.g. 1-cyano-2,3,4,5-tetrabromopyrrole absorbs at 2260 cm^{-1}). Saturated N-cyanoheterocycles[7] by contrast absorb at lower frequencies, reflecting the availability of the N lone pair.

DISCUSSION

Concerted vs *nitrene reaction.* Ring contraction in the tetrazoles X, XV and XVII could in principle be either concerted with N_2 loss or a subsequent reaction of the generated nitrenes VI, VII and VIII. In the analogous cases of benzotriazoles[8] and tetrazolo[1·5-*a*]pyridines,[9] in which we have proposed iminocarbene and nitrene intermediates, discussion of this question was pointless, in that there was no possibility of distinguishing between the two mechanisms. However, in the case of the tetrazolo[1·5-*a*]pyrimidines the possibility does at least exist, and we have attempted to design experiments to cast some light on the question.

The isomerization of tetrazolo[1·5-*a*]pyrimidines (X) to the 2-azidopyrimidines (XI) occurs at slightly elevated temperatures* (indeed, XIc is the preferred isomer at 20°), and it seems reasonable to assume that ring opening to the azido-form could well precede any other reaction in pyrolysis. Certain aspects of the pyrolysis of X (and also of XVc, which exists as the azide at 20°) are strongly suggestive of azide pyrolysis.[4] Thus the extensive carbonization, and the CN loss observed in Xa itself are reactions we have previously observed in the generation of "hot" nitrenes by violent azide pyrolysis. The formation of 2-aminopyrimidines from X is also a strong argument against a concerted N_2 elimination/ring contraction. The triazolo[1·5-*a*]pyrimidine Xc was prepared in an attempt to provide less circumstantial evidence; the nitrene VIc should be capable of forming two ring contractions products (XIIc and XXVII) whereas concerted reaction would give only the one isolated (XIIc).



* The factors governing the ease and extent of this isomerization are discussed in a forthcoming paper.[3] For our present purposes it suffices to know that the energy barrier between X and XI is not extraordinarily high, i.e. the interconversion may reasonably be assumed possible at 400–600°.

Although only one† product was isolated, the high yield of the 2-aminopyrimidine indicated that nitrene participation must have been extensive and it is possible that electronic effects direct the collapse of the nitrene. Similar experiments with Xe were slightly more successful. Pyrolysis at 300°/0·001 mm caused 50% carbonization, the rest of the material being recovered in the azido-form[3] XIe. Under more vigorous conditions (Table 1) 80% carbonization (with some chlorine loss) occurred; the NMR spectrum of the resultant nitriles indicated the presence of two compounds τ 3·83(H), 7·70(3H) (75%) and τ 3·88(H), 7·48(3H) (25%) which could not be readily separated. The chemical shifts are in good agreement with those listed in Table 3, and the mass spectrum indicated M^+ 141/143 (consistent with $C_5H_4N_3Cl$) but no *m/e* 107 (methylcyanopyrazole MW 107). Such evidence as there is thus indicates that the reaction does in fact proceed through the nitrene VII.

In the case of tetrazolo[1·5-*c*]pyrimidines XV, as with the tetrazolo[1·5-*a*]pyridines, both nitrene and concerted reactions would lead to the same ring contraction products. The absence of 4-aminopyrimidines in this series could be taken as evidence against nitrene production, were it not for the fact that XVc and d are known to exist as the azides. In this connection the two methylthiotetrazolopyrimidines Xd and XVd are of interest. Xd is stabilized in the tetrazole form, whereas XVd is stabilized in the azide form. In the first case, ring contraction is reduced to zero and only the 2-aminopyrimidine XIIId results; in the second case facile ring contraction results. Evidently these findings cannot be explained simply in terms of ring contraction in tetrazoles and amine formation in azides. One point of similarity, however, emerges—both compounds readily decompose on GLC at 300°, i.e. N_2 loss is certainly facilitated by the presence of the MeS substituent.

An alternative explanation of the results emerges from a consideration of the detailed processes which may be involved in nitrene collapse. We regard this as being initiated by a disrotatory motion about the 1,6- and 3,4-bonds in VI with the ultimate development of 1,3-overlap in the nitrenoprefulvene type intermediate VI″. From this point the reorganization of the electron cloud occurs to consolidate the C≡N, with concomitant cleavage of one of the C_2N_1 or C_2N_3 bonds to produce XII. In the transformation VI → VI′ → VI″ the relatively weak N—N bond (~39 kcal $mole^{-1}$) is formed, whereas in the corresponding transformation VII → VII′ → VII″ a C—N bond (~73 kcal $mole^{-1}$) results. During the "cooling" of the two nitrenes by collision processes, the potentialities for reversal VI″ → VI should be greater than the corresponding VII″ → VII, as suggested in the energy diagram (Fig 1). With this reasoning we conclude that the decomposition and H-abstraction in pyrolysis of X are due to what is essentially a longer lifetime in the nitrene form VI. A more rapid transformation to VII″ occurs in pyrolysis of XV, resulting in less carbonization and H-capture, with high yields of ring contraction products.

While this broad generalization can be reasonably made to cover the distinction between the two classes of tetrazolopyrimidines X and XV, it is apparent that the nature of the substituents in each has a substantial effect on the processes. We have previously[9] ascribed the ease of ring contraction in XVd to the stabilizing effect of MeS— upon the intermediate VII″d.

† The crude pyrolysate did in fact show an IR band at 2250 cm^{-1} additional to that of XIIc, but only one product was isolated.

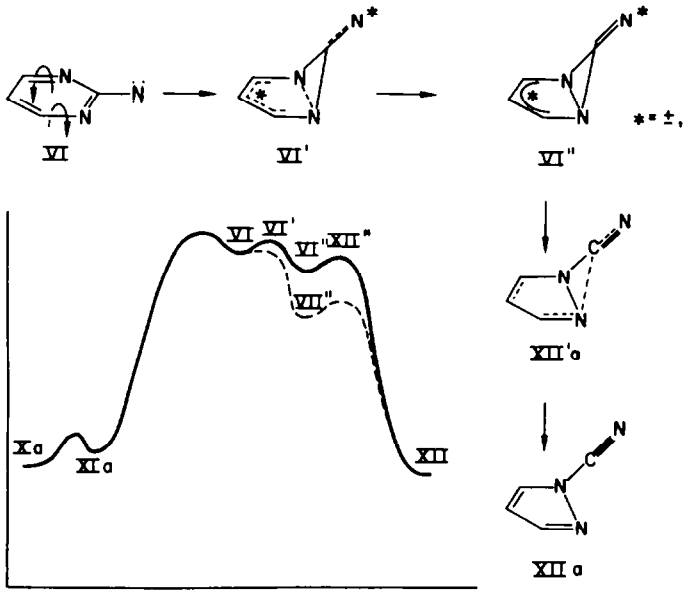
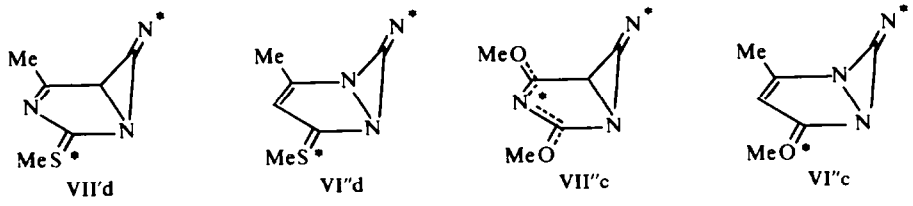


FIG 1



Inspection of the corresponding intermediates VI"c,d and VII"c lead to the expectation that similar effects should be operative; Table 1 shows that this is not necessarily true. The effects of substituents may involve any stage of the process, from stability of the azide to ability of the products to survive the conditions of the experiment,* and clearly need more investigation.†

Nitrene interconversion by ring expansion

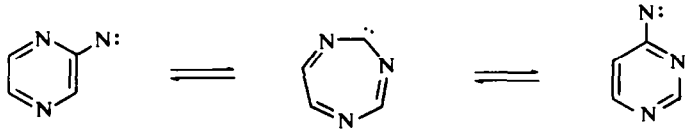
The similarity observed between pyrolysis of tetrazolo[1·5-*c*]pyrimidine (XV) and tetrazolopyrazine (XVIII) raises the possibility that VII → VIII interconversion occurs

* Note the low recovery on pyrolysis of Xd and XVc in particular.

† This point is well illustrated by the effects of substituents on azide-tetrazole isomerisms.

i.e., VI should remain "nitrene-like" for a greater part of its lifetime in the conversion to XII, whereas VII should more rapidly pass to VII", and hence through to final product.

via ring expansion[2] of the nitrenes (*cf* IV → V). In this case ^{15}N-labelling experiments would be required to establish the existence of the process. The ring cleavage products,* which gave a clear indication in the case of tetrazolopyridines,[2] are here not susceptible to structural assignment. In the corresponding comparison between pyrolysis of tetrazolo[1·5-*a*]pyrimidine (Xa) and tetrazolopyridazine (XXI), the complete absence of ring contraction in the latter makes us more confident that the ring expansion/isomerization cycle VI → IX is not involved. Here we must assume that ring cleavage of IX is favoured over other reactions and that the product XXII instantly loses N_2 under the conditions of its generation. The mass spectrum of XXI offers some confirmation of this belief. Even at 12 eV the base peak is the ion $C_4H_3N\cdot$ rather than the expected $C_4H_3N_2^+\cdot$ or $C_4H_3N_4^+\cdot$. It is of significance also to note that the ring contractions and expansions we have reported have formal analogies in the reactions of the heterocyclic N-oxides.[10] The ring-opening of the nitrene IX which we have proposed above is no exception, as 3,6-diphenylpyridazine-N-oxide is reported[11] to give a transient diazo-enone on photolysis. The question of ring cleavage *vs* cyclic



VIII VI

reorganization in the general area of high energy intermediates is not susceptible to meaningful discussion at this stage. Many of the reactions could be rationalized in terms of acyclic biradicals (e.g. XXVIII), possibly still involving azatropylidene intermediates. Any decision on this point needs more sophisticated experimentation than we can currently bring to bear upon the problem.

EXPERIMENTAL

Pyrolysis apparatus. This consisted of a silica tube (30 × 2 cm) packed with 5–10 mm pieces of 4 mm silica tubing, heated by an electric furnace, which was calibrated with a Chromel–Alumel thermocouple. The whole was evacuated with a high-capacity oil pump capable of an ultimate vacuum of 10^{-5} mm, the pressure being recorded on a Vacustat gauge near the traps. Volatile materials were collected in liquid N_2 cooled traps, and gasses sampled by adsorption in cooled, degassed Molecular Sieve 5A. Pressures quoted are self-pressure except where carrier gas was employed.

Analysis of pyrolysis mixtures. Liquid products were extracted with ether, decolourized with carbon or distilled as required, and examined by GLC using an FM 500 gas chromatograph equipped with a thermal conductivity detector. When preparative GLC was necessary, an Aerograph Autoprep 705 was used. In general, samples were collected in m.p. capillaries from the analytical instrument, and submitted to analysis by IR, UV, NMR and mass spectrometry. It was necessary to check by reinjection to establish the purity of the samples. The standard column used was 20% Carbowax 20M on Embacel (*Column A*, 12′ × $\frac{1}{8}$″), using helium as the carrier gas. In special cases other columns were used: *Column B*, SE 30 on firebrick (5′) gave shorter retention times and poorer resolution. *Column C*, 5% Carbowax 20M on Aeropak (5′) was used for high-boiling components.

A typical analytical run would start at 120°, programmed at 2°/min to 240°, with injection port and block at 250°. Identification was checked when possible by comparison of retention times with authentic specimens.

* The fact that ring cleavage *does* occur in XVIII, but not in XV, is not necessarily diagnostic of structural difference in the intermediates. It may well be a function of the excess thermal energy carried by the generated nitrenes,[4] for example.

Solid products usually crystallized or deposited just outside the furnace, and were crystallized, sublimed or subjected to GLC as appropriate.

UV spectra were measured on a Unicam SP800 in 96% EtOH unless otherwise stated. IR spectra were measured on a Unicam SP200G, or (where high resolution was required) on a Grubb–Parsons DB1/GS4 instrument. 60 Mhz NMR spectra were measured with a Perkin–Elmer R-10 spectrometer, and results are quoted as τ-values. The solvent was CCl_4 unless stated otherwise. Mass spectra were recorded on AEI MS902 and MS10C2 or CEC 21-490 instruments as stated; all abundances are as % base peak. Microanalyses were by the Australian Microanalytical Service at the University of Melbourne.

Preparation of tetrazoles. These are described in Ref 3 (following paper).

Preparation of cyanoazoles. The method was adapted from the literature.[5] Cyanogen bromide (2·27 g, 0·021 mole) in benzene (20 ml) was added with stirring to 3,5-dimethylpyrazole (4·10 g, 0·042 mole) in benzene (100 ml) at 60°, then refluxed for 1 hr. The mixture was cooled, the dimethylpyrazole hydrobromide (3·51 g, 93%) filtered off, the solvent removed under reduced press and the residue distilled at 60° (bath)/ 0·001 mm to give 1-*cyano*-3,5-*dimethylpyrazole* (XIIb; 2·08 g, 80%) m.p. 37–38°; λ_{max} (C_6H_{12}): 232 nm; ν_{CN} 2256 cm^{-1}; mass spectrum: M^+ 121 (100), M-H (21), M-15 (32), M-27 (3). The NMR spectrum is recorded in Table 3. The product was >99% pure by GLC, and was in all respects identical with that obtained from pyrolysis of Xb.

1-*Cyanopyrazole* (XIIa) was similarly prepared from pyrazole. In this case the filtered benzene soln was diluted with a large volume of petroleum and evaporated, as the product co-distils with benzene, yield 78%, m.p. 37°, ν_{CN} 2264 cm^{-1}; λ_{max} (C_6H_{12}) 231 nm; mass spectrum: M^+ 93 (100), M-27 (35), M-40 (19). The NMR spectrum is recorded in Table 3.

1-*Cyano*-2,4-*dimethylimidazole* (XVa) and 1-*cyano*-2,5-*dimethylimidazole* were prepared in the same way as a 5:2 mixture from 2,4-dimethylimidazole in 82% yield. The major isomer crystallized and was isolated by filtration, m.p. 63–64°; the structure XVa was assigned on the basis of the lower chemical shift of H_5 and higher chemical shift of the 4-CH_3 (Table 3), and on the expectation that steric factors would favour the formation of this isomer; λ_{max} (C_6H_{12}) 233 nm; ν_{CN} 2253 cm^{-1}; mass spectrum: M^+ 121 (100), M-H (17), M-15 (1), M-27 (17), M-41 (17), M-54 (18), M-68 (60).

The filtrate was a 1:1 mixture of the two isomers according to NMR analysis.

Pyrolysis of tetrazoles

The tetrazole was sublimed into the pyrolysis tube from a heated flask under the conditions stated. The product yields are stated in Tables 1 and 2 and the general analytical procedure has been described above. Only those cases requiring special comment are described below.

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

2-Amino-4-methoxy-6-methylpyrimidine was identified by its IR and mass spectra. It had m.p. 154–156° (lit.[12] 153–154°, 155·5–157°). The structure of the lachrymatory XIIc was based mainly on the NMR spectrum (Table 3); the mass spectrum showed M^+ 137 (100), M-H (60), M-29 (35).

5-*Methylthio*-7-*methyltetrazolo*[1·5-a]*pyrimidine* (Xd)

Pyrolysis resulted in extensive carbonization, and yielded a reddish solid with a sulphurous odour. A chloroform extract of this showed more than 96% as one compound on GLC. The product was identified as XIId from its mass spectrum and the similarity of its IR spectrum to those of other 2-aminopyrimidines. The molecular ion occurred at *m/e* 155·05139 (calc for $C_6H_9N_3S$: 155·05172) and the product had m.p. 151–152° (lit.[13] 152°); λ_{max}: 233, 300 nm (EtOH or pH 1 in water); 232 (12,000), 298 (10,300) at pH 11.[13]

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

The pyrolysate was extracted with CCl_4, and the soluble products were examined by mass spectrometry, using a direct probe. The more volatile components (unheated probe) showed *m/e* 141/143 and 106 (M-Cl, base peak); there was no peak at *m/e* 107 (methylcyanopyrazole). On heating the probe to 110°, a further spectrum appeared, corresponding to that of Xe. Formation of HCl during pyrolysis resulted in isolation of the amine XIIIe as its hydrochloride. The amine (m.p. 183–183°, lit.[19] 182–183°) was recovered and showed M^+ 143/145 as required for the formula.

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

Tetrazole at 320°/0·01–0·02 mm (0·205 g) gave 0·170 g (100%) lachrymatory nitrile (XVIIb) which was

>99·5% pure by GLC (Column C); NMR: (Table 3); mass spectrum: M^+ 135 (100), M-H (34), M-CH_3 (7·5), M-HCN (3·7), M-41 (14), M-56 (17), M-41-27 (66).

4-Azido-2,6-dimethoxypyrimidine (XVIc ⇋ XVc)

The lachrymatory nitrile (XVIIc) formed crystallized from ether as colourless needles, m.p. 80–81° after purification by GLC; IR: 3150 (sharp), 2256s cm^{-1}; λ_{max} 235 nm; mass spectrum: M^+ 153 (100), M-CH_3 (68), M-CH_3CO (18), M-CH_3CO-HCN (24); NMR: Table 3.

7-Methyl-5-methylthiotetrazolo[1·5-c]pyrimidine (XVd)

The slightly lachrymatory nitrile (XVIId) formed had m.p. 69–70°; IR: 3100, 2255, 1160, 1095 cm^{-1}; mass spectrum: M^+ 153/155 (90/4·2), M-CH_3 (60), M-HCN (16), M-SH (5), M-40 (100). The last peak was due to loss of CH_2CN or NCN, since the sulphur isotope peak was present; NMR: Table 3.

Tetrazolopyrazine (XVIII)

The tetrazole (0·45 g) was sublimed into the apparatus at 85° over the course of 60 min at 380°/0·10 mm. 1-cyanoimidazole[5] (XIX, 0·224 g, 65%) was collected in the traps and had m.p. 65°; IR: 2260 cm^{-1}; λ_{max}: 223 mn; NMR: Table 3; mass spectrum: M^+ 93 (100), M-HCN (30), M-40 (13·3). Immediately outside the furnace there was deposited in low yield a colourless solid m.p. 175° (possibly the unreported 2-cyanoimidazole); IR ($CHCl_3$): 2235 cm^{-1}; mass spectrum: as for XIX, together with a vitreous, red–orange material (25%, assumed to be polymeric) m.p. >140° dec; IR: 2140, 2210 cm^{-1}; mass spectrum (CEC 21–490, direct inlet, source 180°): as for XIX.

Tetrazolo[1·5-b]pyridazine (XXI)

(a) Tetrazolo (0·50 g) pyrolysed at 380°/0·02–0·03 mm in 3·5 hr (sublimed in at 105°, m.p. 107–108°) gave 0·266 g (99%) of a mixture of the nitriles XXIII–XXVI. The mass spectrum (M^+ 65) of the crude pyrolysate was identical with that of either XXIII or XXIV. The NMR spectrum of the mixture showed peaks due to cyanoallene XXIII (4·6[14]), tetrolonitrile XXIV (8·0[14]), propargyl cyanide XXV (6·64, *d*, 2H; 7·74, *t*, H[14, 15]) and 3-cyanocyclopropene XXVI (2·85, *d*, J = 1·5, H_1, H_2; 8·05, *t*, J = 1·5, H_3. *cf* data for cyclopropenes[16]) in the integrated ratio 7:1:4:1·5. The IR spectrum of the crude mixture also indicated the presence of XXIII, XXIV and XXV.[17] On GLC (Column C, 60°, 2 ml min^{-1} He) two low-boiling nitriles were obtained. The first was identified as tetrolonitrile, m.p. 17–18°;[18] IR (film): 3000–2900, 2160 w, 2270 s, 2330, 1430, 1380 cm^{-1}; λ_{max} (C_6H_{12}): ~220 nm; 100 Mhz NMR: 8·02 (*s*);[14] mass spectrum: M^+ 65 (100), M-H (54), M-HCN (63). The other was identified as cyanoallene from the IR spectrum;[17] λ_{max} (MeOH): 215 (14,200) nm; mass spectrum: as for tetrolonitrile. Cyanoallene partly rearranged to tetrolonitrile.[14] A third nitrile was also separated in low yield, and showed two IR bands (2230 and 2265 cm^{-1}) for CN, presumably due to a mixture of 1- and 3-cyanocyclopropene. The 2265 cm^{-1} band was stronger in the crude nitrile mixture. At higher column temperatures this nitrile did not appear. Its mass spectrum was the same as for the other isomers.

(b) Tetrazole (0·50 g) pyrolysed at 305°/0·01 mm over 4 hr (sublimed in at 105°) gave 67% recovered starting material and 33% nitriles; the proportion of cyanoallene was twice as great as in (a).

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REFERENCES

[1] W. D. Crow and C. Wentrup, *Tetrahedron Letters* 6149 (1968)
[2] W. D. Crow and C. Wentrup, *Chem. Comm.* 1387 (1969)
[3] C. Wentrup, *Tetrahedron* in press
[4] W. D. Crow and C. Wentrup, *Tetrahedron Letters* 5569 (1968)
[5] H. Gieseman, *J. Prakt. Chem.* [4], 1, 345 (1955)
[6] C. Wentrup and W. D. Crow, *Tetrahedron*
[7] C. Wentrup, Ph.D. Thesis, Australian National University (1969)
[8] C. Wentrup and W. D. Crow, *Tetrahedron*
[9] W. D. Crow and C. Wentrup, *Chem. Comm.* 1082 (1968)

[10] O. Buchardt, P. L. Kumber and C. Lohse, *Acta Chem. Scand.* **23**, 159, 2149 (1969) and earlier papers; C. Kaneko, Sa. Yamada, I. Yokoe and M. Ishikawa, *Tetrahedron Letters* 1873 (1967) and earlier papers; J. Streith, A. Blind, J. M. Cassal and C. Sigwalt, *Bull. Soc. Chim. Fr.* 948 (1969) and earlier papers
[11] P. L. Kumber and O. Buchardt, *J. Am. Chem. Soc.* **90**, 5641 (1968)
[12] W. Braker, E. J. Pribyl, J. T. Sheedan, E. R. Spitzmiller and W. A. Lott, *Ibid.* **69**, 3072 (1947); K. Shirakawa, S. Ban and M. Yoneda, *J. Pharm. Soc. Japan* **73**, 598 (1953)
[13] H. C. Koppel, R. H. Springer, R. K. Robins and C. C. Cheng, *J. Org. Chem.* **26**, 792 (1961)
[14] H. Waltz and P. Kurtz, *Z. Naturforsch* **18b**, 334 (1963)
[15] G. S. Reddy, L. Mandell and J. H. Goldstein, *J. Am. Chem. Soc.* **83**, 4729 (1961)
[16] M. Vidal, J. L. Pierre and P. Arnaud, *Bull. Soc. Chim. Fr.* 2864 (1969)
[17] P. Kurtz, H. Gold and H. Disselkötter, *Liebigs Ann.* **624**, 1 (1959)
[18] R. Vessiere and F. Theron, *C.R. Acad. Sci., Paris* **255**, 3424 (1962); J. Sheridan and L. F. Thomas, *Nature, Lond.* **174**, 798 (1954)
[19] S. Gabriel and J. Colman, *Ber. Dtsch. Chem.* 2921 (1899)