*Tetrahedron.* Vol. 27, pp. 1281 to 1286. Pergamon Press 1971. Printed in Great Britain

# NITRENES DERIVED FROM POLYMETHYLENETETRAZOLES

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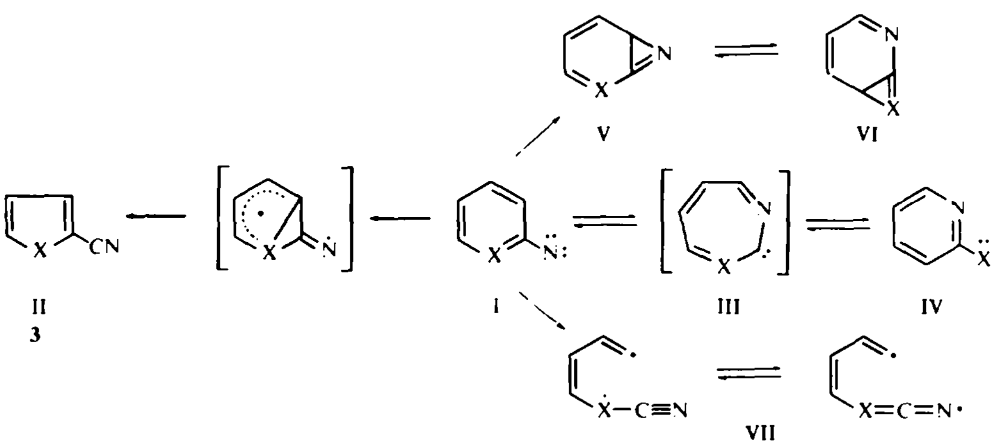
(*Received in the UK* 31 *July* 1970; *Accepted for publication* 20 *August* 1970)

**Abstract.** Pentamethylenetetrazole (VIII) on gas-phase pyrolysis eliminates nitrogen and gives 4-pentenylcyanamide (IX). The latter undergoes ring closure to 1-cyano-2-methylpyrrolidine (X). Tetramethylenetetrazole (XII) similarly gives 3-butenylcyanamide (XIII) and 1-cyanopyrrolidine (XIV). Trimethylenetetrazole (XVI) gives nitrogen, ethylene, and a compound $C_2H_2N_2$, which most likely is N-cyanoformimine, $CH_2{=}N{-}CN$.

## INTRODUCTION

THE thermal gas-phase reactions of aromatic nitrenes (I) have been described.[1] Most important are the ring contractions to 5-membered ring nitriles (II), and the ring isomerisations (to IV) which proceed through an intermediate which has an arrangement of atoms as in the tropylidene (III).




There is at present no clear way to decide whether the bicyclic intermediates[2] (V and VI) are involved instead of, or in addition to III. There is some evidence[1e] that in some cases ring opening to VII may take place; this biradical intermediate readily provides pathways both for production of the ring contraction product (II), and for ring expansion to III. Ring opening pathways to ring contraction in 2-azido-*p*-quinone,[3] and to ring contraction and ring enlargement in phenanthridine N-oxide[4] have also been proposed.

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The hydroaromatic nitrenes described in the present paper are shown to undergo ring contraction *via* ring opening, at least in one case. This provides an additional reason for seriously considering the role of the species (VII) in aromatic nitrene reactions.

## RESULTS AND DISCUSSION

Pyrolysis of pentamethylenetetrazole (VIII) at 450–675° produced two compounds*, 4-pentenylcyanamide (IX) and 1-cyano-2-methylpyrrolidine (X). IX is supposedly formed by ring opening of VIII as indicated in Scheme I. The yield of IX decreases, and the yield of X increases with temperature (Table 1). Furthermore, IX rearranges partly (10%) to X on injection onto a gas chromatography port at 210°, indicating that X arises from internal addition in IX. No trace of the direct nitrene ring contraction product, 1-cyanopiperidine (XI) was detected.

SCHEME I

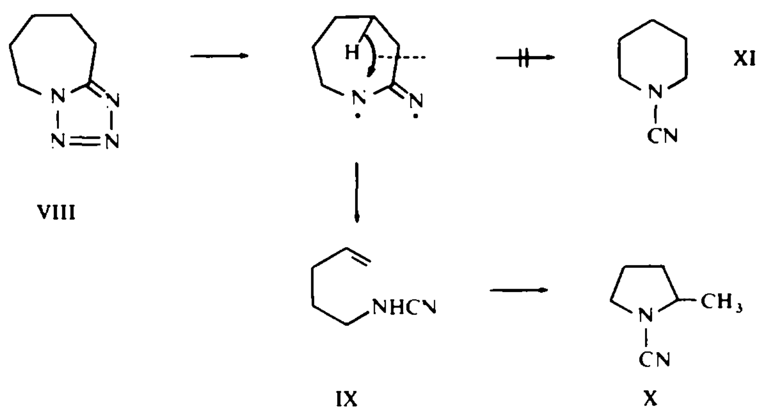
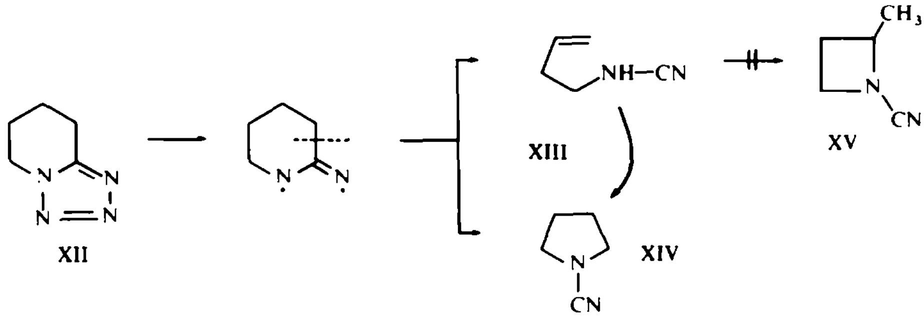



TABLE 1. PYROLYSIS PRODUCTS OF PENTAMETHYLENETETRAZOLE

| Temp °C/Press mm | IX | Yield % | X |
|---|---|---|---|
| 450/0·05 | 1 | | 1·7 |
| 500/0·05–0·10 | 18 | | 49 |
| 500/0·1–0·30 | 20·6 | | 20·6 |
| 550/0·05–0·30 | 30 | | 20·6 |
| 600/0·30 | 13·5 | | 42 |
| 675/0·30 | 8·4 | | 44·5 |

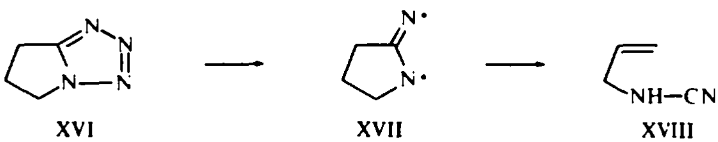
In a similar manner, tetramethylenetetrazole (XII) gave at 500°/0·01–0·10 mm 20% 3-butenylcyanamide (XIII) and 4·5% 1-cyanopyrrolidine (XIV). The latter may arise directly by nitrene ring contraction or by addition in XIII. None of the strained 1-cyano-2-methylazetidine (XV) was found. Gas chromatography revealed at least fourteen low boiling and poorly resolved components. The most abundant of these,

* At very low degrees of conversion, at 400–450°, and unidentified 'isocyanide' was formed. Hydrolysis gave an unidentified 'formamide' (Experimental).

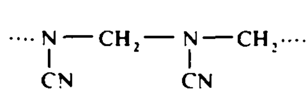



which had a strong piperidine smell and no UV spectrum was found by mass spectrometry at 13 eV to consist of a mixture of piperidine and tetrahydropyridine (*ca* 1 : 1·5). This result is analogous to the formation of phenyl radicals from phenyl azides[1b] and suggests that the first step in tetrazole pyrolysis may be isomerization to the azido-form.

Trimethylenetetrazole (XVI) gave at 500°/0·10 mm 1% product with IR absorption at 2130, 2224 and 3200 $cm^{-1}$, indicative of formation, in low yield, of the same type of products as above:




The main product was a polymer, the physical data of which (Experimental) are consistent with poly-N-cyanoformimine:




which could arise by elimination of ethylene from XVII or XVIII. Ethylene was indeed formed; it was trapped in molecular sieve at liquid nitrogen temperature and identified by its IR (gas) spectrum; yield *ca* 10%.

Further evidence for production of N-cyanoformimine was obtained by pyrolysis in the all-glass heated inlet system of the MS 9 mass spectrometer coupled with high resolution mass measurement of the products.

The mass spectrum of trimethylenetetrazole, obtained by cold, direct inlet, indicates loss of $N_2$ and $N_2$ + H, but the main fragment peak is *m/e* 54 for which the formula $C_2H_2N_2$ was confirmed by high resolution measurement. Using a heated inlet at 150° the compound decomposed completely: no 'parent peak' was observable; and the spectrum featured only ethylene (*m/e* 28), $C_2H_2N_2$ (*m/e* 54), and *m/e* 53 which is formed by loss of H from *m/e* 54, as indicated by a meta-stable peak. The compositions of these peaks were confirmed by high resolution, and the spectrum was also scanned

TABLE 2. 70eV MASS SPECTRUM OF TRIMETHYLENETETRAZOLE USING HEATED INLET

| m/e | Composition of peaks | | | | Relative intensity |
|---|---|---|---|---|---|
| 26 | CN | 10% | $C_2H_2$ | 90% | 24 |
| 27 | HCN | 25% | $C_2H_3$ | 75% | 28 |
| 28 | $N_2$ | 50·5% | $C_2H_4$ | 46·5% | 100 |
| | | | $CH_2N$ | 3·0% | |
| 53 | $C_2HN_2$ | 100% | | | 48 |
| 54 | $C_2H_2N_2$ | 100% | | | 38 |
| 55 | $C_2H_3N_2$ | 40% | $CC^{13}H_2N_2$ | 60% | 1·7 |

at medium resolution for accurate measurement of intensities. The results are given in Table 2, and indicate beyond doubt that the tetrazole decomposes into nitrogen, ethylene, and $C_2H_2N_2$.

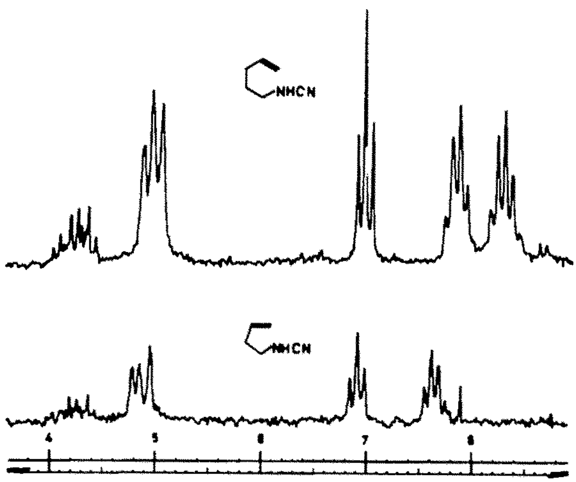



FIG. 1. 100 MHz NMR Spectra of 4-pentenylcyanamide and 3-butenylcyanamide in $CCl_4$

## EXPERIMENTAL

The pyrolysis technique has been described.[7] A packed quartz tube was used throughout. The recorded pressures are those of gases escaping the traps. The tetrazoles were distilled into the pyrolysis tube at 120–140°, and the pyrolysates were analysed on a 5' column of Carbowax 20M on Aeropak at 100°, programmed at 2°/min to 190°; carrier gas He at 60 ml/min (F & M instrument with thermal conductivity detection). Retention times: 1-cyano-2-methylpyrrolidine (X) 30 min, 1-cyanopiperidine (XI) 32 min, 4-pentenylcyanamide (IX) 58 min; 1-cyanopyrrolidine (XIV) 28 min, 3-butenylcyanamide (XIII) 48 min.

Mass spectra were recorded on an AEI MS 902 (high resolution) or MS 10C2 (low resolution) instrument.

*Identification.* The cyanamides IX and XIII were identified by IR, lack of UV; NMR and high resolution mass spectra and by comparison with the spectra of 1-hexene and pentylcyanamide.

The 100 MHz NMR spectra are shown in Fig IX. The vinylic pattern of XIII is almost identical with that of 1-hexene. For better comparison, pentylcyanamide was prepared from pentylamine and cyanogen bromide. Its NMR spectrum indicated the N–H resonance at 4·85 ppm, i.e. it will be hidden under the resonance lines of the vinylic protons in the spectra of IX and XIII. Pentylcyanamide shows the following unresolved peaks at 60 Mc: $\tau$ 7·0 ($CH_2(\alpha)$, broad triplet), 8·6 ($CH_2$ ($\beta, \gamma, \delta$)), 9·1 ($CH_3$).

Assuming $J_{\alpha\beta} = J_{\beta\gamma} = J_{\gamma\delta} = 7$ cs in IX and XIII, the spectra are readily interpreted as follows:

*4-Pentenylcyanamide*: (IX). $\tau$ 4·3 (centre, vinylic H), 4·97 (centre, vinylic H plus NH), 6·98 (t, $CH_2$ ($\alpha$)), 7·84 (q, $CH_2$ ($\gamma$)), 8·27 (quintet, $CH_2$ ($\beta$)).

*3-Butenylcyanamide*: (XIII). $\tau$ 4·3 and 4·9 (vinylic H + NH), 6·90 (t, $CH_2$ ($\alpha$)), 7·62 (q, $CH_2$ ($\beta$)).

*IR spectra*

*4-Pentenylcyanamide* (IX; $CCl_4$, $cm^{-1}$): 3220 (broad, NH), 3070 (=C—H), 2930 ($CH_2$), 2227 (vs, CN), 1640 (C=C), 1470 ($CH_2$), 1170, 925 (=$CH_2$), and 1850 (=$CH_2$, 2 $\nu$). Dilution caused a new, sharp band at 3400 $cm^{-1}$ to appear (NH).

*3-Butenylcyanamide* (XIII) identical beyond distinction with the above.

*Pentylcyanamide.* 3200 (broad), 3370 (w, NH), 2223 (vvs, CN), 1170, 735 ($\nu_s$ CNC). No UV spectrum.

*Mass spectra*

The base peaks are due to loss of 40 mass units (NCN) from the molecular ions.

*1-Cyanopyrrolidine* (XIV) was identical with a specimen prepared from pyrrolidine and cyanogen bromide. The structure of 1-cyano-2-methylpyrrolidine (X) follows from spectral comparison:

*NMR spectra*

*1-Cyanopyrrolidine* (XIV): $\tau$ 6·60 (t, $J \cong 7$ cs, $CH_2$ ($\alpha$), 4H), 8·07 (apparently two overlapping triplets with identical shift, $J \cong 8$ and $J \cong 4$ cs, 4H).

*1-Cyano-2-methylpyrrolidine* (X): $\tau$ 6·47 (q, $J \cong 6$ cs, H (2), 1H), 6·58 (t, $J \cong 6$ cs, H (5), 2H), 8·1 (m, 4H), 8·70 (d, $J \cong 6$ cs, $CH_3$(2)).

*1-Cyanopiperidine* (XI): $\tau$ 6·8 (m, 4H), 8·35 (m, 6H). None of these compounds exchanged with deuterium oxide.

*IR spectra*

Compound X ($CCl_4$ or liq. film, $cm^{-1}$) 2210; spectrum almost identical with that of XIV except for a new band at 1375 $cm^{-1}$ ($CH_3$).

UV spectra: no absorption above 210 mμ.

*Mass spectra*

Compound XIV: $M^+$ 96, 100%, [M-1] 50%, [M-27] 35%, [M—H—NCN, *m/e* 55] 26%. Compound X: $M^+$ 110, 49% [M-1] 15%, [M-15] 100%, [M-15-27, m*] 20%, [M—H—NCN, *m/e* 69] 10. Compound XI: $M^+$ 110, 100%, [M-1] 82%, [M—H—NCN, *m/e* 69] 70%.

*Preparations and pyrolyses*

(i) *Pentylcyanamide* was prepared by a variation of a known method:[8] cyanogen bromide (5·3 g; 0·05 mole) in ether was added with stirring to pentylamine (8·7 g; 0·10 mole) in ether (100 ml) at 0°. The mixture was stirred at 22° for 30 min and filtered. The ether was removed *in vacuo* and the residue distilled at 180° in a high vaccum to yield pentylcyanamide (5·0 g; 89%). Spectral data are presented in the Identification section. The *compound* crystallised to a white solid, m.p. 47–49°, after several months at − 10°. This compound showed no CN-absorption in the IR, distilled with difficulty and partial decomposition at 260° in high vacuum, and was, according to the mass spectrum, tripentylmelamine ($M^+$ 336: MS 902, direct inlet).

(ii) *1-Cyanopyrrolidine* (IXV) and *1-cyanopiperidine* (XI) were prepared[9] as in (i). Physical data are given in the Identification section.

(iii) *Pentamethylenetetrazole* (VIII; Aldrich Chemical Co.) (a) Pyrolysis conditions are given in Table 1. The reaction is synthetically useful for the preparation of X which distils from the less volatile IX at 80°/$10^{-3}$ mm. The sample of X so obtained was gas chromatographically pure. The reaction can be run on a 1–10 g scale in the present apparatus.[7]

(b) Compound VIII (1·5 g) was pyrolysed at 400°/0·005 mm in the course of 60 min. Extraction of the product with ether left the unreacted starting material behind and gave a trace of an 'isocyanide', $\nu_{max}$ 2100 $cm^{-1}$.

(c) Compound VIII (1·5 g) at 450°/0·05 mm in 60 min gave 0·357 g of a liquid containing X (1·7%), IX (1%), and the "isocyanide" (*ca* 3%), retention time 33 min. The "isocyanide" was stable for at least 24 hr at room temp (neat or in $CCl_4$), had no distinct UV spectrum, and had a pungent but not typical isocyanide smell. A distinct mass spectrum could not be obtained either with heated or direct inlet; apparently the compound polymerised, giving peaks up to *m/e* 288. The crude product had $\nu_{max}$ 2107 ($CCl_4$) or 2125 (liq film) $cm^{-1}$. After gas chromatography it had $\nu_{max}$ 2135 ($CCl_4$), and also 915 (C=C) and possibly a very weak band at 1830 $cm^{-1}$ (2 $\nu$ C=C).

(d) The crude "isocyanide" from (b) was treated with water and allowed to stand at room temp until the water had evaporated, leaving a white solid which sublimed in needles at 105–20°. The remainder melted partly at 120°. The needles melted at 145–50° and crystallised from chloroform as colourless needles, m.p.

150–152°; $\nu_{max}$ (CHCl$_3$) 1640 vvs (several narrow bands), 3200–3300 (NH, bonded) 3430 cm$^{-1}$ (NH, free). The IR spectrum showed some similarities with that of N-formamidovalerimine, Bu-CH=N—NHCHO, prepared from valeraldehyde and formhydrazide. The mass spectrum (MS 902, direct inlet) showed M$^+$ 128 = 110 + 18, which corresponds to addition of water to an isocyanide isomeric with IX and X (neither IX or X added water under the described conditions). Apparent formation of isocyanides by distillation of cyanamides has been reported.[5]

N-Formamidopiperidine and N-formamido-2,5-dimethylpyrrolidine have m.p. 74–76° and 114·5–117° respectively, and the corresponding N- isocyanides have $\nu_{max}$ 2088–2092 cm$^{-1}$ (Ref 10). 2,8-Diazacyclo-octanone[11] has m.p. 270–272°. The structures of the "isocyanide" and "formamide" *in casu* remain uncertain. The retention time of the "isocyanide" is inconsistent with N-isocyano-4-pentenylamine, and $\nu_{max}$ is inconsistent with N-isocyano-2-methylpyrrolidine. The NMR spectrum of the "formamide" was indistinct, showing broad, unresolved bands at τ 6·6 and 8·4, and a sharp signal (CH$_3$) at 8·2.

(iv) *Tetramethylenetetrazole* (XII) was prepared[12] by reduction of tetrazolo[1.5-*a*]pyridine. Conditions of pyrolysis are given in the text.

(v) *Trimethylenetetrazole* (XVI) was prepared by Boyer and Miller[13] from 2-mercaptopyrrolidine by conversion to the thioether and then displacement by hydrazoic acid. These workers obtained a 30% yield of the free thioether by extraction of the neutralised soln of the hydriodide with ether. In the present work a quantitative yield was obtained by extraction from a strongly alkaline soln. The thioether was treated with hydrazoic acid (2 moles) at 40° (stoppered) for 8 hr, and then under reflux for 5 hr. The soln was evaporated and the product recrystallised from xylene to give the pure tetrazole, m.p. 109–110° (4·32 g from 8·15 g thioether; 55·8% yield). From the filtrate was obtained a second crop of 0·41 g (5·25%), m.p. 106° from chloroform/light petroleum. Thus the reported yield[13] was tripled, and the reaction time reduced to one third.

Pyrolysis of XVI at 500°/0·10 mm gave 1% of a liquid with IR absorption at 2130, 2224 and 3200 cm$^{-1}$. The main product (74%) was a hard, transparent, insoluble polymer with IR absorption at 2215 (CN, broad, strong), 1470 (C=N), 1330 ($\nu_s$NCN), 1425, 1160, 1140, 1000 ($\nu_s$CNC), 950, 800, 720 ($\nu_s$CNC) cm$^{-1}$ (*cf* Ref 5). Elemental analysis gave the approximate formula (CHN)$_x$. (Found: C, 43·29; H, 4·07; N, 49·92. Calc. for CHN: C, 44·44; H, 3·73; N, 51·83%; Calc. for $C_4H_6N_4$: C, 43·6; H, 5·45; N, 50·8%; Calc. for $C_4H_6N_2$: C, 58·51; H, 7·37; N, 34·12%). No mass spectrum could be obtained on direct inlet. The compound darkened above 200° on slow heating, not melting at 360°, and exploded on fast heating to 200°. The fumes smelt strongly of aliphatic amine. The compound was not identical with any of the polymers of hydrogen cyanide.[6] The data are consistent with a polymer of N-cyanoformimine.

*Acknowledgements*—I thank Professor W. D. Crow for stimulating discussions, Dr. J. K. McLeod for the high resolution mass spectra, and the A.N.U. for the award of a Postgraduate Scholarship.

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