PYROLYSIS OF 1(H)-TRIAZOLOARENES

RING CONTRACTION TO 5-RING NITRILES, AND CN-GROUP MIGRATION

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Abstract—Vapour phase pyrolysis of 1(H)-benzotriazoles, naphthotriazoles and pyridotriazoles results in N_2-loss and formation of cyanocyclopentadienes, cyanoindenes and cyanopyrroles respectively. The mechanism of the ring contraction is discussed in terms of a Wolff rearrangement of the 1,3-biradicals formed initially. The CN group in the products is shown to undergo sigmatropic shifts at elevated temperatures; thus 9,10-phenanthrotriazole gives 9-cyanofluorene, which is converted to the 1-cyanoisomer at 1000°. Similar CN migrations, mainly to the *ortho* positions are observed in benzyl cyanide and diphenylacetonitrile. Methylcyanocyclopentadienes undergo symmetry—allowed H_2-loss and ring expansion to benzonitriles above 700°.

INTRODUCTION

IN PRELIMINARY communications we have reported contraction of aromatic 6π-systems in the vapour phase pyrolysis of phenylazides[1] and triazoloarenes.[2,3] The present paper gives full details of the latter work, and considers the mechanisms in terms of nitrene and biradical intermediates. Much of the interest in nitrene[4] and


$$X = CH \text{ or } N$$

carbene[5] chemistry has been centred on the spin state of the species—a problem which is inherently difficult to study. The ambiguities introduced by working in the condensed phase have frequently made interpretation of nitrene work difficult, and for this among other reasons we have confined our work to low pressure gas phase experiments.

The aromatic nitrenes appear to differ from the carbenes and the aliphatic nitrenes[6,7] in that they have not so far been reported to insert in Ar-H bonds, or add to multiple bonds, except in the rather special intramolecular cases of azepine formation[8-10] and carbazole,[11] indoline[12] or indole[13] formation. In all cases the reacting bond is held in close proximity to the nitrene centre at the moment of generation, and is often conjugated with it. The formation of carbazoles can for example be regarded as an intramolecular electrocyclic reaction (4 + 2), followed by a 1,5-H shift. The more usual products from condensed phase reactions of aromatic nitrenes are anilines, azobenzenes and polymeric tars—typical radical products which led to the

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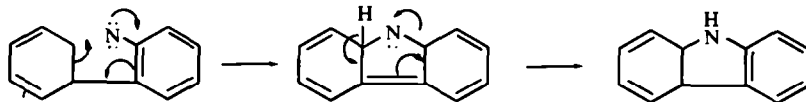
early conclusion that the triplet state was involved.[14] Present ideas on the spin states of aromatic nitrenes are still far from clear; intermolecular insertion in aliphatic C-H bonds[15] appears to be a reaction of the triplet state, whereas intramolecular insertion[12] may be, at least in part, a reaction of the singlet state.* In the presence of suitable nucleophiles phenylnitrene undergoes intramolecular insertion
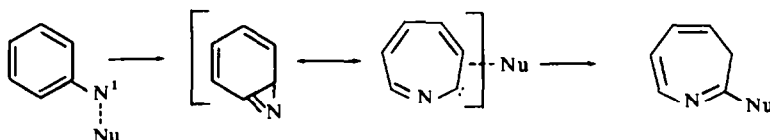
to give azepines,[8-10] a reaction which can be ascribed to stabilization of the singlet state[16] by interaction with the nucleophiles.[10, 17] A similar type of singlet stabilization by overlap with a π-system, could be involved in the formation of carbazole, a neighbouring group effect.

In recent studies of gas-phase nitrene reactions we[1-3, 18-20] and others[21] have shown that a variety of isomerizations can be observed on the C_6H_5N (Chart 1) and related energy surfaces, the exact nature of the bonding in the intermediates being as yet unknown. Under relatively mild conditions[1] only the usual[14] dimerization and
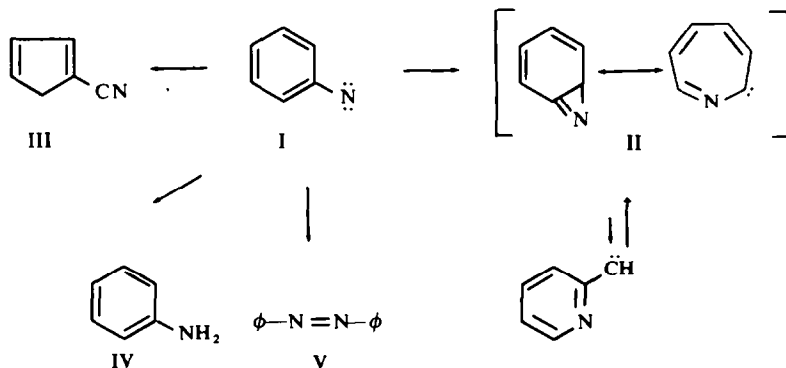

H-abstraction products (V and IV) were obtained, arising presumably[14, 16] from the triplet nitrene.

In order to gain further insight into the C_6H_5N transformations we pyrolysed a number of 1(H)-benzotriazoles (VI) isomeric with the phenyl azides, in the expectation

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* "Insertion" refers rather to the nature of the product than to the mechanism, which, in the case of the triplet, appears[15] to be a two step radical process. Since the singlet is first generated, it is logical that intramolecular insertion should compete with decay to the triplet state. The evidence, relying on retention in an asymmetric reaction centre,[12] could however be interpreted as H abstraction by the triplet, with rapid recombination in the solvent cage competing with radical racemization at the abstraction site.

that these would give rise to 1,3-biradicals (VII) isomeric with the phenylnitrenes (I). The two species I and VII are formally related by a simple 1,3H-shift.

VI   VII
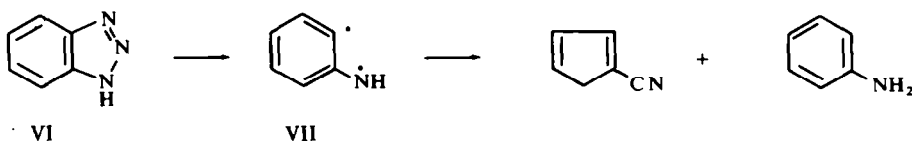
Pyrolysis of 1(H)-*benzotriazoles*

Pyrolysis of benzotriazole (VI) at 600–900° under a variety of conditions (Table 1) gave 1-cyanocyclopentadiene (III)* in up to 99% yield. By contrast, phenyl azide gives no more than 50% yield[21] in an almost explosive reaction with many other products.[1, 21, 22] Formation of aniline from the 1,3-biradical VII is consistent with the observation[23] that photolysis of benzotriazole gives 1,3-biradicals which abstract H from the solvent. In the related case of 3,3-dimethyl-3(H)-indazole similar biradical formation was implicated by ESR detection of a triplet biradical arising from reaction of the first formed species with an alkene.[24]

Attempts to demonstrate the spin state of the reactive intermediate by the use of carrier gas (Table 1) were in general of dubious value. Inert carrier gas (Ar, N_2, CO_2) in general produced an increase in yield of III coupled with a decrease in aniline yield, but the effects were not large. The increase in III is to be expected on the grounds of its more rapid removal from the furnace, and the lower frequency of collisions suitable for H-abstraction would be expected to lower aniline yields. The use of radical trap carriers such as oxygen and nitric oxide resulted in lower yields due to reaction with products; this was confirmed in the latter case by exposing normal reaction products to NO. The resultant dark red mixture gave a GLC trace indistinguishable from that of the products when this gas was used as a carrier, with the notable exception that benzonitrile was absent. The heavy-atom effect, successfully applied in solution nitrene chemistry,[25] cannot be so readily applied in high temperature gas phase work. In the present case the use of methylene bromide vapour as carrier gas results in formation of HBr, with consequent invalidation of the results. An alternative approach to the problem was attempted by incorporating the heavy atom in the triazole itself. 5(6)-Chlorobenzotriazole (VIIIa; see Table 2 and Chart 2) was pyrolysed, but even under the mildest effective conditions chlorine loss was observed (20% in the ring contraction products).

Pyrolysis of substituted benzotriazoles (VIIIa–e and IXe) gave the corresponding cyclopentadienes (X and XI) as outlined in Table 2 and Chart 2. The formation of two biradicals, and hence two anilines, is to be expected from the tautomerism in the parent triazoles. It will be noted that, except under more vigorous conditions, only *one*† cyanocyclopentadiene (X or XI) results in each case.

* The structures of the cyanocyclopentadienes present a problem in its own right, and will be discussed in a succeeding paper. Their formation from benzotriazole pyrolysis constitutes a necessary introduction to the problem and is thus presented first.

† The cyanocyclopentadienes (X–XI), unlike the simple alkylcyclopentadienes,[26] undergo very facile H-shifts—too readily to permit GLC isolation of the tautomers. Thus there are effectively only *three* methylcyanocyclopentadienes (5,5-, 1,2- and 1,3-substituted). Compositions of the tautomeric mixtures were determined by NMR spectroscopy. The H-shifts were readily demonstrated by pyrolysis of benzotriazole-1-d_1, which gave III in which the deuterium was uniformly scrambled throughout the ring.

TABLE 1. EFFECT OF CARRIER GAS ON PYROLYSIS[a] OF BENZOTRIAZOLE

Carrier gas	p(mm)	Cyanocyclopentadiene (%)	Aniline (%)	Benzonitrile (%)
—	0·15	92	2·1	—
—[b]	0·15	96	2·0	—
Ar	0·5	99	1·0	—
Ar	5·0	87[c]	0·5	—
air[d]	0·5	60	0·5	0·2
O$_2$	0·15	58	1·6	1·0
O$_2$	0·25	37	trace	2·0
N$_2$	0·5	95	1·8	—
CO$_2^d$	0·5	90	1·3	—
CO$_2^d$	4·0	86[c]	0·4	—
HCN	0·5[e]	99	1·0	—
NO	0·1[f]	(20)[g]	trace[g]	trace[h]
CH$_2$Br$_2$ (16 g)[i]	0·05–0·1	(35–50)	0	5

[a] 0·5 g pyrolysed at 760° in a packed tube, products trapped in three liquid N$_2$ traps, unless otherwise indicated.
[b] Unpacked tube.
[c] Trapping incomplete due to high gas flow.
[d] Trapping in CO$_2$/acetone.
[e] ~0·1 mm sample pressure.
[f] ~0·1 mm NO, maximum recorded pressure 0·1 mm.
[g] Decreases rapidly due to reaction with NO.
[h] Other products formed.
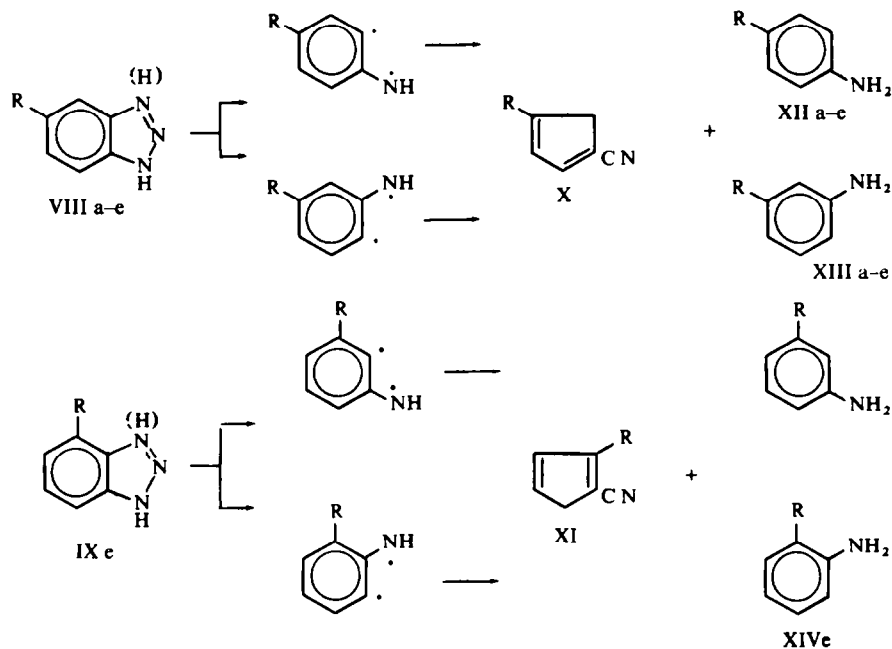[i] HBr evolved, KOH trap inserted; black solids formed.

CHART 2

TABLE 2

Compound	R	T°C	Pmm	% Conversion	III	X	XI	XII	XIII	XIV	ØCN
VIIIa	Cl	550	0·1	50	18	72	0	0	0		
VIIIb	CN	600	10^{-3}	46		73	0	0	0		
VIIIc	CF$_3$	500	10^{-2}	18		75^b					
VIIId	F	600	0·1	100		40	trace	5	5		
Xd	F	800	10^{-3}			6:1					
XId	F	800	10^{-3}			6:1					
VIIIe	Me	500	0·02	2		80	0	trace	trace		
VIIIe	Me	600	0·05	70		56	11	~0·5	~0·5		~1
VIIIe	Me	650	0·10	100		70	20	trace	trace	.	7
VIIIe	Me	700	0·05	100		14	7	0	0		70
IXe	Me	500	0·01	5		0	80		0·1	0·1	
IXe	Me	700	0·05	100		14	7		0	0	70
Xe	Me	655	10^{-4}			72	12				trace
Xe	Me	780	10^{-2}		trace	2	1				75
XIe	Me	655	10^{-4}			40	40				trace
XIe	Me	780	10^{-2}		trace	2	1				75

^{a} Corrected for recovered starting material.

^{b} Not examined by VPC (containing HF).

Although the structures of some of the cyanocyclopentadienes presented a problem, the coarse features of the mechanism (*vide infra*) can be based on known cases. Thus cyanobenzotriazole (VIIIb) gave the fully conjugated tautomer Xb. On regeneration from the anion, this gave a 10:1 mixture of Xb and the cross conjugated isomer XV, in full agreement with the findings of Webster.[27]
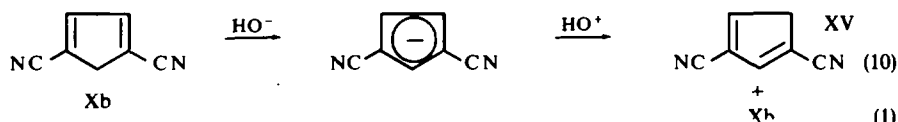
Reference to Table 2 shows that at higher temperatures group migration occurs in the cyanocyclopentadienes, a topic which is discussed more fully below. For this reason the degree of conversion in triazole pyrolysis was deliberately kept low, so as not to obscure the structural findings.

Pyrolysis of annelated triazoles and triazolohetarenes

Since the ring contraction of the benzotriazoles appeared to constitute a convenient synthesis of cyclopentadienes, we were prompted to extend the reaction into the area of larger molecules and more particularly into the heterocyclic series. In most cases the reaction followed the expected course in good yield (Tables 3, 4), and the results are adequately summarized in Chart 3.

The product from pyrolysis of 1,2-naphthotriazole (XVI) was readily identified with the known 3-cyanoindene,[28] while that from 2,3-naphthotriazole (XVIII) could be readily assigned as 2-cyanoindene from spectroscopic data. No naphthylamines were detected in pyrolysis of these two triazoles. The isomeric [1·8-*de*]naphthotriazine

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TABLE 3. Pyrolysis of annelated triazoles and cyanoindenes

| Compound	T°/P(mm)	Products (relative peak areas by GLC)					
		Indene	XIX	XVII	4(7)-CN-indene	5(6)-CN-indene	Total Yield %
XVI	600/0·025		1·0	5·9			100
	740/0·08		1·68	1·0	0·04	trace	96
	800/0·05		1·0	1·73			85
	1000/0·25	0·5	1·3	1·0	1·8	1·6	40
XVIII	650/0·2		6·33	1			a
	740/0·01		1·67	1	0·07	trace	a
	800/0·02		2·02	1	0·24	0·25	92
	1000/0·25	0·5	1·3	1	1·8	1·6	40
XVII	800/0·02		1	1·5			100
	1000/0·25	1·5	1·3	1	1·8	1·6	100
XIX	1000/0·25	0·5	1·3	1	1·8	1·6	100
XXI	550/0·005	XXII (92%)					
XXII	800°/0·01	XXII (93%), fluorene (4%), HCN					
	1000/0·08	fluorene, XXII, 1-cyanofluorene, HCN (30%)					

XX although it possesses the necessary thermal leaving group, is structurally unsuited for ring contraction, and afforded only 1-naphthylamine.

Pyrolysis of 2,3-fluorenotriazole (XXIII) gave a mixture of 2- and 3-amino-fluorenes together with a nitrile to which was assigned the structure 2-cyano-1,4-dihydrobenz[a]pentalene XXIV, largely on spectroscopic evidence (Experimental). The mass spectrum of the nitrile XXIV showed a pronounced $[M-2]^+$ ion—formally the 2-cyanobenz[a]pentalene radical cation. Similar reactions[29] are seen in the mass spectra of 2,-3- and 4 aminofluorenes (loss of 2H + HCN) and of the fluorenotriazole XXIII (loss of N_2 + HCN), leading to m/e 152 (formally the benz[a]pentalene radical cation).

In the heterocyclic series, the triazolopyridines XXVI and XXVIII were smoothly converted to the cyanopyrroles XXVII and XXIX, which in turn were interconvertible at higher temperatures. Triazolo[4,5-d]pyrimidine ("8-azapurine") XXX, however, did not give the expected 4(5)-cyanoimidazole XXXI, the only identifiable products being HCN and NH_3. Apparently the pyrimidine ring fragments under the pyrolysis

TABLE 4. Pyrolysis of pyridotriazoles and cyanopyrroles

Compound	T°/Pmm	Product (relative peak areas by GLC)		Total Yield %
		XXVII	XXIX	
XXVI	800/0·05	1	0	99·5
	800/0·04	2·3	1	97
XXVIII	600/0·04	0	1	97
	800/0·05	1	1	95
XXVII	800/0·01	2	1	98
XXIX	800/0·01	1	2	98

CHART 3
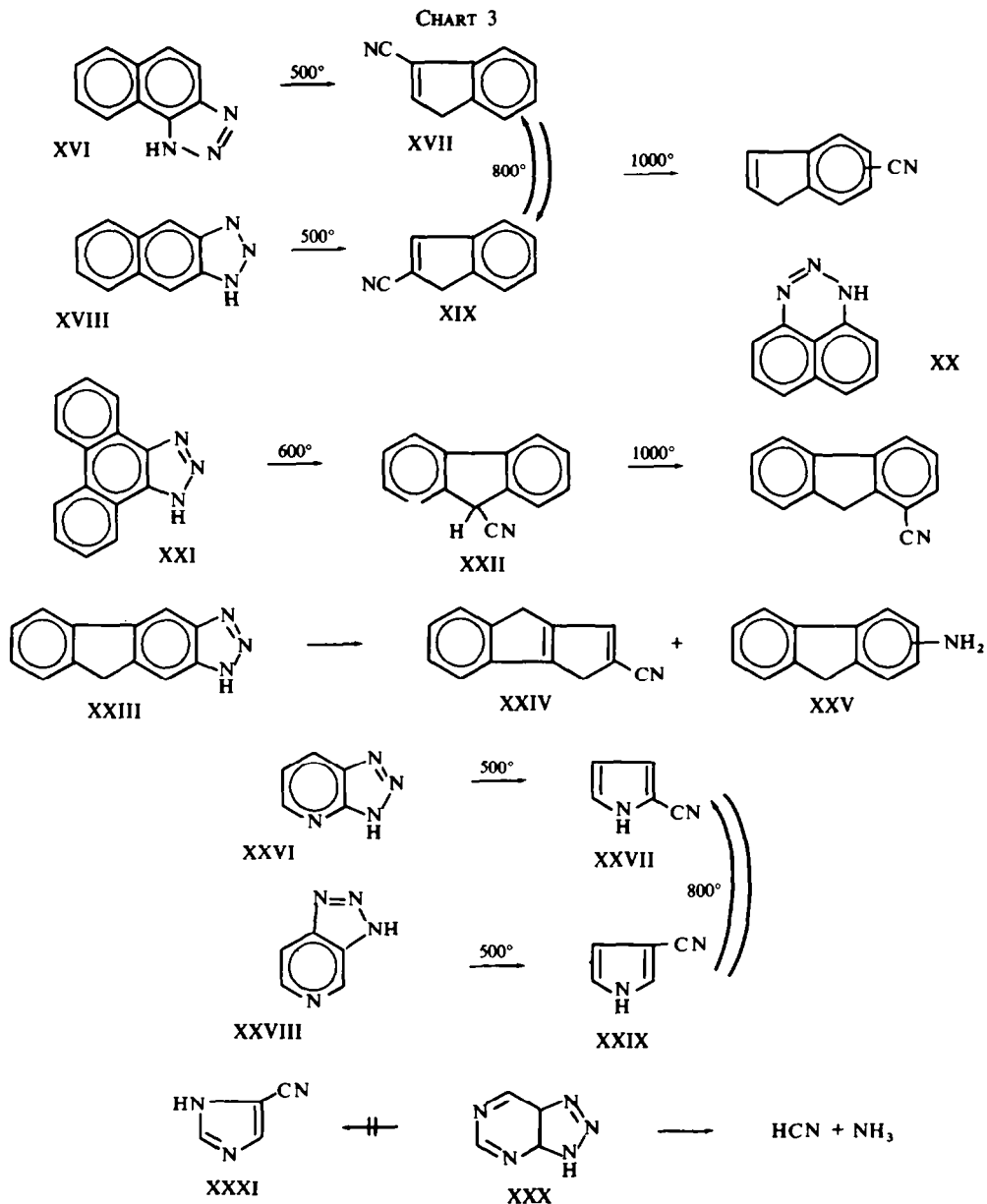
conditions; other workers[30, 31] have encountered pyrimidine ring opening in solution chemistry of XXX.

CN-*Group migrations and ring expansions*

The problem of CN migration was first encountered in the cyanocyclopentadienes. Quite apart from the facile H-shifts which equilibrate isomers, it was found that

CN-shifts occurred at higher temperatures, and the situation with the methyl-cyanocyclopentadienes is summarized in Chart 4. Similar shifts were observed in the fluorocyanocyclopentadienes, the cyanoindenes and the cyanopyrroles. Sigmatropic shifts of H and CH$_3$ in cyclopentadienes have been reported previously[32] and CN-shifts in cycloheptatrienes are known.[33] In the present case the migrations may involve radical pairs, ion pairs, or be true sigmatropic shifts. While σ-bonded groups normally undergo 1,5 thermal shifts[34] the CN group may undergo any shift through p-orbital participation.[35]

A possible mechanism for the migration is already inherent in the intermediate XXXIII previously proposed[21, 22] for the ring contraction of phenylnitrene, and has an analogy in the recently reported[36] degenerate rearrangement of the heptamethyl-benzononium ion. The reversal of the sequence I → III is a possibility we plan to investigate.

A somewhat different type of CN migration is observed in the benzyl cyanides. In the cyanoindenes the normal migrations within the cyclopentadiene system, analogous to those in Chart 4, are observed at 800°, but at higher temperatures migration into the benzenoid system is observed. This reaction (Chart 3) is accompanied by loss of the CN group and formation of indene, and probably involves free radicals. Since 9-cyanofluorene (XXII) gives only 1-cyanofluorene, a fairly tight radical pair is

CHART 4
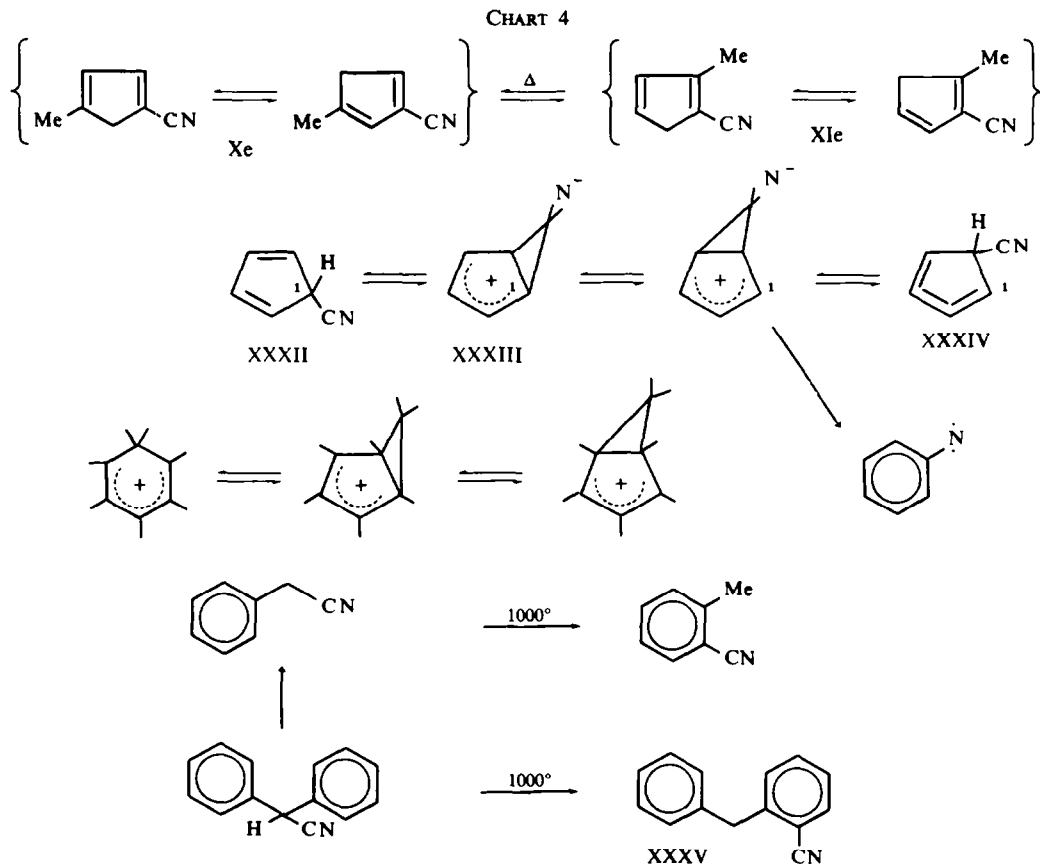
probably involved.* Model experimental systems were employed in benzyl cyanide and diphenylacetonitrile. The former gave, at 1000°, predominantly o-tolunitrile, with low yields of m- and p-tolunitrile, benzene, toluene and benzonitrile. The latter gave 2-benzylbenzonitrile (XXXV), benzyl cyanide, o-tolunitrile, benzonitrile, benzene, biphenyl and fluorene.

In all cases where the product of ring contraction was a methylcyanocyclopenta-diene (Xe, XIe), it was found that pyrolysis of the benzotriazole (VIIIe, IXe) at temperatures greater than 600° gave increasing amounts of benzonitrile. The reaction was evidently clean, and not likely to involve radicals. Pyrolysis of either Xe or XIe at higher temperatures established that these products readily eliminated H_2 to form benzonitrile. A similar conversion of methylindene to naphthalene has been reported.[37]

The stage at which H_2-loss occurs is a matter for conjecture; a symmetry-allowed elimination from an intermediate 1-cyano-1,4-cyclopentadiene (XXXVI), while substantiated by the literature,† suffers from the disadvantage that the formation of the precursor is difficult to rationalize. The mechanism is more likely to involve the cyanofulvene XXXVIII, whether formed by a concerted or stepwise process. Measurement of the mass spectra of Xe and XIe using a metal inlet system shows a dramatic rise in the abundance of m/e 78 (benzene) with time, due to catalysed loss of HCN. A
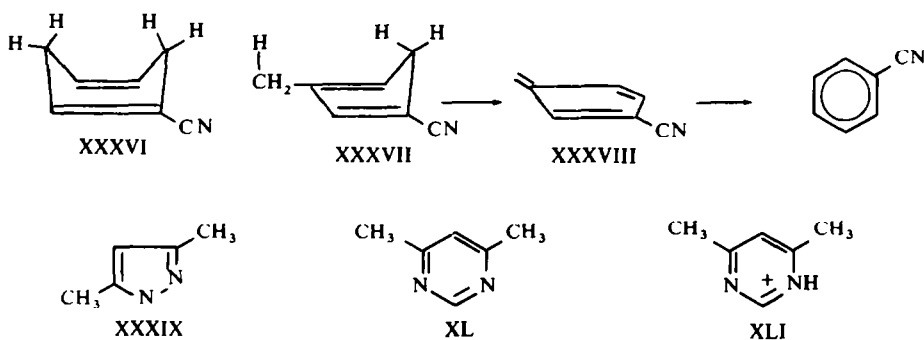

similar thermal ring expansion is seen in the conversion[22] of XXXIX to XL, and has analogies in the mass spectral ring expansions[41] of the benzyl cation and the $(M-1)^+$ ions derived from N-methylpyrrole and N-methylindole. Prominent (M-1) peaks observed in the mass spectra of Xe, XIe and XXXIX (Experimental) are possibly due to protonated ring-expanded species (e.g. XLI).

Mechanism of the ring contraction

The formation of m- and p-substituted anilines from the benzotriazoles VIIIa–e (and o- and m-substituted anilines from IXe) clearly proves the existence of *both* the

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* It is reasonable to assume that the transition between the dipolar transition state XXXIII and a "tight radical pair" is gradual with increasing energy, i.e. with increasing separation of the CN moiety from the hydrocarbon system.

† Attempts to prepare XXXVI above 150° are reported[39] to give only benzonitrile. It has been reported[40] as a product (in low yield) from pyrolysis of 3-diethylamino-4-cyanocyclohexene hydrochloride.
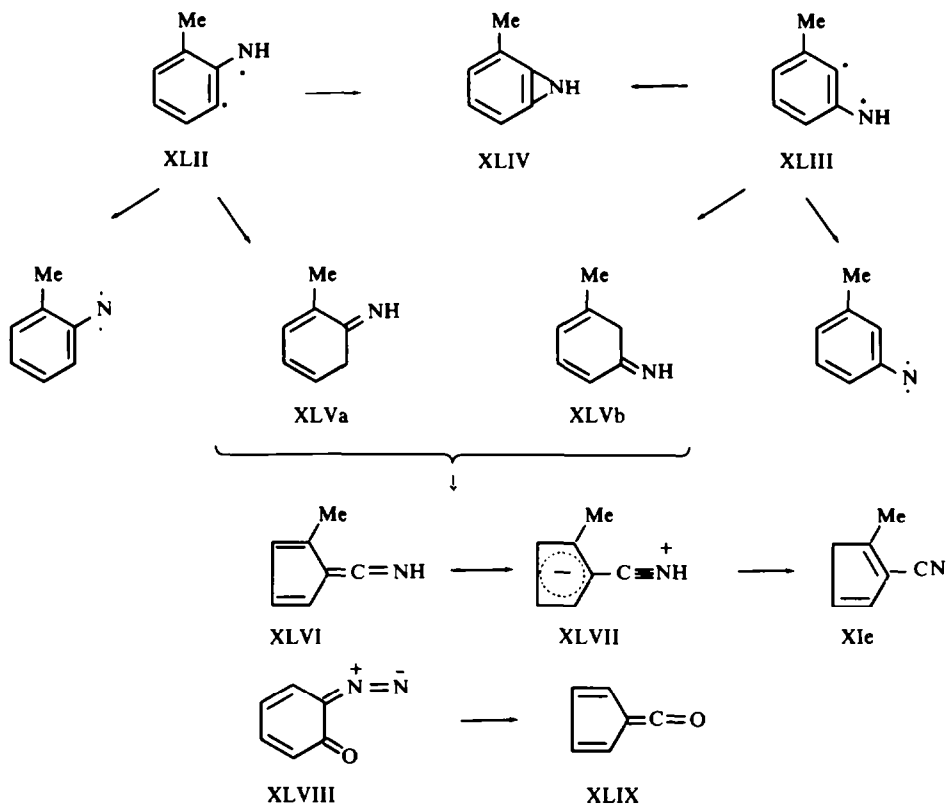
biradicals XLII and XLIII. Spin conservation requires that these be initially in the singlet state. There are three mechanistic possibilities which might be considered :*

(1) H-shift to the corresponding o- and m-tolylnitrenes
(2) Electronic reorganization to the iminocarbenes XLVa and XLVb
(3) Formation of the azirine XLIV.

We have previously shown[1] that nitrenes give azobenzenes under mild pyrolysis conditions, that o-tolylnitrene behaves this way under more violent conditions, and that m-tolylnitrene gives mixtures of Xe and XIe under violent conditions. The pyrolysis of benzotriazoles has no points in similarity with such reactions, and we therefore feel confident in rejecting the possibility[42] of H-shift in XLII and XLIII.

The intermediacy of the azirine XLIV appears to be most unlikely, but cannot be definitely excluded without more detailed knowledge of the exact mechanism of its collapse to products. Any mechanism which involved H-shift in the azirine ring system, alone or coupled with ring expansion (e.g. to the system II) would produce a mixture of cyanocyclopentadienes. This would be contrary to the experimental results. The most suitable rationalization of the results would be in terms of a Wolff rearrangement[5]

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* We recognize that all these structures, and others, are probably only contributors to a total, fluxional, structure of the intermediate under the conditions of high vibrational energy involved. Our purpose is to consider the type of structure which most closely corresponds to the relevant saddle point on the energy surface. In this connection the distinction between the "structures" is still relevant.

of the iminocarbenes XLV (XLVI → XLVII → XIe). The *o*-diazooxides XLVIII undergo a similar photolytic reaction[43] to give ketenes XLIX; in one such case the reaction has been reported to go thermally.[44]

The iminocarbenes XLV can be written in a number of ways, all of which merely express the same idea—that the original carbon radical site carries a p-orbital which will permit some degree of overlap with adjacent atoms. On this basis we would explain[3] the specificity of the ring contraction as arising from orbital overlap in a transition state such as L, in which only *one* of the bridgehead C-atoms is capable of supporting such overlap. Such a postulate is adequate to explain the observed facts, but raises yet another point for consideration. This concerns the ring contraction of triazolo[4,5-*b*]pyridine to 2-cyanopyrrole. The intermediate in this case would be L, and carries available orbitals on both C and N atoms in the three-membered ring. Thus it may be possible that the first formed product would be 1-cyanopyrrole, an as yet unknown compound which may be expected to readily rearrange to the 2-cyano-pyrrole under mild conditions, or to a mixture with 3-cyanopyrrole under more drastic conditions. These are exactly the results we have observed, although they can be satisfactorily explained on the basis of thermal interconversion of the isomers.

L   LI

Although the reactions reported here have been solely concerned with thermal activation, there are a number of parallels observed in the photochemical field. Thus the irradiation of pyridine-N-oxide has been reported to result in a variety of reactions, including[45] ring contraction to 2-formylpyrrole, and it is proposed that this proceeds through an oxazirane intermediate. Subsequent evidence[46] suggests that the N-formylpyrrole may be an intermediate in this reaction also (cf. LI). Our results do not suggest an azirine intermediate, since this could result in a mixture of products, contrary to what is observed. We thus prefer to propose a 2,6-bonded intermediate; it is quite possible that this difference merely reflects a difference in the opportunities for energy dissipation by the intermediates. Thus in *gas phase* photolysis[47] of pyridine-N-oxide it is reported that oxygen loss occurs; there is no solvent present in this case to assist in collisional deactivation processes.

The difference between gas phase and condensed phase experiments has interesting implications as far as the Wolff Rearrangement itself is concerned, and tends to support the idea that small differences in the energy levels of the intermediates may have large effects upon the mechanism. Franzen[48] has examined the mechanism of this rearrangement by isotopic labelling techniques, and has concluded that the oxiirene intermediate is not involved in solution decomposition. More recently, Csizmadia, Font and Strausz[49] have carried out a similar analysis on the gas phase

Wolff Rearrangement of simple ketocarbenes, and report in this case that the cyclic oxiirene *is* definitely involved. In the work reported here, we tentatively conclude that the azirene intermediate XLIV is not involved as a discreet stage in the mechanism.

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-pressures 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′ × ¼″), using He as the carrier gas. In special cases other columns were used: Column B, SE30 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 90°, programmed at 2°/min to 240°, with injection port and block at 250°. Identification was checked as far as possible by comparison of retention times with authentic specimens.

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 instruments; all abundances stated are % base peak. Microanalyses were by the Australian Microanalytical Service at the University of Melbourne.

Preparation of compounds. Benzotriazoles were prepared by diazotization of the appropriate diamine in AcOH. The method used was adapted from that of Damschroder and Paterson.[50]

(1) 9,10-*Phenanthrotriazole* (XXI) was prepared in 10% yield by Epsztein;[51] the method below was found to be more efficient.

9,10-Diaminophenanthrene dihydrochloride (5·0 g) in glacial AcOH (70 ml) was cooled to −10° with stirring, and gradual addition of water (20 ml) to prevent freezing. Powdered $NaNO_2$ (1·70 g) was added all at once, the cooling bath was removed and the soln was allowed to warm to room temp. The product was precipitated with vigorous evolution of nitric oxide. The dried solid contained some 18% phenanthroquinone, which was sublimed out at 180°/0·005 mm; the triazole sublimed at 200°/0·005 mm as a colourless solid m.p. 315–316°, leaving a residue (13%) presumed to be phenanthrazine. The molecular ion occurred at *m/e* 219, as required.

(2) *Fluoreno*[3,2-a]*triazole* (XXIII). This compound was available from diazotization of 2,3-diaminofluorene. 2-Amino-3-nitrofluorene was prepared in 72% yield by the following modification of the method of Diels.[52] 2-Aminofluorene (30 g, 0·166 mole) was added in portions to Ac_2O (300 ml) with stirring, and acetylation was completed by heating on the waterbath for 30 min. The mixture was stirred and cooled and nitrated at 10–15° by the addition over 30 min of HNO_3 (18·6 ml, *d* = 1·42). The product was filtered, washed with 50% AcOH, then water, and dried at 110°, giving 40 g (90%) mixed nitro compounds. These were refluxed with EtOH (1·7 l.) containing conc HCl (100 ml) for 1 hr, cooled to 0° and filtered. A further crop was obtained by dilution of the filtrates with water to precipitation. The combined solids were boiled with AcOH (2 l.), cooled and filtered. The red filtrate was diluted with water (3 l.), filtered, and the solid recrystallized from AcOH to give the desired 2-amino-3-nitrofluorene (24·4 g) m.p. 200–203°, λ_{max} 274, 296 (sh), 304 (sh), 440–450[53] nm. Reduction with Zn[54] gave the 2,3-diamine, m.p. 192–193 (lit. 192–193°).

2,3-Diaminofluorene (4·9 g) in AcOH (50 ml) was cooled to 14° and powdered $NaNO_2$ (4·0 g) was added; the operation was conducted under N_2. The soln was heated on the waterbath to 80°, cooled to room temp

and filtered. The filtrates were diluted with water (200 ml), filtered, washed with water and the product dried at 110°, giving 2,3-*fluorenotriazole* (4·05 g, 78 %) m.p. 225°. Sublimation at 180°/0·01 mm gave colourless prisms m.p. 235–237°. (Found: C, 75·2; H, 4·7; N, 19·8. Calc for $C_{13}H_9N_3$: C, 75·3; H, 4·4; N, 20·3 %). The molecular ion occurred at m/e 207, and showed successive losses of 28 (N_2) and 27 (HCN), supported by metastable peaks. IR (Nujol): 3500 br, 1710 w, 1640 m, 1595 m, 1530 w, 1405 s, 1325 s, 1265 s, 1232 s, 1198 s, 1098 s, 1011 s, 9920 m, 842 s, 750 s, 760 s, 660 s, cm^{-1}.

(3) 5(6)-*Fluorobenzo-1H-triazole* (VIIId) was prepared in 45 % yield by the diazotization process[50] and sublimed at 110°/0·001 mm (cf. ref. 55).

(4) 5(6)-*Cyanobenzo-1H-triazole*[56] (VIIIb) was prepared in 76 % yield, and had m.p. 222–223° after sublimation at 120°/0·001 mm.

(5) 5(6)-*Trifluoromethylbenzo-1H-triazole*[57] (VIIIc) was prepared in 79 % yield, and had m.p. 132–133° after sublimation at 120°/0·001 mm.

(6) *Triazole[4,5-b]pyridine* (XXVI). 2,3-Diaminopyridine was diazotized in AcOH as described,[50] and the triazole was obtained in 86 % yield, m.p. 201–202° (dec), after recrystallization from EtOH. Diazotization in HCl afforded 45 % yield, m.p. 195°.[58] The mass spectrum showed a molecular ion at m/e 120 (72 %), with peaks at M-28 (100 %) and M-28-27 (35 %).

(7) *Triazole[4,5-c]pyridine* (XXVIII) was similarly prepared in 83 % yield, m.p. 241–242° (lit. 240,[59] 244[60]). The mass spectrum showed the molecular ion at m/e 120 (100 %), with peaks at M-28 (77 %) and M-28-27 (43 %).

(8) 1-*Cyanocyclopentadiene* (III) was prepared by a modification of the method of Peters.[61] Thiele's acid (dimeric 1-carboxycyclopentadiene—3·0 g) and ethyl chloroformate (3·02 g) in dry THF (50 ml) was treated at 0° (dropwise, stirring) with Et_3N (2·76 g). After 3 hr standing, ammonia gas was passed at 0° for 30 min, the mixture was left overnight, and the thick ppt filtered off. Soln of the solid in water and acidification afforded Thiele's amide (2·3 g; 77 %, m.p. 200–202°; lit.[61] 202°). The dimeric nitrile was prepared from this in the usual way,[61] and depolymerized by GLC (Column B 100–125°, injection port 250°, 60 ml/min He). It was in all respects identical with the product from benzotriazole pyrolysis.

PYROLYSIS EXPERIMENTS

(1) *Benzotriazole*

The liquid product from pyrolysis of benzotriazole (5·0 g) at 760° in a stream of argon (0·4 mm) weighed 3·8 g (100 %). Analysis on Column A or B indicated approximately 1 % aniline. This product was freed from aniline and dimerized nitrile by repeated distillation under reduced press from a 45° bath, collecting the nitrile in liquid N_2-cooled receivers. Dimeric nitrile could be de-dimerized by distillation at 180° (bath)/10 mm, but the process was relatively slow (3 g in 2 hr). The cyanocyclopentadiene was redistilled at 65° *in vacuo* and stored at liquid N_2 temp; it had m.p. -45 to $-42°$, and was identical with the product reported by Webster;[27] v_{max} (CCl$_4$): 3070 m, 2980 m, 2900 w, 2215 vs, 1620 s, 1500 s, 1370 s, 1360 s, 1290 w, 1170 s, 1120 m, 1005 s, 960 s, 902 s, 830 s, 692 s, cm^{-1}; λ_{max} (C$_6$H$_{12}$): 268 (8000) in H$_2$O; 266 (8260) in EtOH; 264 (7600) mm. Previous reports[61, 62] give substantially lower extinction coefficients, and this is believed to be due to the presence of dimer in the samples; 100 MHz NMR (CDCl$_3$): 2·73 (quintet, H); 3·35 (multiplet, 2H); 6·74 (quintet, 2H); The last signal (—CH$_2$—) collapsed to an unsymmetrical triplet on irradiation at 2·73 (H$_2$) and to a doublet on irradiation at 3·35 (H$_3$ and H$_4$). A full discussion of this and related systems will appear in a later paper; *Mass spectrum*: M$^+$ = 91 (100 %), 65 (5), 64 (46), 63 (10), 51 (2), 50 (2) at 70 eV.

(2) 5(6)- *and* 4(7)-*Methylbenzotriazoles* (VIIIe and IXe)

In order to prevent interconversion of the nitrile in each case, pyrolysis was conducted at 95 % recovery of starting material, which was recycled to accumulate samples of nitriles. Each nitrile was freed from toluidines in the usual way, and purified by GLC (Column A or B), for spectroscopic analysis.

1-*Cyano-4-methylcyclopentadiene*: (Xe) λ_{max} 276 (8000) nm; v_{max} (CCl$_4$): 3070 w, 2980 m, 2213 s, 1450 s, 1380 s (1390 and 1370 sh), 1140 m, 930 m, 910 m, 890 m, cm^{-1}; 100 MHz NMR (CDCl$_3$): 2·90 (m, H); 3·80 (m, H); 6·80 (m, 2H); (7·65 + 7·97) (two triplets, CH$_3$). The spectrum was accumulated on a PDP/8 computer. The existence of two methyl signals is due to the prototropic shift which equilibrates 3-methyl and 4-methyl-1-cyanocyclopentadienes; both signals are distinct from that of the 1,2-isomer (*vide infra*). A sample of the nitrile used still gave a single GLC peak after 30 hr at 30° (probe temp); *Mass spectrum*: M$^+$ = 105 (100 %), 104 (88), 103 (20), 92 (5), 91 (10), 90 (5), 80 (63), 79 (80), 78 (80), 77 (40), 65 (42), 52 (37), 50 (22) at 70 e.

1-*Cyano-2-methylcyclopentadiene* (XIe). λ_{max} 268 (8000) nm; ν_{max} (CCl$_4$): 3070 w, 2980–2900 m, 2210/2215 s (doublet), 1440 s, 1390 m, 1380 s, 1360 m, 1175 m, 960 w, 890 w, cm^{-1}. The doublet CN band may be due to tautomerism, although only one tautomer was detected by NMR; 60 MHz NMR (CDCl$_3$): 3·46, 3·52 (irregular multiplet, 2H); 6·75 (multiplet, 2H); 7·77 (crude triplet, 3H); *Mass spectrum*: identical with that of 1-cyano-4-methylcyclopentadiene at 70 eV.

(3) 5(6)-*Fluorobenzotriazole*

The pyrolysate was separated by GLC (Column A).

1-*Cyano-4-fluorocyclopentadiene* (X); λ_{max} (C$_6$H$_{12}$): 272 nm; ν_{max} (CCl$_4$): 3100 w, 2200 s, 1620 vs, 1530 s, 1360 s, 1340 s, 1185 s, 1120 m, 940 s, 922 m, 910 m, 897 m, cm^{-1}; 60 MHz NMR (CDCl$_3$): 3·00 (multiplet, H); 4·23 (multiplet, H); 6·66 (multiplet, 2H); *Mass spectrum*: M$^+$ = 109 (100%), 89 (13), 82 (45), 63 (24), 62 (24), 57 (57), 54·5 (M^{++}, 2·8), 52 (12), 51 (13), 50 (12).

1-*Cyano-2-fluorocyclopentadiene* (XI) was not fully characterized, and its identity rests on the similarity of the mass spectrum to that of the 4-fluoro isomer. (M$^+$ was of much higher intensity, and m/e 57 was of lower intensity; λ_{max} (C$_6$H$_{12}$): 268 nm; ν_{max} CCl$_4$: 2100–2205 (doublet), 1642 s, 1530 s, 1385 s, 1365 w, 1300 m, 1030 w, 950 w, cm^{-1}.

(4) 5(6)-*Trifluoromethylbenzotriazole*

The triazole (2·0 g) was pyrolyzed at 500°/0·1 mm, giving 0·23 g liquid nitrile, which evidently contained free HF, and for this reason was not fully investigated; ν_{max}: 2228 cm^{-1}; λ_{max} (C$_6$H$_{12}$): 265 nm. The spectrum was qualitatively similar to that of 1-cyanocyclopentadiene itself, with four faint shoulders on the long wavelength side; 60 MHz NMR (CDCl$_3$): 2·76 (multiplet, H); 2·84 (multiplet, H); 6·47 (multiplet, 2H); *Mass spectrum*: M$^+$ 159 (100%), M-F (21), M-HF (48), M-CF (72), M-CF$_3$ (37).

(5) 5(6)-*Chlorobenzotriazole*

Pyrolysis of the triazole (1·0 g) at 550°/0·1 mm gave 0·5 g unreacted triazole and 0·346 g liquid nitriles. The presence of 1-cyanocyclopentadiene (20%) in the mixture was detected by its NMR and mass spectra, but the two compounds were not separated by GLC (Column A); no other amines or other impurities were detected. Signals other than those due to 1-cyanocyclopentadiene were assigned to 4-*chloro*-1-*cyanocyclopentadiene* (Xa); ν_{CN} 2215 cm^{-1}; λ_{max}: 277 nm, (EtOH), 275 nm, (C$_6$H$_{12}$), 267 nm, (NaOH aq); 60 MHz NMR (CDCl$_3$): 2·87 (multiplet, H); 3·56 (multiplet, H); 6·57 (multiplet, 2H); *Mass spectrum*: M$^+$ = 125, 127 (100%), M-Cl (70%).

(6) 1,2-*Naphthotriazole*

The triazole (3·0 g, sublimed 140°/0·001 mm, m.p. 187–188°) was pyrolyzed at 550°/0·05 mm over the course of 3 hr. The product was freed from unreacted triazole by distillation. Analysis (GLC Column A) indicated the presence of pure 3-cyanoindene[28] (XVII, 0·86 g, 34%); λ_{max} (C$_6$H$_{12}$): 227 (7260), 234 (6950), 262 (3860), 270 sh (3570), 294 (370) nm; ν_{CN} (CCl$_4$): 2231 cm^{-1}; *Mass spectrum*: M$^+$ = 141 (100%), 140 (45), 112 (17); 100 MHz NMR (CDCl$_3$): 2·5–2·85 (multiplet, 4H); 2·91 (triplet, H$_2$); 6·50 (doublet, 2H); $J_{1,2}$ = 2 hz. The use of less pure triazole resulted in an increased yield (74%).

(7) 2,3-*Naphthotriazole*

This was treated exactly as for the 1,2-isomer. The triazole was more stable, and pyrolysis was not complete even at 800°. The product was separated from a little 3-cyanoindene by GLC (Column A, 150° → 200° at 2°/min 86 ml/min He Rt = 46 min (3-CN) and 50 min (2-CN)). 2-*Cyanoindene* (XIX) was obtained from GLC as colourless plates m.p. 39–40; λ_{max} (C$_6$H$_{12}$): 220 (10,530), 222·5 (13,590), 232·5 (12,900), 275 (12,490), 281 sh (12,410), 294 sh (7660) nm; ν_{CN} (CCl$_4$): 2215 cm^{-1}; *Mass spectrum*: 141 (100%), 140 (45), 112 (17); 100 MHz NMR (CDCl$_3$): 2·5–2·8 (multiplet, 5H), 6·48 (doublet, 2H); Irradiation at 6·48 showed collapse of a triplet ($J_{1,3}$ = 2 Hz) at 2·57 within the low field signal, thus identifying H$_3$.

(8) 2- *and* 3-*Cyanoindenes* (XIX *and* XVII)

Pyrolysis conditions for these compounds are set out in Table 3. The mixture of isomers was separated by GLC as described above; R_T values for 4(7)-cyanoindene and 5(6)-cyanoindene were 41 and 53 minutes respectively.

5(6)-*Cyanoindene*. λ_{max} (C$_6$H$_{12}$): 218 (27,800), 225 (27,900), 231 sh (9340), 259·5 (12,600), 264 (12,800), 268·5 sh (13,300), 273 sh (12,000), 278 sh (10,370), 287 sh (5480), 294 sh (3420), 307 sh (798) mm; ν_{max} (CCl$_4$):

2231 cm^{-1}; 100 MHz NMR (CCl$_4$): 2·3–2·9 (m 3H-benzenoid), 3·1–3·4 (m H$_2$ and H$_3$), 6·57 (s, CH$_2$). The signal at 6·57 appeared as two overlapping triplets at 100 Hz sweep width, due to the presence of the two tautomers.* Unlike 2- and 3-cyanoindenes, 5(6)-cyanoindene did not undergo rapid H/D exchange with D$_2$O in the mass spectrometer inlet system. Indene behaved similarly.

4(7)-Cyanoindene. ν_{max} (CCl$_4$): 2231 cm^{-1}; 100 MHz NMR (CCl$_4$): 2·4–2·9 (m, 3H, benzenoid), 2·9–3·1 and 3·1–3·6 (m's 2H), 6·48 and 6·58 (s's CH$_2$). The duplication of signals is due to the existence of the two tautomers.* 4(7)-Cyanoindene similarly did not show rapid H/D exchange in the mass spectrometer inlet system. The mass spectra of all four cyanoindenes were essentially identical.

(9) 9,10-Phenanthrotriazole

The triazole (0·87 g) yielded 9-cyanofluorene (XXII) (92%) on pyrolysis at 550°/0·005 mm over 4 hr. The product was deposited as colourless prisms m.p. 145–146° outside the furnace, and was identical with a sample prepared by Vorländers method.[62] Both samples had m.p. 152–153° after recrystallization from EtOH, then benzene; ν_{CN} (CCl$_4$): 2237(2257 cm^{-1} (doublet). The 2257 cm^{-1} band increased markedly in CHCl$_3$. Repeated purification failed to remove the splitting; *Mass spectrum*: M$^+$ = 191 (100%), M-H (60), M-HCN (5), M-H$_2$CN (5), M^{2+} (6).

(10) 2,3-Fluorenotriazole

The triazole (1·0 g) was pyrolized at 570°/0·02 mm over 1·5 hr, giving yellow crystals m.p. 70–75° (0·2 g; ν_{max} 3500, 3400, 2210, 1630 cm^{-1}). Recrystallization from light petroleum afforded a mixture, presumed to be 2- and 3-aminofluorenes (M$^+$ = 181: ν_{max} = 3500, 3400, 1630 cm^{-1}) which had m.p. 75–80° (2-amino,[63] m.p. 130°; 3-amino;[64] m.p. 150°). Repetition at 600°/0·05 mm (0·55 g, triazole in 1 hr) gave 0·36 g product, which was chromatographed on silica gel in CCl$_4$. The first, rapidly eluted, band was collected and gas chromatographed (Column C, 200–235°, 60 ml/min He) to give a compound R_t = 36 min, solidifying to yellow crystals m.p. ca 70° (XXIV); λ_{max} (C$_6$H$_{12}$):·244 (20,500), 261 (12,800), 270 (13,800), 280 (10,600), 316 (4300), 326–329 (4900), 342 (3500), 352 (900); ν_{max} (CCl$_4$): 2210 s cm^{-1}, transparent 2800–3000 and 3400–35000 cm^{-1}; 60 MHz NMR (CDCl$_3$, C.A.T.): 2·80 (multiplet, 4H-aromatic); 3·72 (multiplet, H$_3$); 6·85 (multiplet, 2H); 7·35 (multiplet, 2H); *Mass spectrum*: M$^+$ = 179 (40%), M-1 (42), M-2 (100).

(11) Triazolo[4,5-b]pyridine and Tria–olo[4,5-c]pyridine

Conditions of pyrolysis, and product yields (%) were as shown below in Table 4. Products were separated by GLC (Column C, 125° at 2°/min, 60 ml/min He).

2-Cyanopyrrole:[65] b.p. 118–120°/10 mm; ν_{max}(CCl$_4$): 3470, 3300 br, 2229 cm^{-1}; λ_{max}: 247 (12,200) nm; 60 MHz NMR (CDCl$_3$):[67] −0·2 (NH); 3·17 (multiplet, H$_3$ and H$_5$); 3·82 (multiplet, H$_4$).

3-Cyanopyrrole:[66] m.p. 54–55°; ν_{max} (CCl$_4$): 3480, 3300 br, 2239 cm^{-1}; λ_{max}: 216 (7440) nm; 60 MHz NMR (CDCl$_3$):[66] 0·4 (NH); 2·68 (multiplet, H$_2$); 3·20 (multiplet, H$_5$), 3·55 (multiplet, H$_4$). The mass spectra of 2- and 3-cyanopyrroles were identical: M$^+$ (100%), M-27 (23).

(12) 2- and 3-Cyanopyrroles (XXVII and XXIX)

Pyrolysis of either cyanopyrrole gave quantitative recovery at 800°/0·01 mm. The product was in each case a mixture of the starting material (2/3) and the isomerized derivative (1/3).

(13) Triazolo[4,5-d]pyrimidine[67] (XXX)

The triazole was recovered unchanged on pyrolysis at 320°, and partial decomposition occurred in the range 380–500°. At 600°/0·05 mm the triazole (0·5 g sublimed in at 130° over 1 hr) gave a dark red pyrolysate, of which 0·02 g was soluble in chloroform, showing weak CN absorption at 2220 cm^{-1}. No tractable product was isolated. The condensable gas in the traps was identified (IR, mass spectrum) as a mixture of ammonia and hydrogen cyanide.

Benzyl cyanide. Pyrolysis at 1000°/0·01 mm gave the following products: benzene (0·4%), toluene (2·6%), benzonitrile (0·8%), o-tolunitrile (8·2%), m-tolunitrile (1·2%), p-tolunitrile (1·8%), HCN, and recovered benzyl cyanide (66%).

Diphenylacetonitrile. Pyrolysis at 1000°/0·08 mm gave HCN and 56% w/w yield of ether soluble materials consisting of (relative peak areas by GLC): benzene (3·6), benzonitrile (1·0), o-tolunitrile (2·1), benzyl cyanide (7·6), biphenyl (1·05), fluorene (2·6) and o-cyanodiphenylmethane (XXXV, 0·63).[68]

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* The spectra will be discussed in detail in a later publication.

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