SEVEN MEMBERED INTERMEDIATES IN THE
ISOMERISATION OF ARYL CARBENES
AND NITRENES

A Thesis

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Author's statement

This thesis represents the author's original
work. Where the work of others is discussed,
acknowledgement is made and due reference given

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Abbreviations

CCPD	1-Cyanocyclopentadiene
M$\overset{\cdot}{+}$	Molecular ion
n.m.r.	Nuclear Magnetic Resonance
i.r.	Infra Red
g.l.c.	Gas Liquid Partition Chromatography
m.s.	Mass Spectrum
g.l.c./m.s.	Gas Liquid Partition Chromatography - Mass Spectrometry
t.l.c.	Thin Layer Chromatography
E.H.T.	Extended Hückel Theory
C.N.D.O.	Complete Neglect of Differential Overlap
Hückel-M.O.	Hückel Molecular Orbital
u.v.	Ultra Violet

(v)

CONTENTS

Summary

The literature on aryl nitrenes and carbenes is reviewed. A novel rearrangement of the s-triazolo(4,3-a) pyridines to the pyrazolo(3,4b)pyridine ring system is proposed, the products observed being derived from the migration of hydrogen in.the pyrazolo(3,4b)pyridine ring system. The products obtained indicate a duality of mechanism with the competing pathways involving 1,3 diradicals or carbene intermediates.

The hydrogen shift mechanism for the decomposition of the pyrazolo(3,4b)pyridine is further explored by the pyrolysis of 1H-pyrazolo(3,4b)pyridine. This pyrolysis gave support to the hydrogen shift mechanism proposed for the s-triazolo(4,3-a)pyridine pyrolysis and also demonstrated the carbene/1,3 diradical duality by giving azafulvenallenes, ethynylpyrroles and CCPD. The CCPD was attributed to the intermediacy of 3-pyridylcarbene; a proposal which conflicted with the results from v-triazolo(1,5-a) pyridine.[29] This investigation of the hydrogen shift/nitrogen mechnism was extended to the 1H-indazole molecule which gave the phenylcarbene[30] ring contraction products fulvenallene and ethynylcyclopentadiene. Pyrolysis of pyrazole also showed this hydrogen shift/nitrogen loss to give methylacetylene and allene.

INTRODUCTION

Electronic Structure and Reactivity of Triplet and Singlet
State Nitrenes and Carbenes

The nucleus of the electron deficient atom found in an unperturbed carbene or nitrene is enclosed in a six electron system having two non-bonding electrons, (the nitrene possessing an additional lone pair). Therefore both carbenes and nitrenes can exist in singlet and triplet spin states; with the triplet normally being assigned as the ground state (vide infra).

Considering the linear methylene, it can be seen that there are two identical 2p orbitals and the total angular momentum (L) will assume the values of 0 and 2 (obtained by vector addition of the l values). For L=0, S can have the values of 1 or 0 hence there will exist a triplet $(^3\Sigma)$ and a singlet $(^1\Sigma)$. For L=2 the spins are paired (as the quantum numbers n, l, m are equal) giving S=0 so that the singlet state $^1\Delta$ is obtained.

Consideration of Hund's rules gives the ground state as the triplet $^3\Sigma$ and the lowest singlet state being $^1\Delta$. As the state $^1\Delta$ is doubly degenerate, it splits into two levels when the molecule is bent with one p orbital attaining s character while the other remains unchanged. The energy diagram for methylene (1) is as follows in Fig. 1.

FIGURE 1
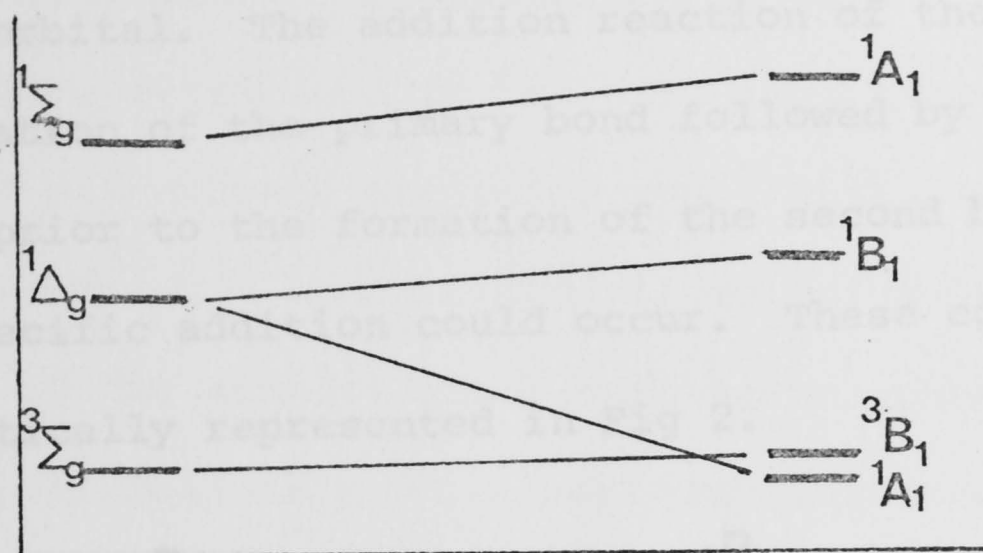
From the energy diagram (Fig. 1) it appears that the lowest singlet $^1A_1$ is the ground state for the bent carbene form; however Hoffmann[2,3] claimed that the small energy difference (between $^3B_1$ and $^1A_1$) is compensated for by the electrostatic energy gained by the separation of the electrons; thus the triplet $^3B_1$, becomes the ground state for both the linear and bent forms of methylene.

For the purpose of discussing the varying reactivity of the two spin states it is necessary only to discuss the reactions of the ground state triplet 1, lowest singlet 2 and first excited singlet 3.
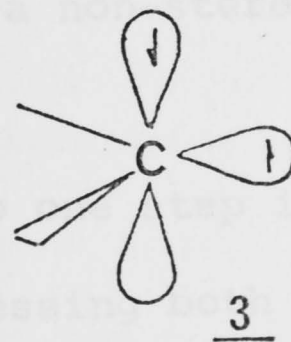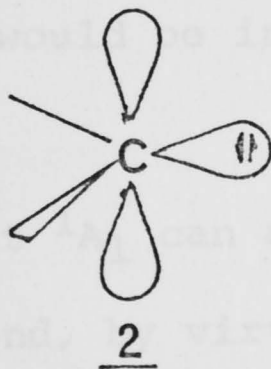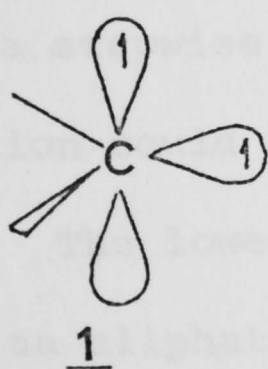
The first consideration of the reactivity of the triplet and singlet states is their ability to undergo addition to C=C double bonds. Skell[4] argued that a singlet carbene could

3.

add stereospecifically to a double bond, as both electrons were

in the same orbital. The addition reaction of the triplet would

require formation of the primary bond followed by spin inversion

or rotation prior to the formation of the second bond; thus

non-stereospecific addition could occur. These considerations

are diagramatically represented in Fig 2.

<u>FIGURE 2</u>
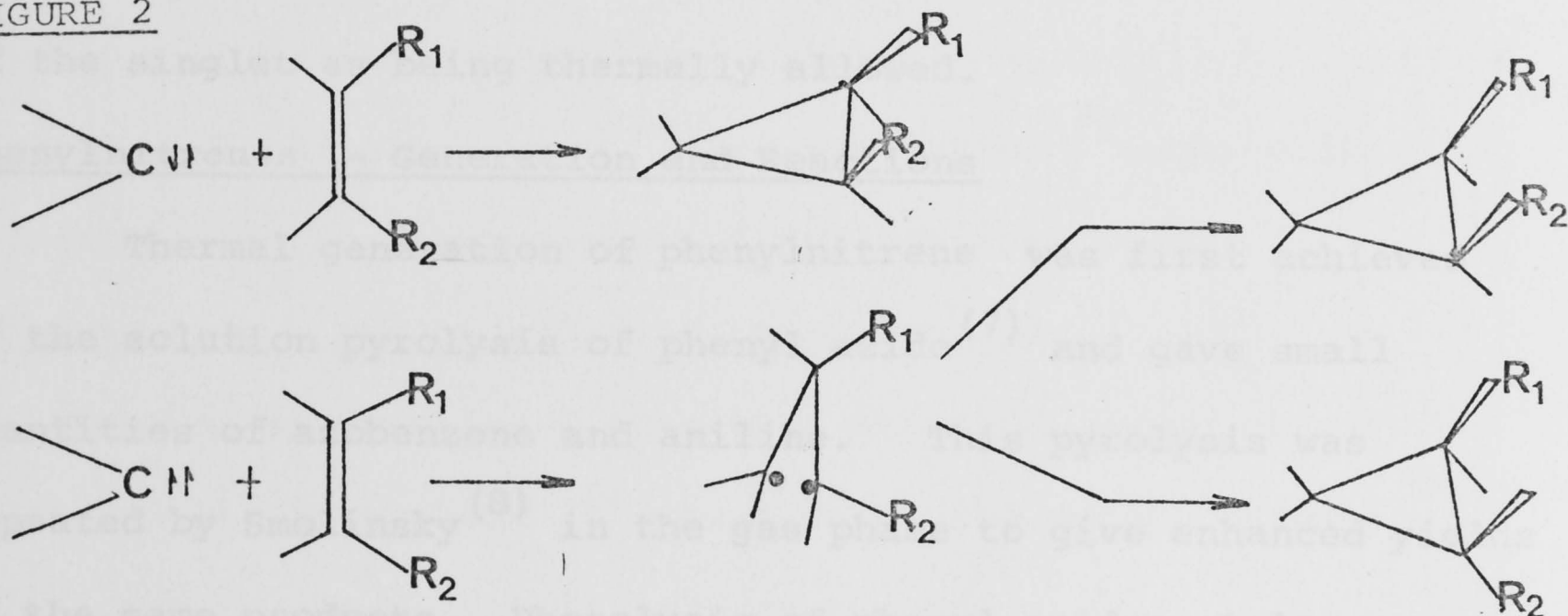
Hoffmann's[2,3] theoretical treatment shows that the lowest

singlet $^1A_1$ attacks with the doubly occupied σ -orbital and

therefore the addition goes in one step as the two electrons

are in the bonding area simultaneously. The triplet $^3B_1$ and

the first excited singlet $^1B_1$ attack head on with only one orbital,

thus a stepwise process would be involved and a non-stereospecific

addition could result.

The lowest singlet $^1A_1$ can also undergo one step insertion

into an aliphatic C-H bond, by virtue of possessing both reacting

electrons in the one orbital, while the triplet $^3B_1$ inserts into

a C-H bond by first abstracting a proton and then undergoing

radical recombination. Dimerisation to give olefin and azo-compounds is attributed to the diradical nature of the triplet state of carbenes and nitrenes. This was further verified by Hoffmann's[5] E.H.T. calculations, which showed the dimerisation of the singlet state carbene was thermally disallowed; however Kollman's[6] C.N.D.O. calculations gave dimerisation of the singlet as being thermally allowed.

Phenylnitrenes - Generation and Reactions

Thermal generation of phenylnitrene was first achieved by the solution pyrolysis of phenyl azide[7] and gave small quantities of azobenzene and aniline. This pyrolysis was repeated by Smolinsky[8] in the gas phase to give enhanced yields of the same products. Photolysis of phenyl azides at low temperature yielded azobenzenes,[9] while at ordinary temperatures no products were observed unless electron donating substituents were present[10]. It was reasoned that electron donation facilitated nitrogen loss and formation of the nitrene. Photolysis of phenyl azide[11] has also been reported to form benzotriazole.

The fact that the thermally produced singlet phenylnitrene was giving rise to the typically triplet nitrene products (azobenzene and aniline), was explained as being due to rapid intersystem crossing between the generated singlet and the triplet ground state[12]. The nitrene electrons interact with the system and thus increase the likelihood of intersystem crossing

by enhancing the lifetime of the nitrene.[12]

Calvin and Splitter[13] reported that triplet phenyl-
nitrenes gave only azobenzene and aniline rather than ring

insertion, and attributed the latter reaction to the singlet

state nitrene.   These conclusions were drawn from the authors'

experience[13] with triplet sensitised photolysis of phenyl

azide, (which presumably produced triplet phenylnitrene), as

compared with the photolytic[14] and pyrolytic[15] decomposition

of phenyl azide in the presence of aniline (see below).

Ring Insertion - Nucleophilic Addition Reaction

The first example of this type of reaction was observed
by Huisgen and co-workers[15] who thermolysed phenyl azide in

aniline and obtained 2-anilino-2H-azepine 4.
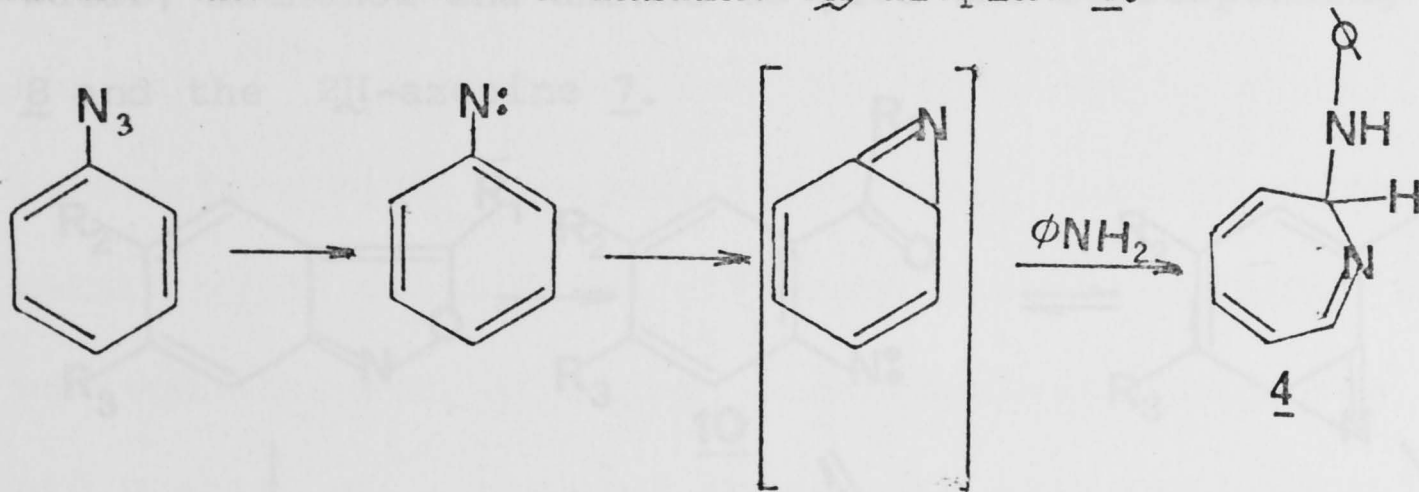

The above mechanism was established by ^{14}C labelling.[15]

The same type of insertion/nucleophilic addition reaction was

also observed in the photo-deoxygenation of nitrobenzenes in

the presence of triethyl phosphite.[16][17]

6.
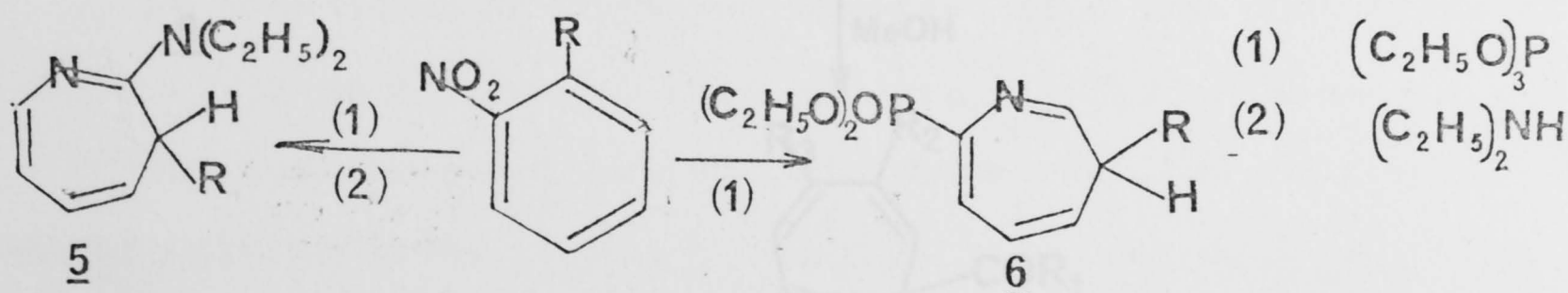
The products 5 and 6 represent the work of Cadogan and co-workers[16], who isolated the 3H-azepinyl-7-phosphonate from the triethyl phosphite reduction of o-nitroethylbenzene. The generation of the nitrene from o-nitrobenzene by deoxygenation with triethyl phosphite by Sundberg and co-workers,[17] although mechanistically similar, gave rise to different products from those observed by Cadogan[16] and will be discussed in relation to 2-pyridylcarbene/phenylnitrene isomerisation later in this introduction. (See expansion/contraction cycle).

Another example of this ring expansion/nucleophile addition reaction for aryl nitrenes was observed by Ogata,Matsumato and Kano[18] by the photolysis of anthranils in the presence of water, methanol and amines to give the corresponding 3H-azepine 8 and the 2H-azepine 7.
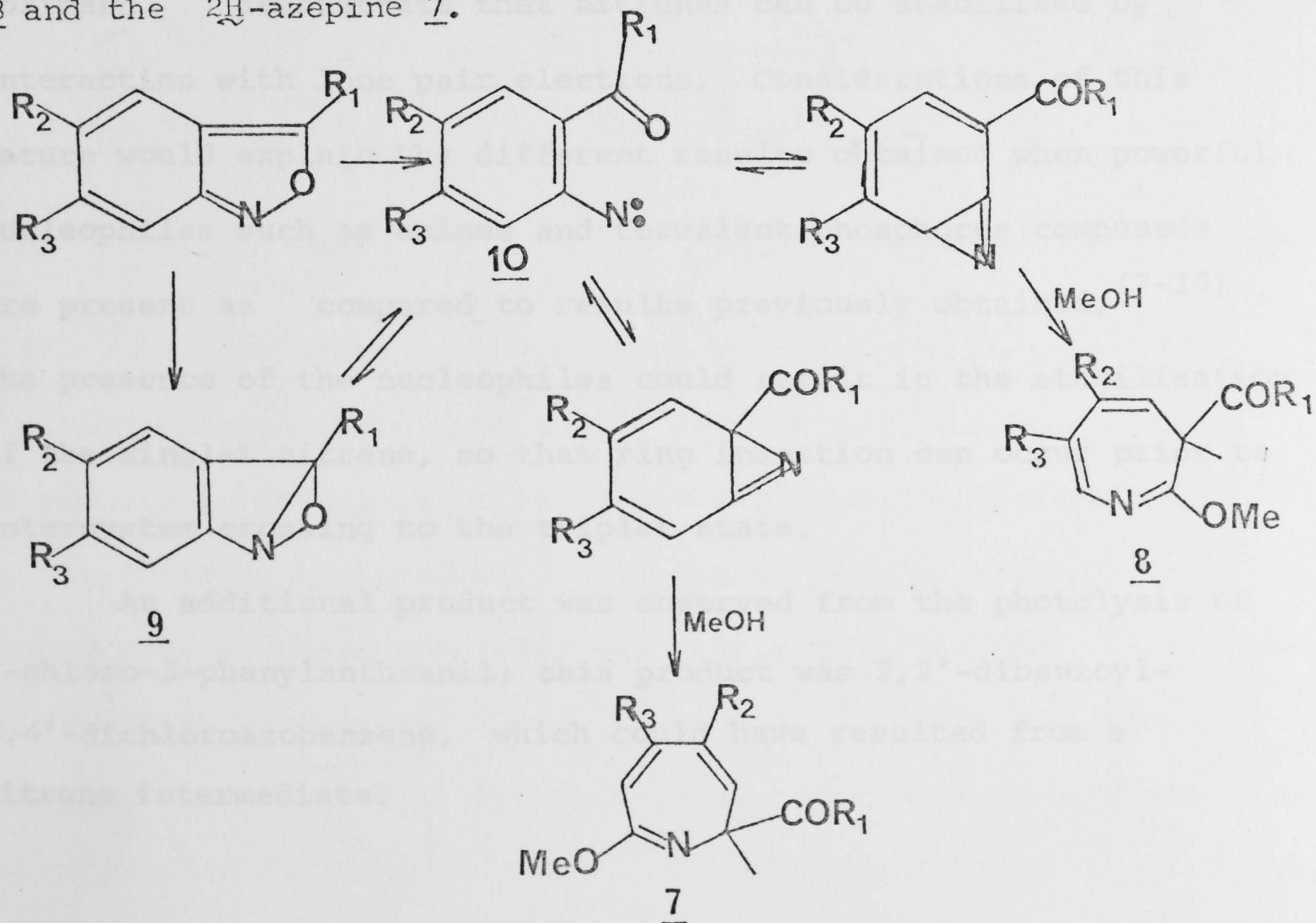
The mechanism proposed for the ring expansion and the subsequent nucleophilic addition was essentially that proposed by Huisgen and Appl[15] for the formation of 2-anilino-3H-azepine from the thermolysis of phenyl azide. The authors proposed the possible intermediacy of the oxaziran[18] 9 prior to ring cleavage to the nitrene 10. The formation of the oxaziran 9 results from the interaction of the π - electron system of the carbonyl group with the nitrene, prior to bond formation to give the intermediate 9; the nitrene would achieve a stabilisation analogous to the stabilisation calculated by Crow, Gregory and Paddon-Row[19] in their theoretical considerations of stabilising singlet carbenes with π - systems.

The extended Hückel-MO calculations by Gleiter and Hoffmann[20] demonstrate that nitrenes can be stabilised by interaction with lone pair electrons. Considerations of this nature would explain the different results obtained when powerful nucleophiles such as amines and tervalent phosphorus compounds are present as compared to results previously obtained.[7-10] The presence of the nucleophiles could result in the stabilisation of the singlet nitrene, so that ring insertion can occur prior to intersystem crossing to the triplet state.

An additional product was observed from the photolysis of 5-chloro-3-phenylanthranil; this product was 2,2'-dibenzoyl-4,4'-dichloroazobenzene, which could have resulted from a nitrene intermediate.

Insertion into Neighbouring π-Surfaces

The photolysis of 7-substituted-3-phenylanthranils[18]

led to the formation of acridone derivatives 11 by C-H insertion

or hydrogen abstraction, followed by radical combination at the o-

position of the adjacent phenyl ring.
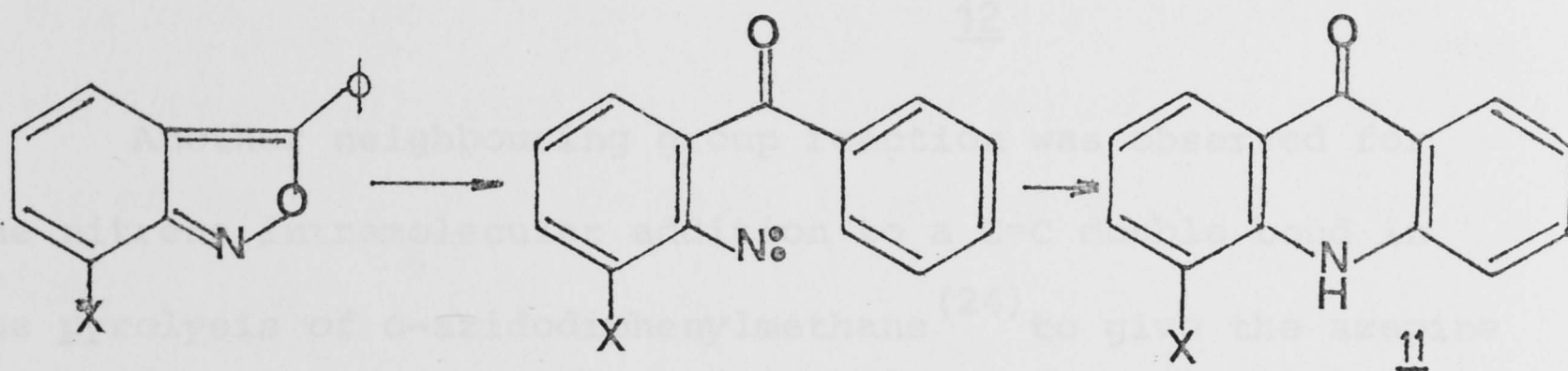
Similar neighbouring group reactions have been observed

for the photolysis[21] and thermolysis[22] of o-azidobiphenyl

to give carbazole.
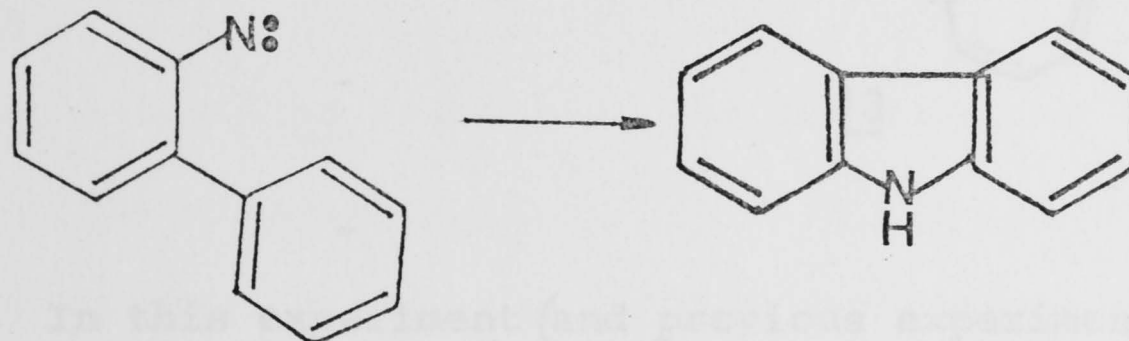
The spin state of the nitrene in this case is not known

although spectroscopic evidence,[21] derived from the production

of photolytic carbazole from o-azidobiphenyl, indicates that

triplet nitrene is involved. Evidence of singlet nitrene gener-

ation from gas phase pyrolysis was obtained by Smolinsky,[8] for when

an optically active centre was introduced[23] total retention of

activity was observed in the product 12 compared with only 65%

retention in the solution phase. The retention of optical activity

was attributed to the concerted nature of the singlet nitrene

insertion into the C-H bond.

12
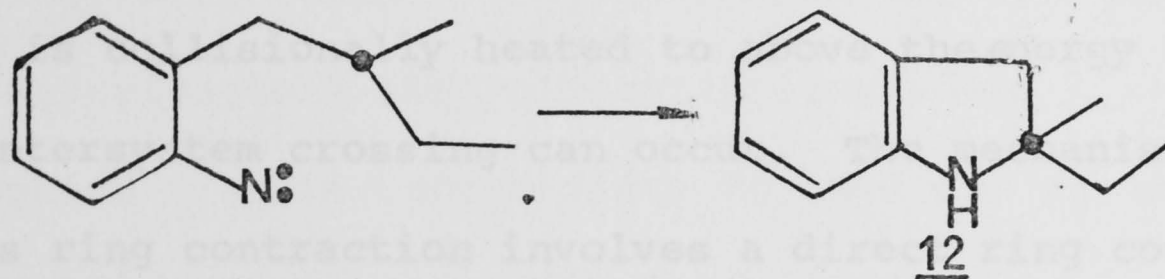
Another neighbouring group reaction was observed for
the nitrene intramolecular addition to a C=C double bond in
the pyrolysis of o-azidodiphenylmethane[24] to give the azepine
derivative 13.

13
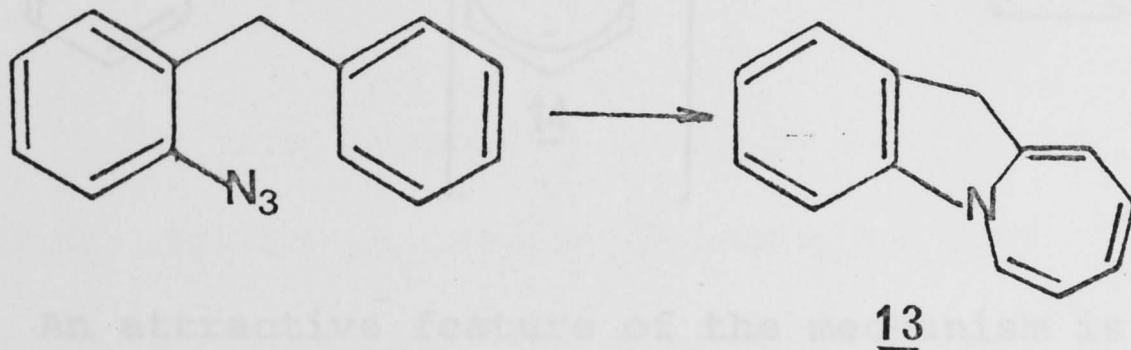
In this experiment (and previous experiment producing
the indoline derivative 12), the geometry of the trapping group
in relation to the attacking nitrene is sufficiently close to
facilitate rapid trapping, so that the singlet nitrene reacts
before deactivation and intersystem crossing can occur.

Contraction of the Aromatic Ring

More recently, singlet phenylnitrene has been reported[25]
to give the ring contraction product CCPD.

These results were achieved by the violent gas
phase pyrolysis of phenyl azide, where the conditions used have

(12)

been described as a "controlled explosion". The explanation

given for the observation of the singlet nitrene was that, under

the extreme conditions used, the thermally produced singlet

nitrene is collisionally heated to above the energy level at

which intersystem crossing can occur. The mechanism proposed[25]

for this ring contraction involves a direct ring contraction

via the nitreno-prefulvene intermediate 14 followed by ring

opening of the bicyclo intermediate 14 and hence to the observed

product.
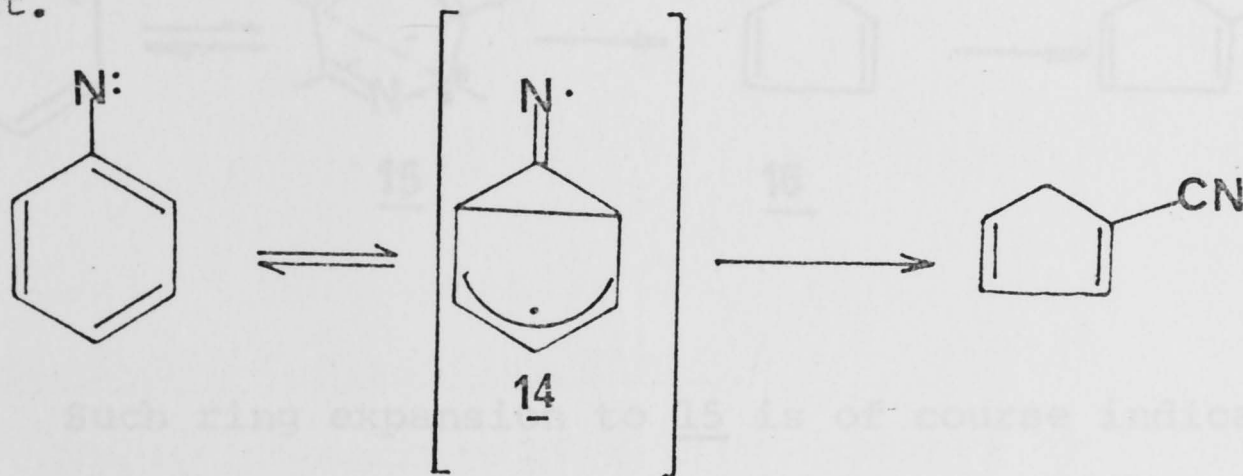
An attractive feature of the mechanism is that it follows

the principle of least motion,[26] with the nitrene leading

directly to ring contraction. Also the nitreno-prefulvene

intermediate is analogous to prefulvene, which has been proposed[27]

as an intermediate in the conversion of the first excited state

of benzene to fulvene. Similar intermediates have also been

proposed for the decarbonylation of phenoxy radicals[28] and for the

elimination of hydrogen cyanide from anilino radicals leading to

cyclopentadienyl radicals. This mode of ring contraction has also

been demonstrated[25] by orbital symmetry considerations to be

thermally allowed; a result which, although gratifying, has

questionable relevance under conditions of such high energy.

The above mechanism is one of a number possible for this ring contraction; the other most likely mechanism being ring expansion to 2-azacycloheptatrienylidene 15 and direct contraction of this intermediate to give the unstable nitrile 16 which rearranges to the product obtained.

15   16
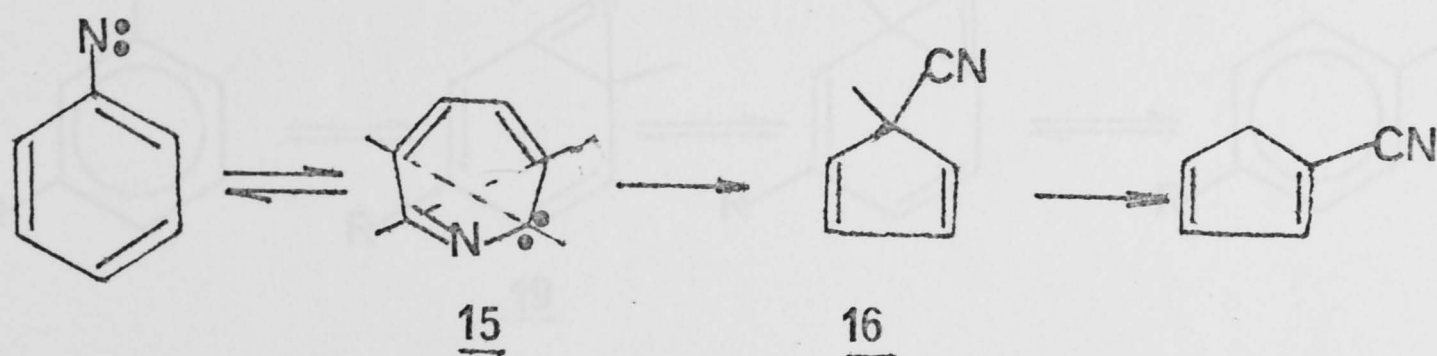
Such ring expansion to 15 is of course indicated by the trapping techniques used by Huisgen and Appl[15] and the products observed from the photolysis of anthranils.[18] This mechanism was not preferred, although a similar ring expansion/contraction cycle, leading to pyridine and picolines was observed.[25]

Pyrolysis of substituted phenyl azides[25] gave mixtures of the nitriles 17, 17a and 18.

17   17a   18
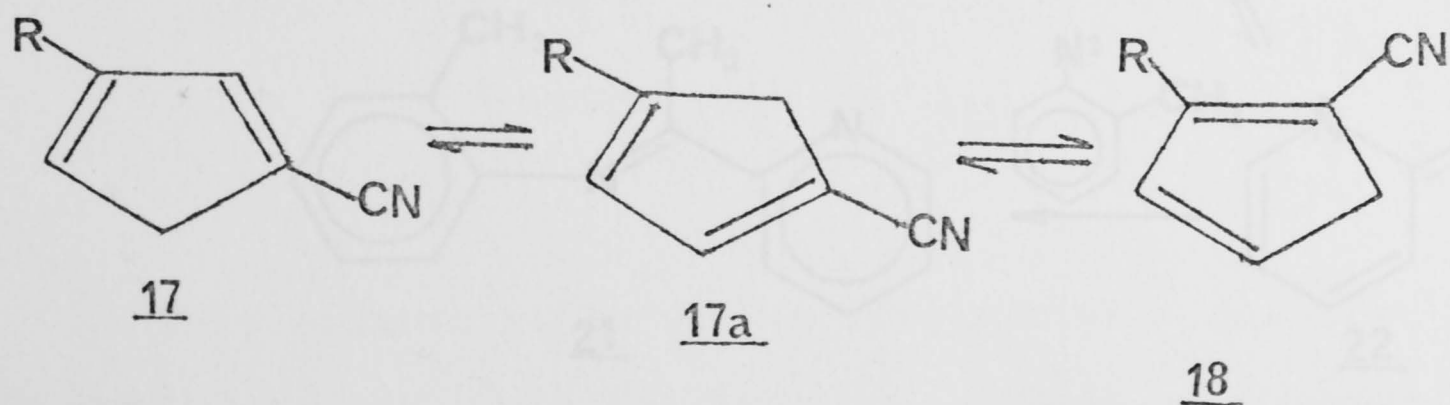
This result was shown to be mechanistically irrelevant, since the nitriles interconvert at high temperature by cyano group migration. However, the possibility of other explanations was not, of course eliminated by this finding; for example rapid cycloperambulatory motion of the nitrene by hydrogen shifts in a benzazirine intermediate 19, prior to the ring contraction.

19
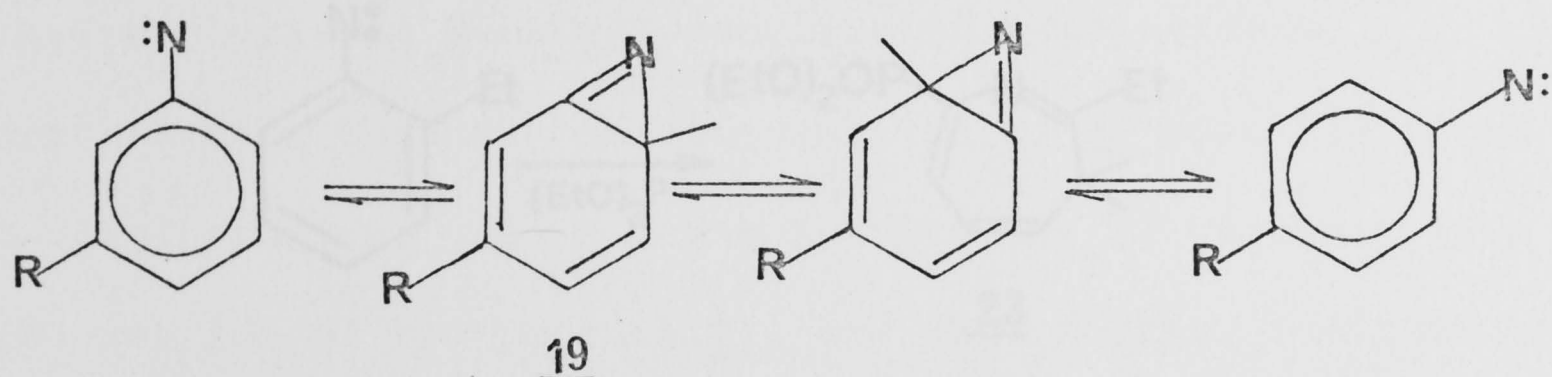
The Expansion-Contraction Cycle

The deoxygenation of o-nitrotoluenes by triethyl phosphite carried out by Sundberg and co-workers[66] involved generation of o-tolyl nitrene 20 which underwent the following sequence of reactions to give the product 21.

20

21

22
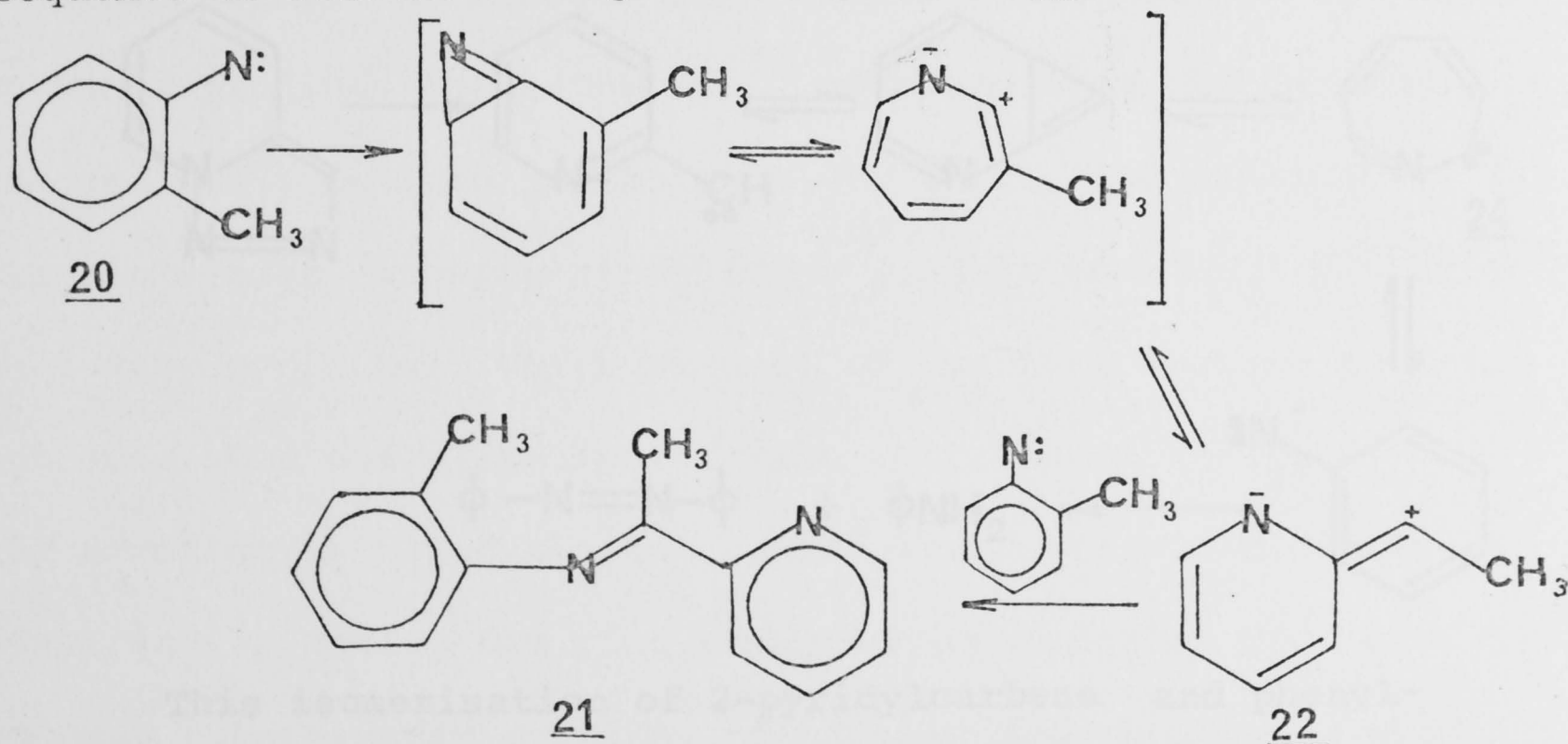
The isolation of the 3H-azepinyl-7-phosphonate <u>23</u> from the deoxygenation of o-nitroethylbenzene by Cadogan and co-workers[16] (<u>via</u> ring insertion/nucleophilic addition), implied that the results observed by Sundberg and co-workers were derived from a nucleophile stabilised ring expansion intermediate[17] ratherthan the discrete intermediate.

<u>23</u>
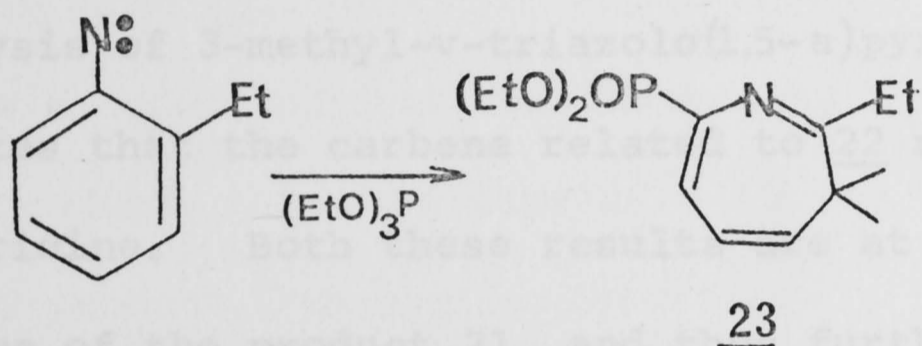
This led Crow and Wentrup[29] to attempt to generate 2-pyridylcarbene in the gas phase, where no such participation could occur. Pyrolysis of v-triazolo(1,5-a)pyridine led to the following results.

<u>24</u>
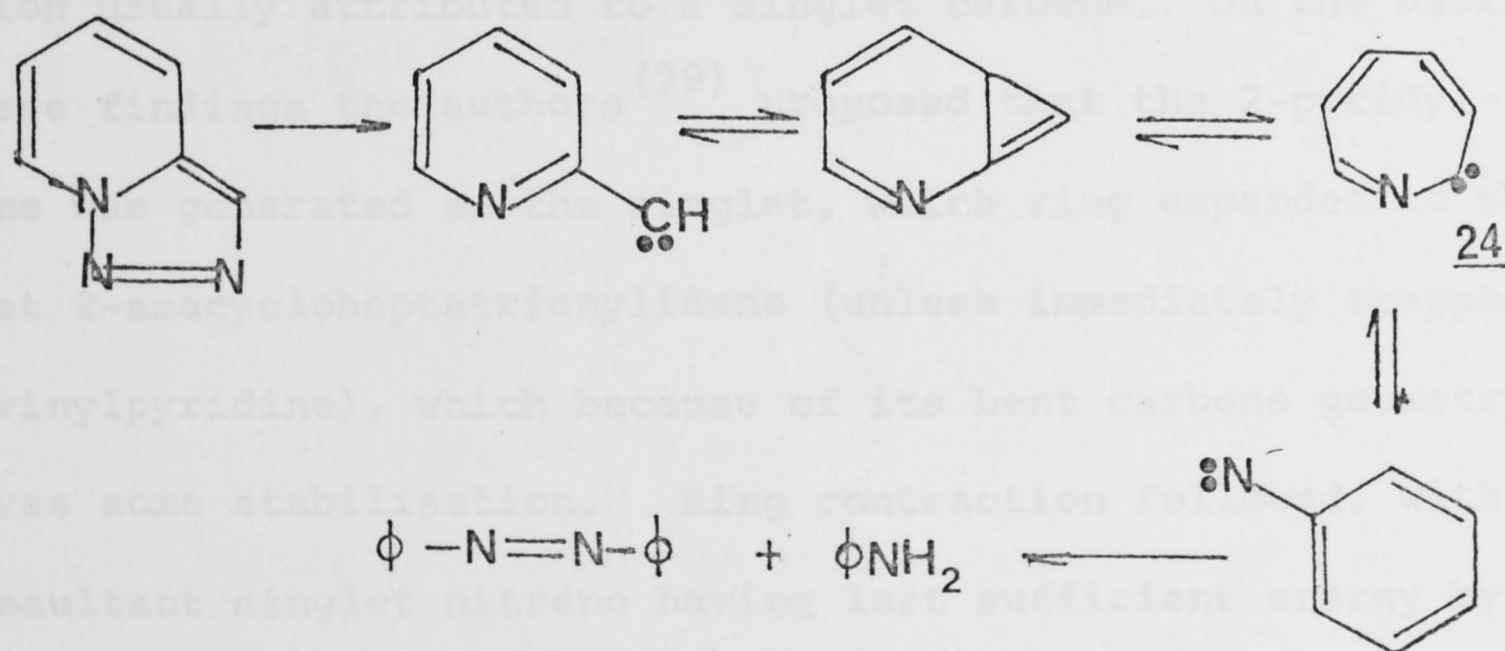
This isomerisation of 2-pyridylcarbene and phenyl-nitrene was explained as a ring expansion to 2-azacycloheptatri-enylidene <u>24</u>, followed by ring contraction to phenylnitrene.

The pyrolysis of 3-methyl-v-triazolo(1,5-a)pyridine [29] gave

2-vinylpyridine in quantitative yield between 500-800°C via

carbene insertion in the C-H bond.   These results demonstrate

that, in the absence of any nucleophilic stabilisation,

isomerisation (2-pyridylcarbene/phenylnitrene) strongly favours

the formation of phenylnitrene.   The result obtained from

the pyrolysis of 3-methyl-v-triazolo(1,5-a)pyridine

demonstrates that the carbene related to 22 normally gives

2-vinylpyridine.   Both these results are at variance with

observation of the product 21 and thus further indicate that

the isomerisation observed by Sundburg was nucleophile-stabilised.

The pyrolysis of v-triazolo(1,5-a)pyridine   gave products

after ring expansion/contraction which were typical of triplet

phenylnitrene, while pyrolysis of 3-methyl-v-triazolo(1,5-a)-

pyridine gave the C-H insertion product (2-vinylpyridine), a

reaction usually attributed to a singlet carbene. On the basis

of these findings the authors [29] proposed that the 2-pyridyl-

carbene was generated as the singlet, which ring expanded to the

singlet 2-azacycloheptatrienylidene (unless immediately trapped

as 2-vinylpyridine), which because of its bent carbene geometry

achieves some stabilisation.   Ring contraction followed, with

the resultant singlet nitrene having lost sufficient energy by

deactivation during the ring expansion-contraction process to

undergo inter-system crossing to triplet phenylnitrene which

was responsible for the products formed and isolated.

2-PyCl Λ $\rightleftharpoons$ azatropilidene $||$ $\rightleftharpoons$ ϕN $||$ $\longrightarrow$ ϕN $||$
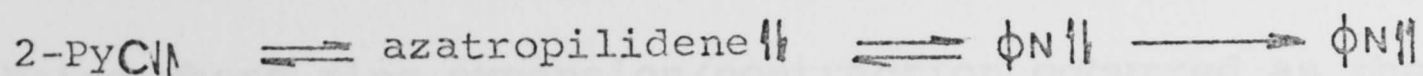
The pyrolysis of 3-phenyl-v-triazolo(1,5-a)pyridine gave carbazole in 94% yield. The formation of this product was also attributed to the generation of the triplet nitrene after ring contraction from 25.

The triplet nitrene then abstracts hydrogen to give the observed product. Methyl labelling in the 6 position resulted in the one product, 3-methylcarbazole 26.

25

26
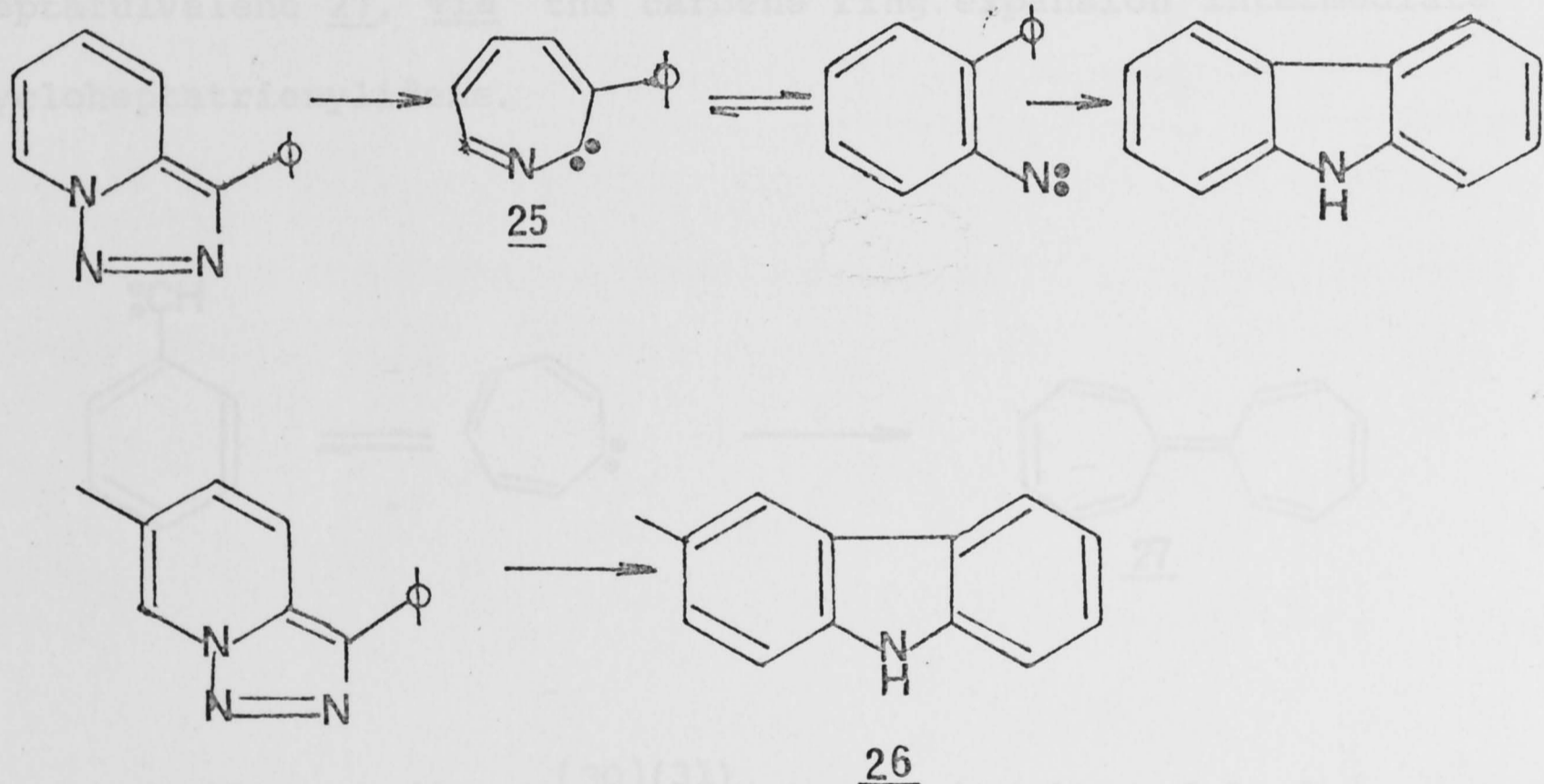
The failure to observe the ring contraction product CCPD from the pyrolysis of v-triazolo(1,5-a)pyridine led the authors to claim[29] that the ring contraction of phenylnitrene to CCPD does not occur via the 2-azacycloheptatrienylidene intermediate 24. This implied that the ring contraction

of phenylnitrene and the ring expansion/contraction cycle were two entirely different competing mechanisms. The postulate being,where ring expansion/contraction occurred as the major pathway, no ring contraction product (CCPD) would be observed.

Aryl Carbenes

The study of aryl carbenes in the gas phase was initiated by the generation of phenylcarbene [30] by the pyrolysis of phenyldiazomethane (generated by heating the sodium salt of benzaldehyde tosylhydrazone), which led to formation of heptafulvalene 27, via the carbene ring expansion intermediate cycloheptatrienylidene.
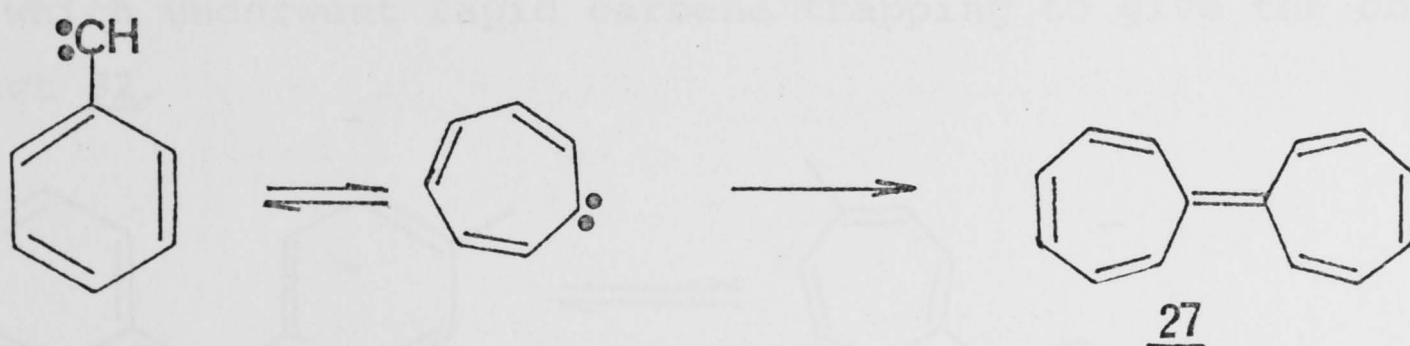
Further studies [30][31] showed that heptafulvalene was formed from the generation of phenylcarbene below 600°. Above 600°C the carbene gave the ring contraction products fulvenallene 28 and ethynylcyclopentadiene 29. The mechanism postulated for this ring contraction was analogous to the one proposed [25] for the formation of CCPD from phenylnitrene,

that is ring contraction involving the bicyclo-intermediate 30.
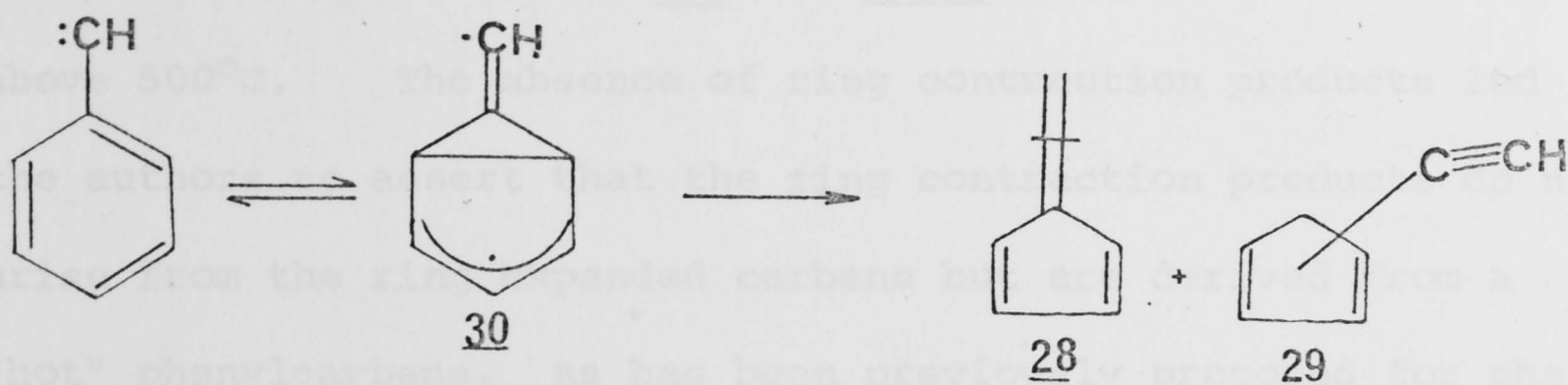
Pyrolysis of diphenyldiazomethane[32] gave fluorene, and when methyl labelled diphenyldiazomethanes were pyrolysed[33][31] the initial carbene formed[31] must have ring expanded to the corresponding 2-tolyl-cycloheptatrienylidene intermediate. This was then followed by ring contraction to give the aryl carbene 31, which underwent rapid carbene trapping to give the observed product 32.
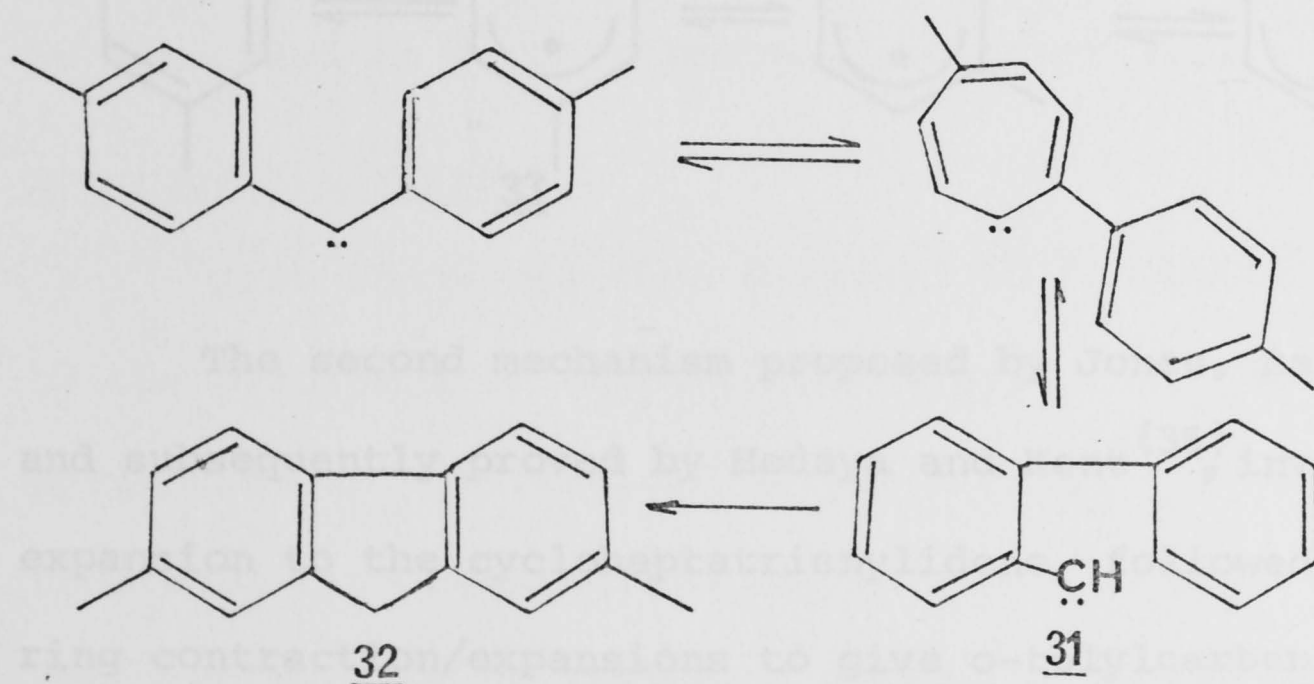
This is a reaction analogous to the reported thermal rearrangement of 2-pyridyl-phenylcarbene.[29] The generation of cycloheptatrienylidene was achieved by Wentrup and Wilczek[31] by the pyrolysis of the sodium salt of tropone tosylhydrazone.

The products observed were heptafulvalene, cis- and trans-stilbene below 500°C, and cis-and trans-stilbene and anthracene above 500°C. The absence of ring contraction products led the authors to assert that the ring contraction products do not arise from the ring expanded carbene but are derived from a "hot" phenylcarbene, as has been previously proposed for phenyl-nitrene.[29]

The pyrolysis of p-, m- and o-tolylcarbenes resulted in the formation of benzocyclobutene and styrene [34][35] with two mechanisms being proposed for their formation. The first mechanism involved a ring flipping pathway involving the prefulvene intermediate 33.
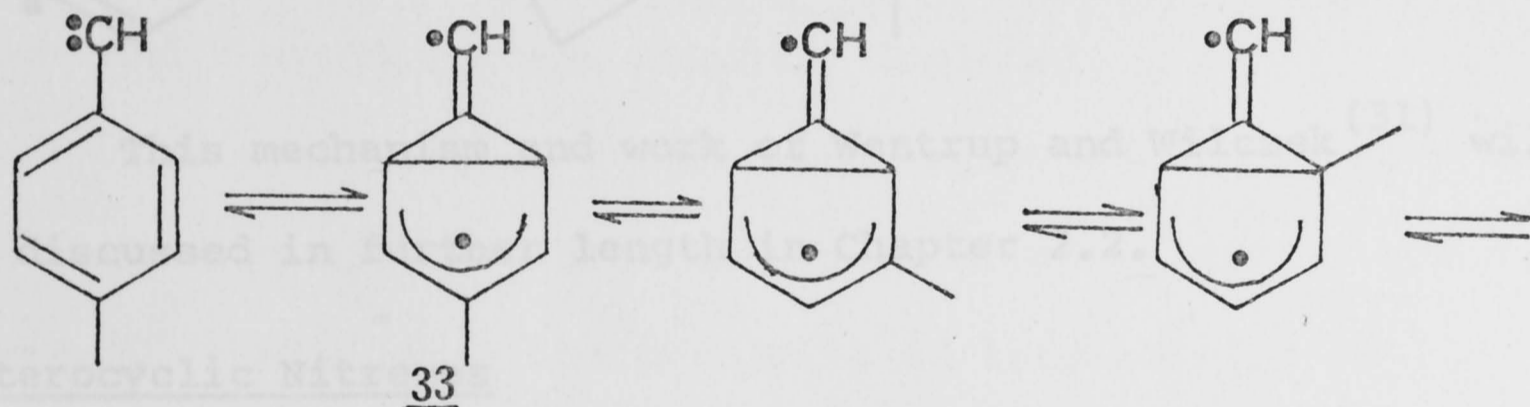
The second mechanism proposed by Jones, Baron and Gasper[34], and subsequently proved by Hedaya and Kent[35], involved ring expansion to the cycloheptatrienylidene followed by further ring contraction/expansions to give o-tolylcarbene and methylphenylcarbene 34. This mechanism was proved[35] by ^{13}C-labelling the initial carbene generated; the mechanism and products are as follows:
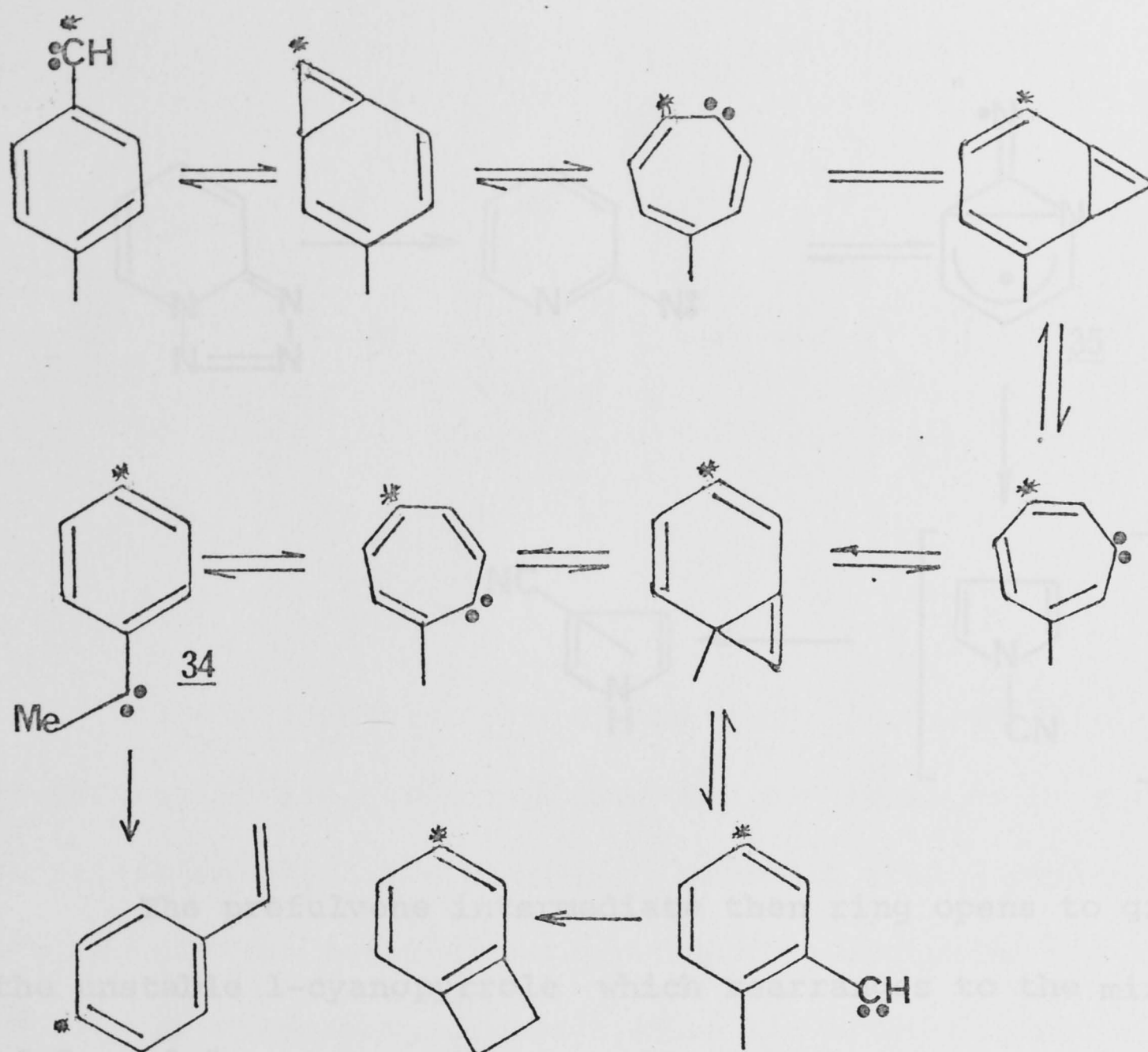
This mechanism and work of Wentrup and Wilczek[31] will be discussed in further length in Chapter 2.2.

Heterocyclic Nitrenes

This study was then extended to the heterocyclic nitrenes by the pyrolysis of tetrazolo(1,5-a)pyridine, tetrazolo(1,5-a) pyrimidine and tetrazolo(1,5-c)pyrimidine;[36] 2-pyridylnitrene underwent ring contraction in 80% yield to give 2- and 3-cyanopyrroles by an analogous mechanism to the one proposed for the formation of CCPD from phenylnitrene, involving the aza-prefulvene intermediate 35.
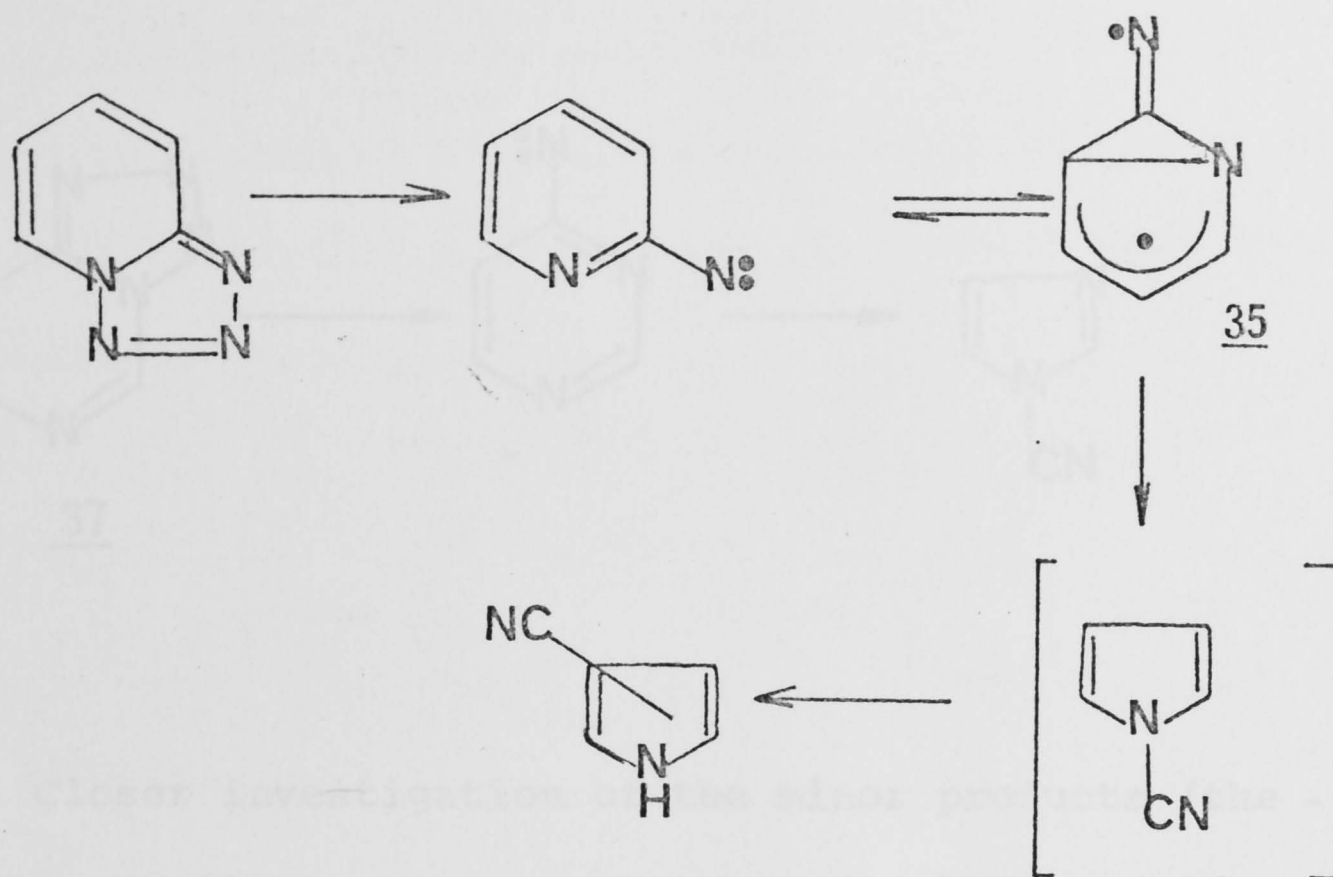
The prefulvene intermediate then ring opens to give the unstable 1-cyanopyrrole which rearranges to the mixture of 2- and 3-cyanopyrroles actually isolated.

The pyrolysis of tetrazolo(1,5-a)pyrimidine 36 gave the corresponding nitrene which ring contracted to give 1-cyano-pyrazole. Similarly the pyrolysis of tetrazolo(1,5-c)-pyrimidine 37 gave the ring contraction product 1-cyanoimidazole.

This ring expansion/contraction mechanism prior to the formation of the prefulvene intermediate 35, was further indicated by examining the amines obtained from the pyrolysis of 6-methyl-tetrazolo(1,5-a)pyridine 39, which gave a mixture of the amines 40 and 41.

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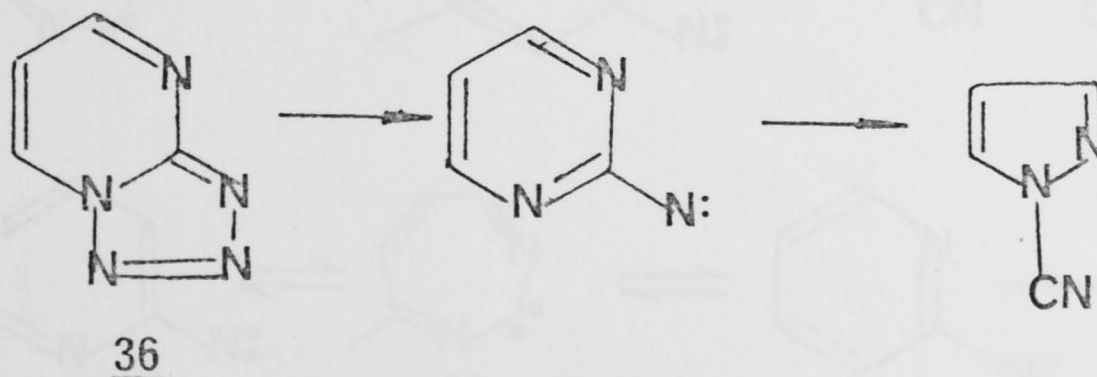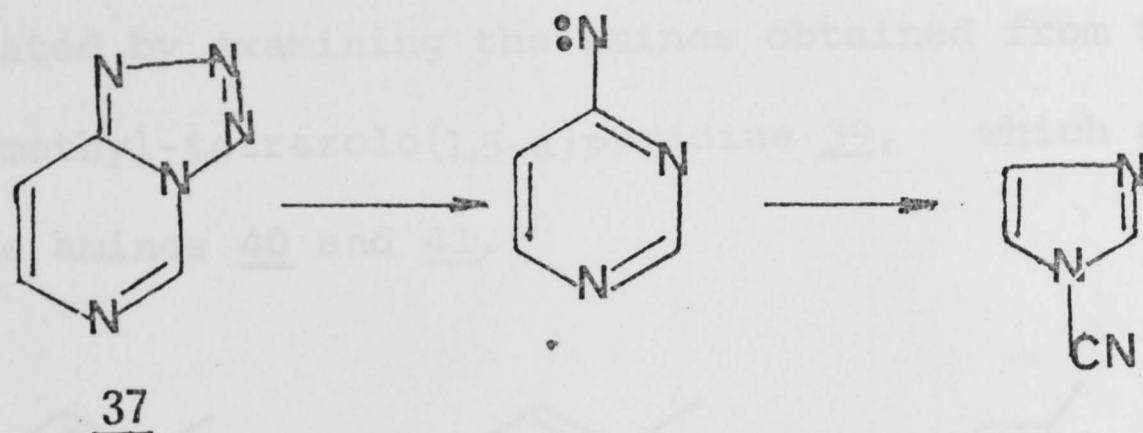
Closer investigation of the minor products (the glutacononitriles) obtained from the pyrolysis of 5- and 6-methyl-tetrazolo(1,5-a)pyridine revealed that 2-pyridyl-nitrene must be passing through the ring expansion intermediate (2, 7 - diazacycloheptatrienylidene 38) prior to ring cleavage to form the glutacononitriles.
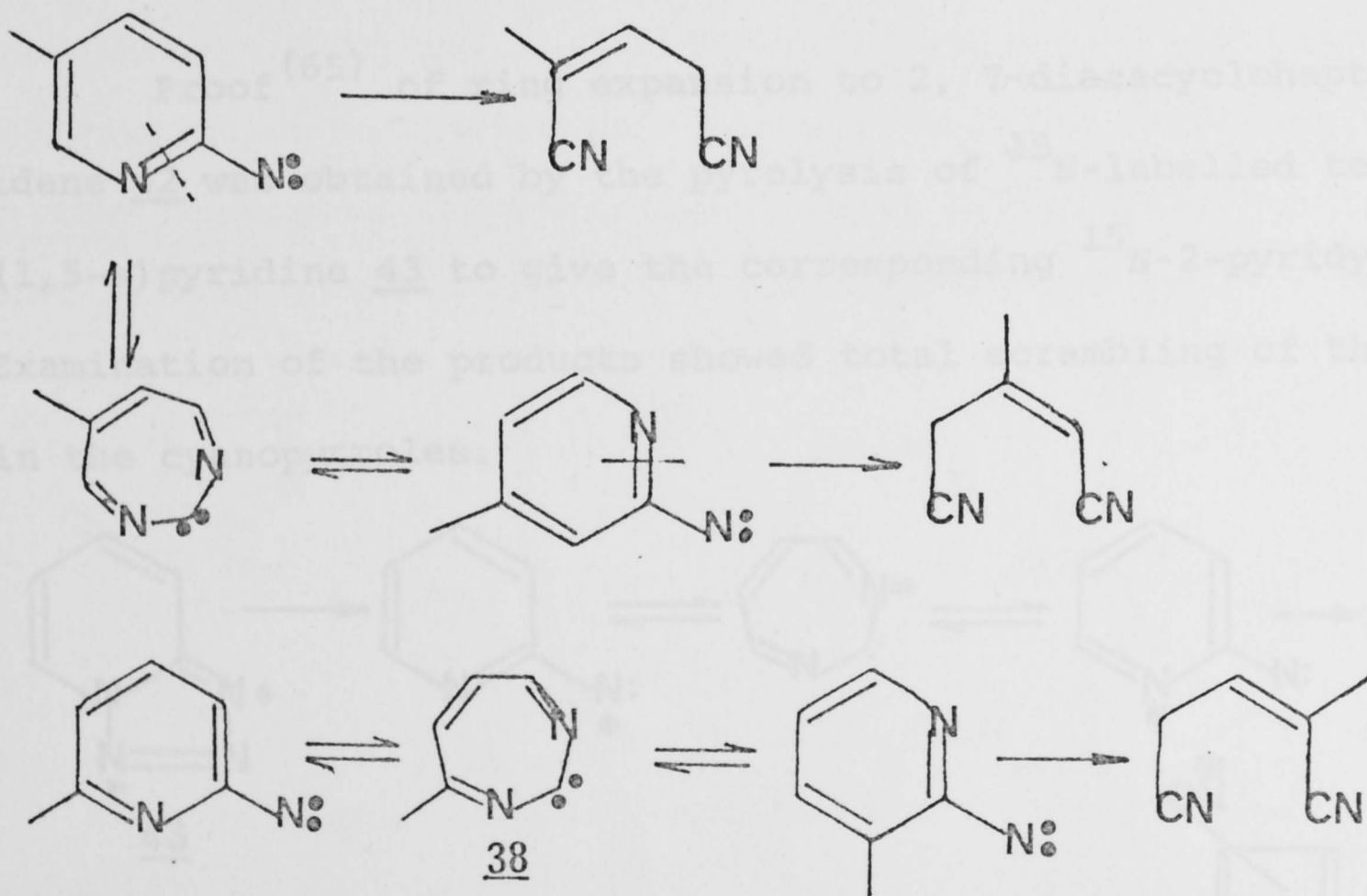
38

This ring expansion/contraction mechanism prior to the

formation of the prefulvene intermediate 35, was further

indicated by examining the amines obtained from the pyrolysis

of 8-methyl-tetrazolo(1,5-a)pyridine 39, which gave a mixture

of the amines 40 and 41.
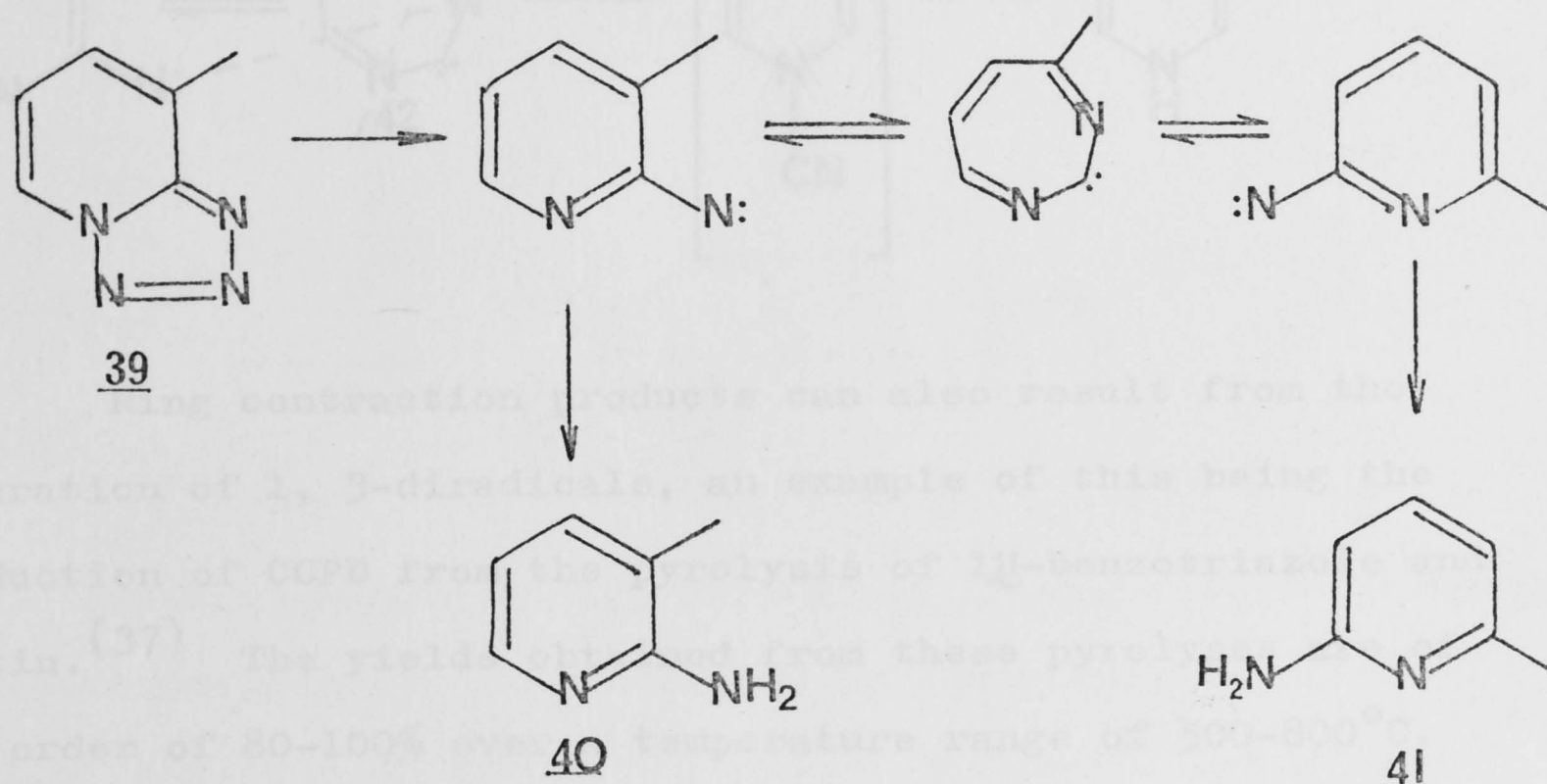
Proof[65] of ring expansion to 2, 7-diazacycloheptatrienyl-

idene 42 was obtained by the pyrolysis of ^{15}N-labelled tetrazolo-

(1,5-a)pyridine 43 to give the corresponding ^{15}N-2-pyridylnitrene.

Examination of the products showed total scrambling of the ^{15}N

in the cyanopyrroles.
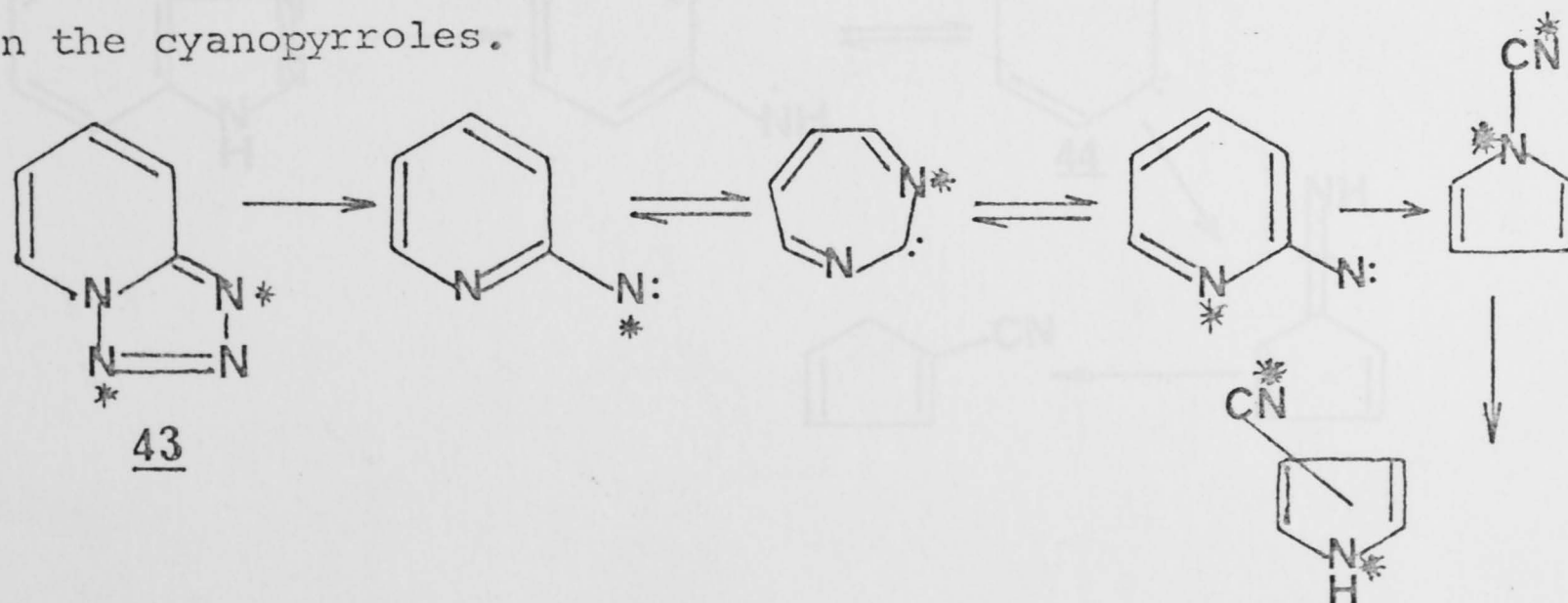
One other mechanism for the ring contraction can also give these same results:- direct ring contraction from <u>42</u> to give the 1-cyanopyrrole which subsequently rearranges to the observed products.
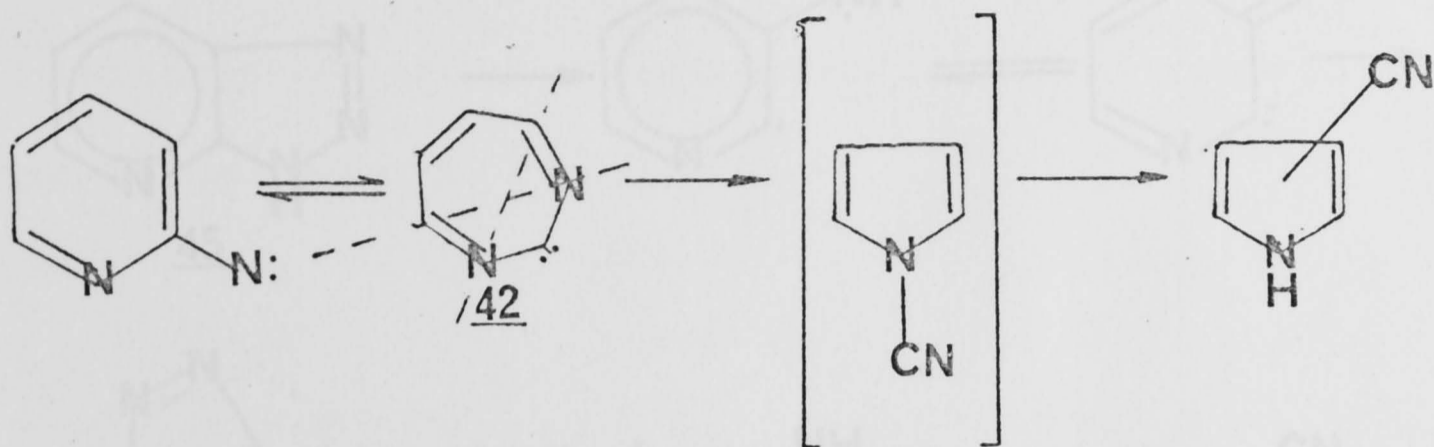
Ring contraction products can also result from the generation of 1, 3-diradicals, an example of this being the production of CCPD from the pyrolysis of 1H-benzotriazole and isatin.[37] The yields obtained from these pyrolyses are of the order of 80-100% over a temperature range of 500-800°C. The mechanism proposed for this mode of ring contraction is the generation of the 1, 3-diradical followed by electronic reorganisation to the singlet carbene 44. The imino-carbene <u>44</u> then undergoes rearrangement to give CCPD. This rearrangement is analogous to the Wolff rearrangement of keto-carbenes.
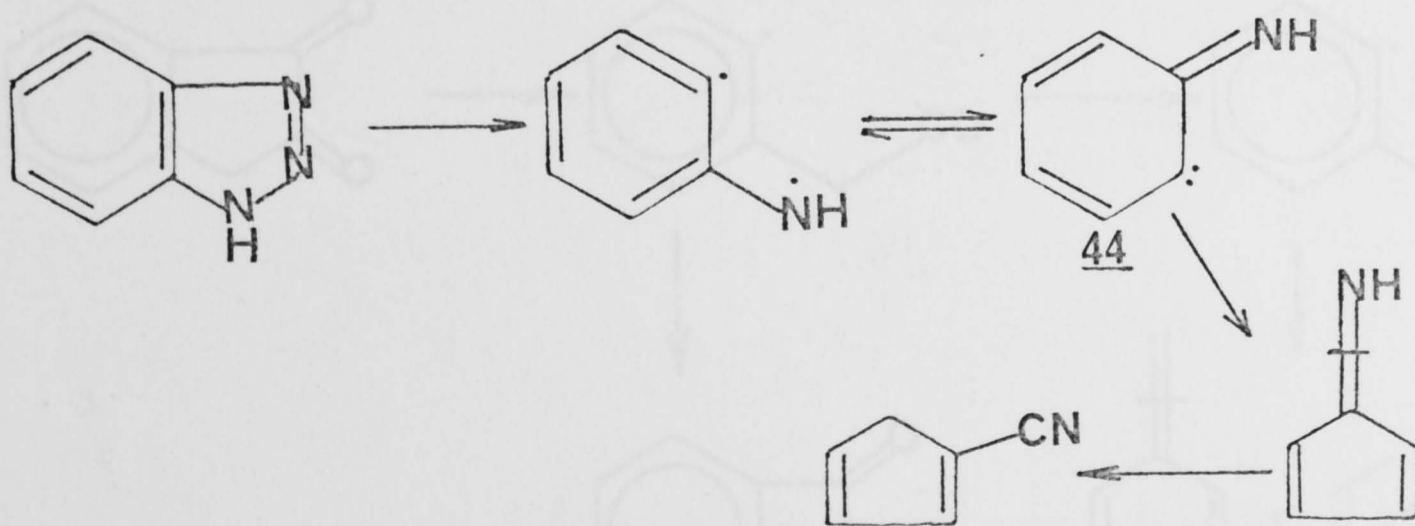
Similar results were obtained from the pyrolysis of triazolo(4,5-b)pyridine 45 and triazolo(4,5-c)pyridine 46[37] to give 2- and 3-cyanopyrrole.
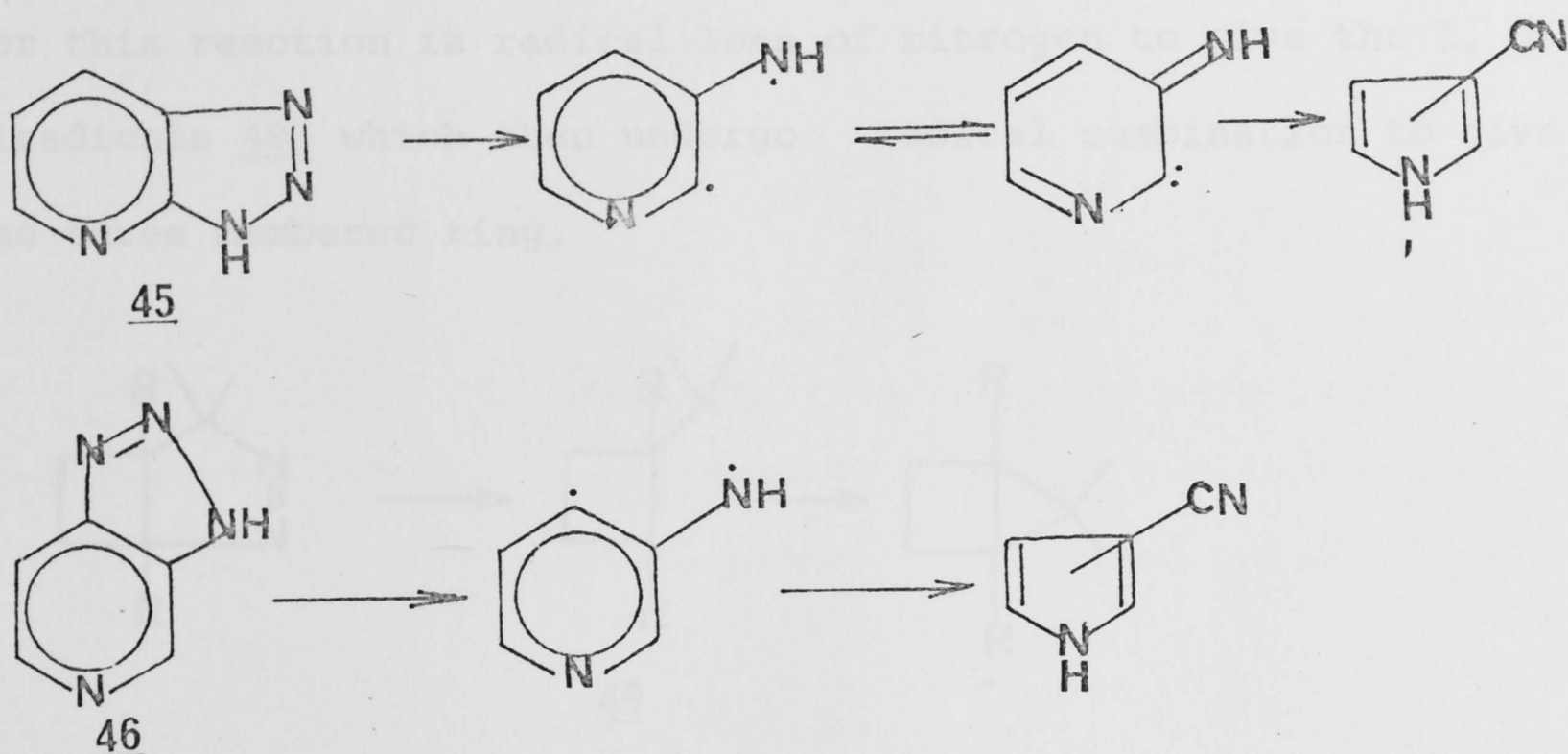
Another example of 1,3-diradicals giving rise to ring contraction products was furnished by the pyrolysis of the carbon analogue of isatin : indan -1,2-dione[38] which gave rise to the phenylcarbene ring contraction products fulven-allene 47 and ethynylcyclopentadiene 48. In this case the authors isolated the benzocyclobutenone (a similar intermediate was proposed for the decomposition of isatin).
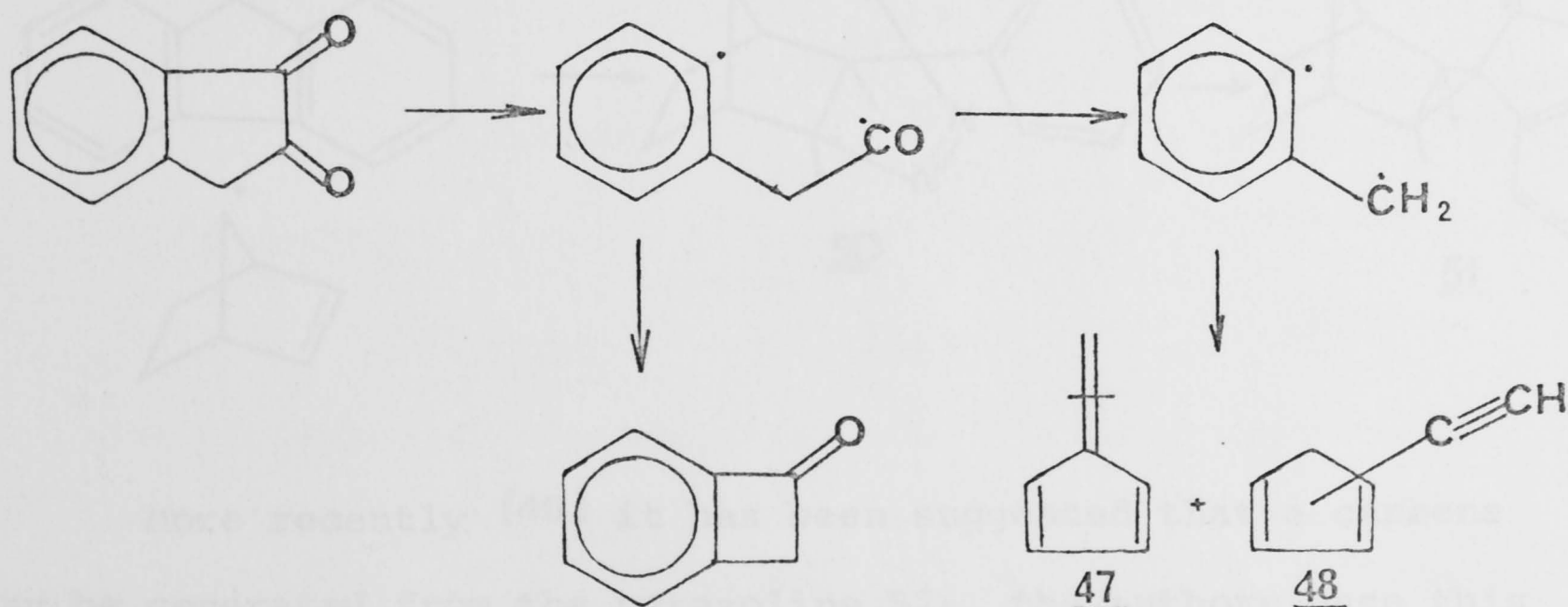
Pyrolysis of Pyrazolines, 3H-Pyrazoles and 1H-Pyrazoles

Pyrolysis of pyrazolines has long been known as a synthetic pathway for the formation of cyclopropanes;[39] the mechanism for this reaction is radical loss of nitrogen to give the 1, 3-diradicals 49 which then undergo radical combination to give the three membered ring.

49
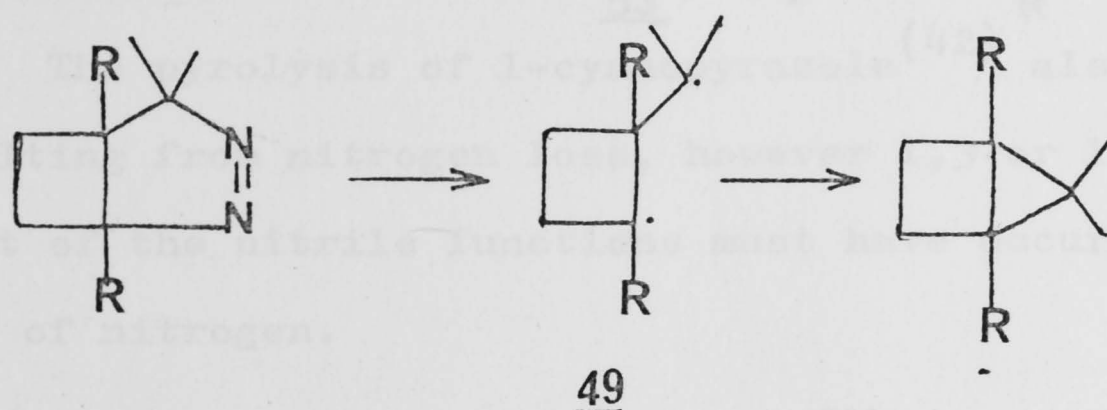
Another example of this reaction was obtained by the pyrolysis and photolysis of 9-diazofluorene in norbornene to give the pyrazoline 50, which then rearranged thermally and photolytically to the spiro-cyclopropane 51.

50

51
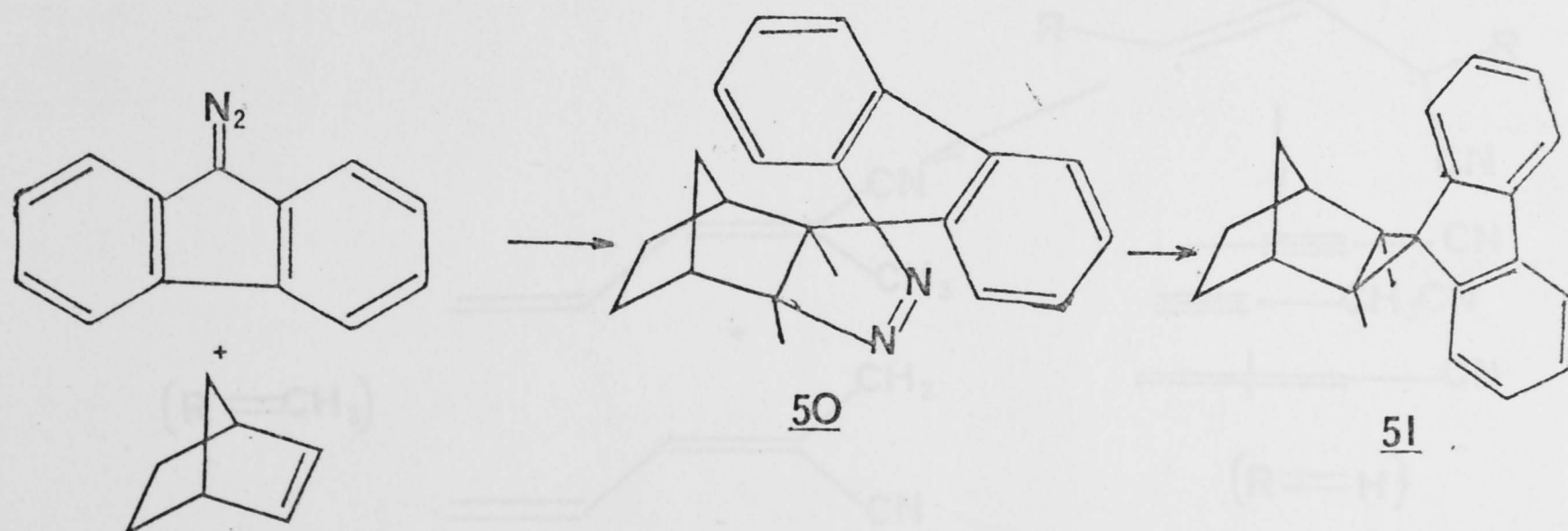
More recently [40] it has been suggested that a carbene may be generated from the pyrazoline 52: the authors base this proposal on the observation of the products 53 and 54 which could arise from the carbene 55.
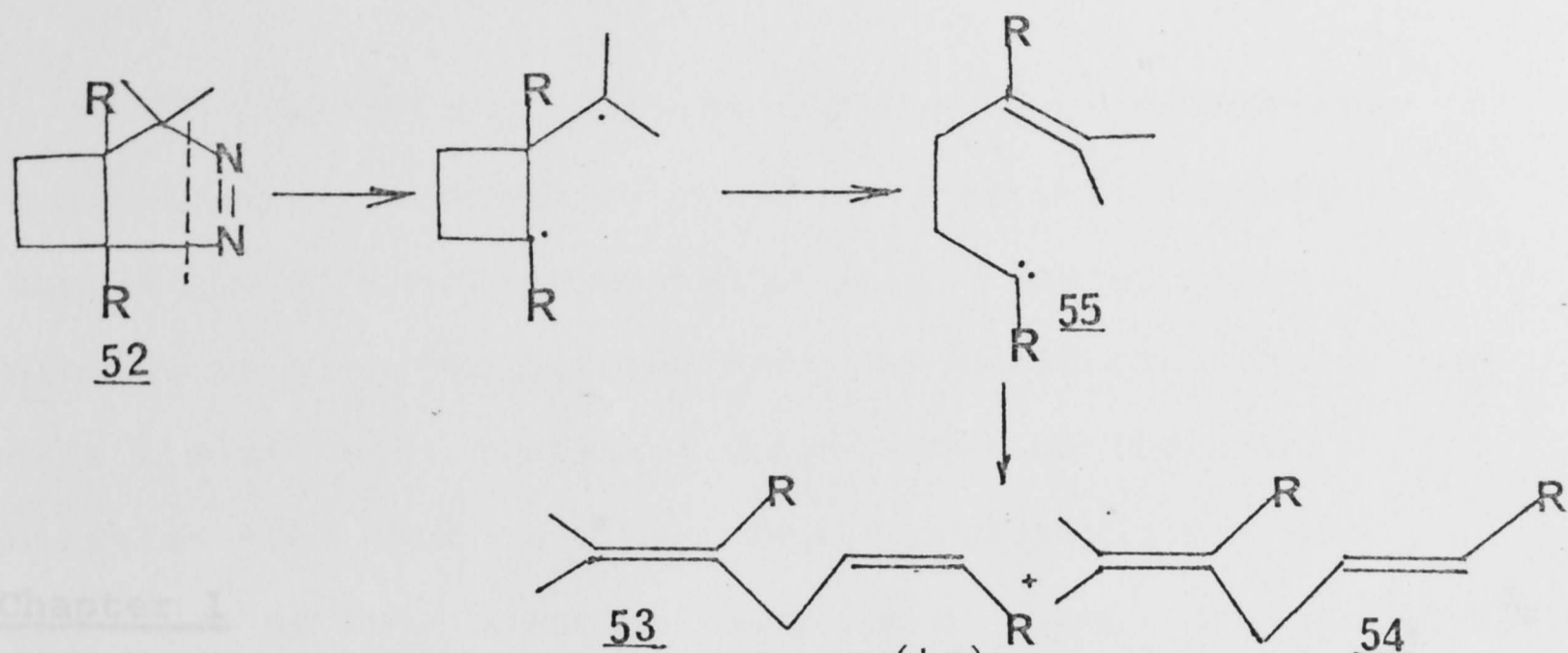
The pyrolysis of 1-cyanopyrazole[(42)] also gave products resulting from nitrogen loss, however 1,3-or 1,5-sigmatropic shift of the nitrile functions must have occurred prior to the loss of nitrogen.
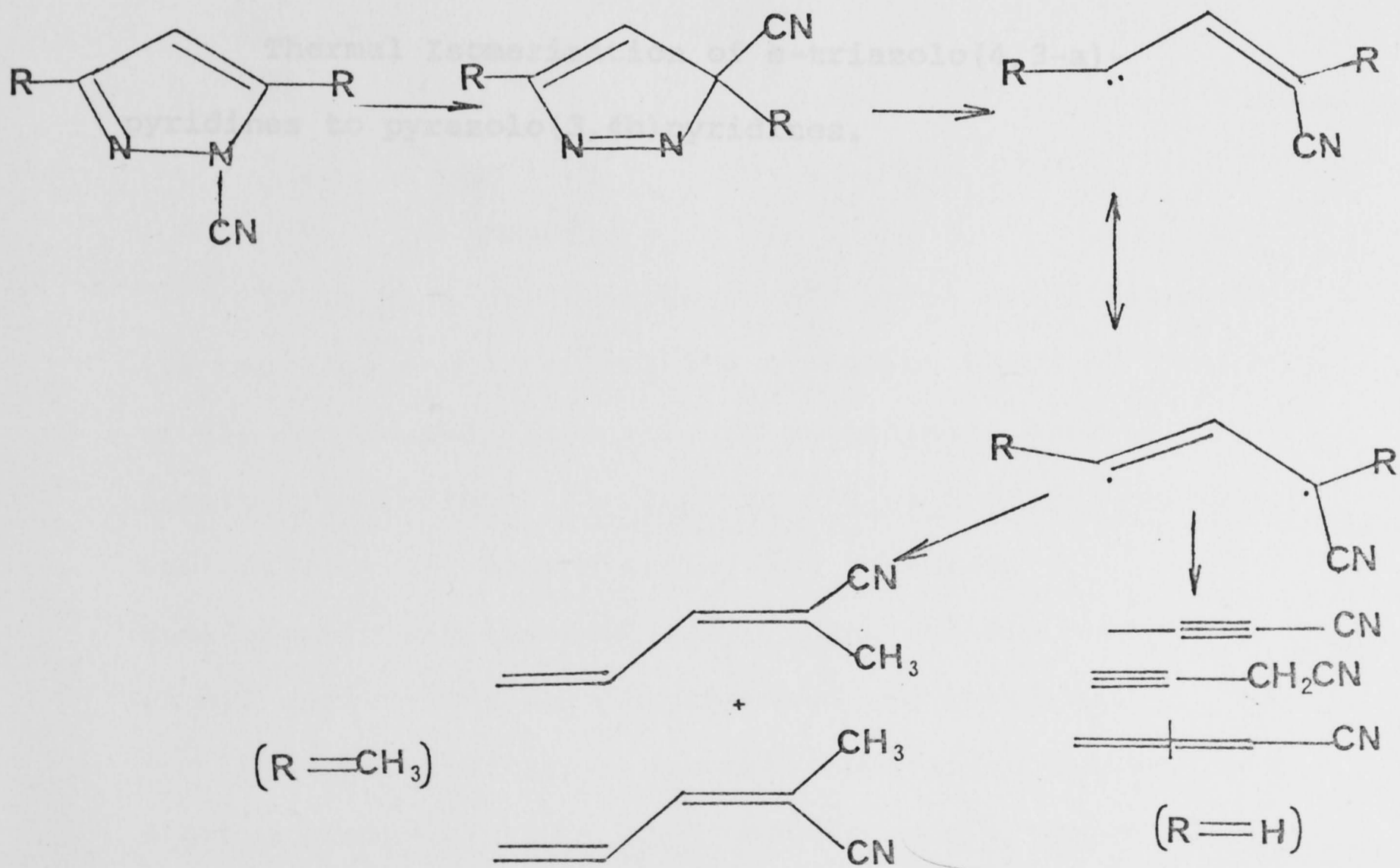
The pyrolysis of 1-methylpyrazoles[(42)] also showed this reaction pathway to give 4-methylpenta-1,3-diene (1-2%) and 2,3-dimethylbutadiene (5%) at 800° and 900° respectively.

Chapter 1

Thermal Isomerisation of s-triazolo(4,3-a)-
pyridines to pyrazolo(3,4b)pyridines.

The relative proportions of the 2-pyridylnitrene rearrangement products 2- and 3-cyanopyrrole may depend on the origin of the 2-pyridylnitrene. Loss of carbon dioxide to give the nitrene from the pyridooxadiazole 109 gave a mixture of different proportions of the two nitriles from that obtained when 2-pyridylnitrene was generated by the loss of nitrogen, e.g. from tetrazolo(1,5-a)-pyridine.
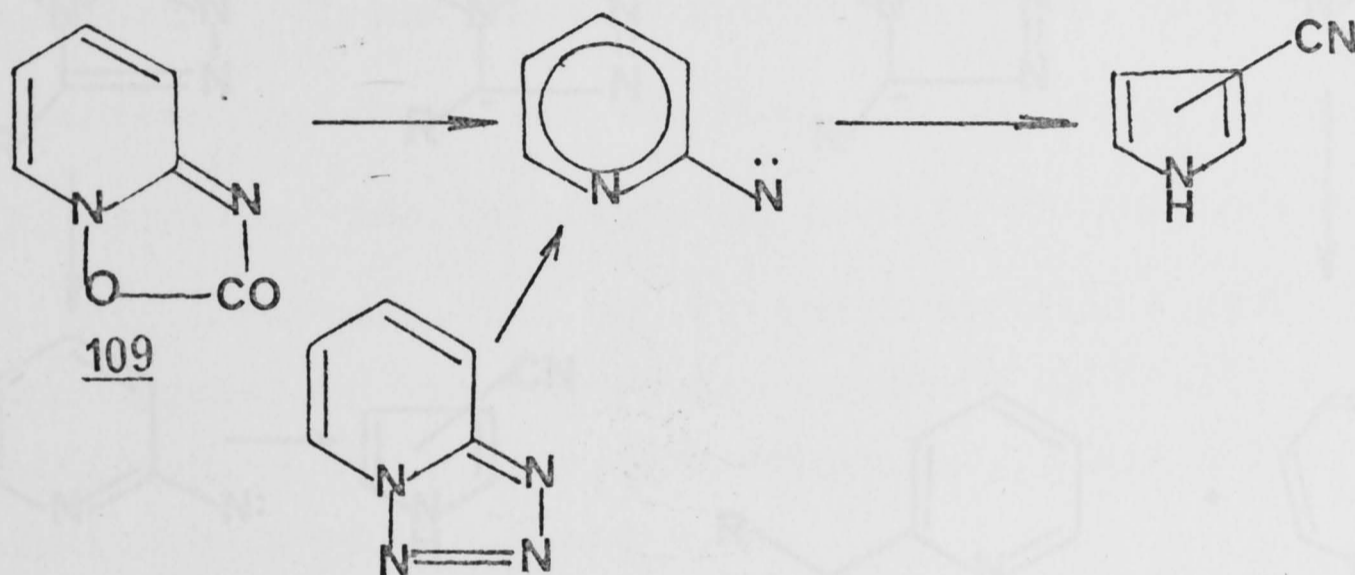
It is possible that these different proportions of the nitriles might reflect the different heats of formation of the two leaving groups. To investigate this possibility further, the leaving groups hydrogen cyanide, acetonitrile and benzonitrile were selected. Consequently s-triazolo(4,3-a)pyridine and its methyl and phenyl derivatives were synthesised and pyrolysed.

The possiblity of internal competition between the leaving groups alkyl or aryl nitriles and nitrogen also existed, with the loss of the nitrogen molecule leading to generation of 2-pyridylcarbene by a method

alternative to that achieved previously.[29] It was considered

of some interest to observe whether the 2-pyridylcarbene

so obtained would also show the products of triplet state

after isomerisation to phenylnitrene, as did the carbene

from v-triazolo(1,5-a)pyridine.[29]
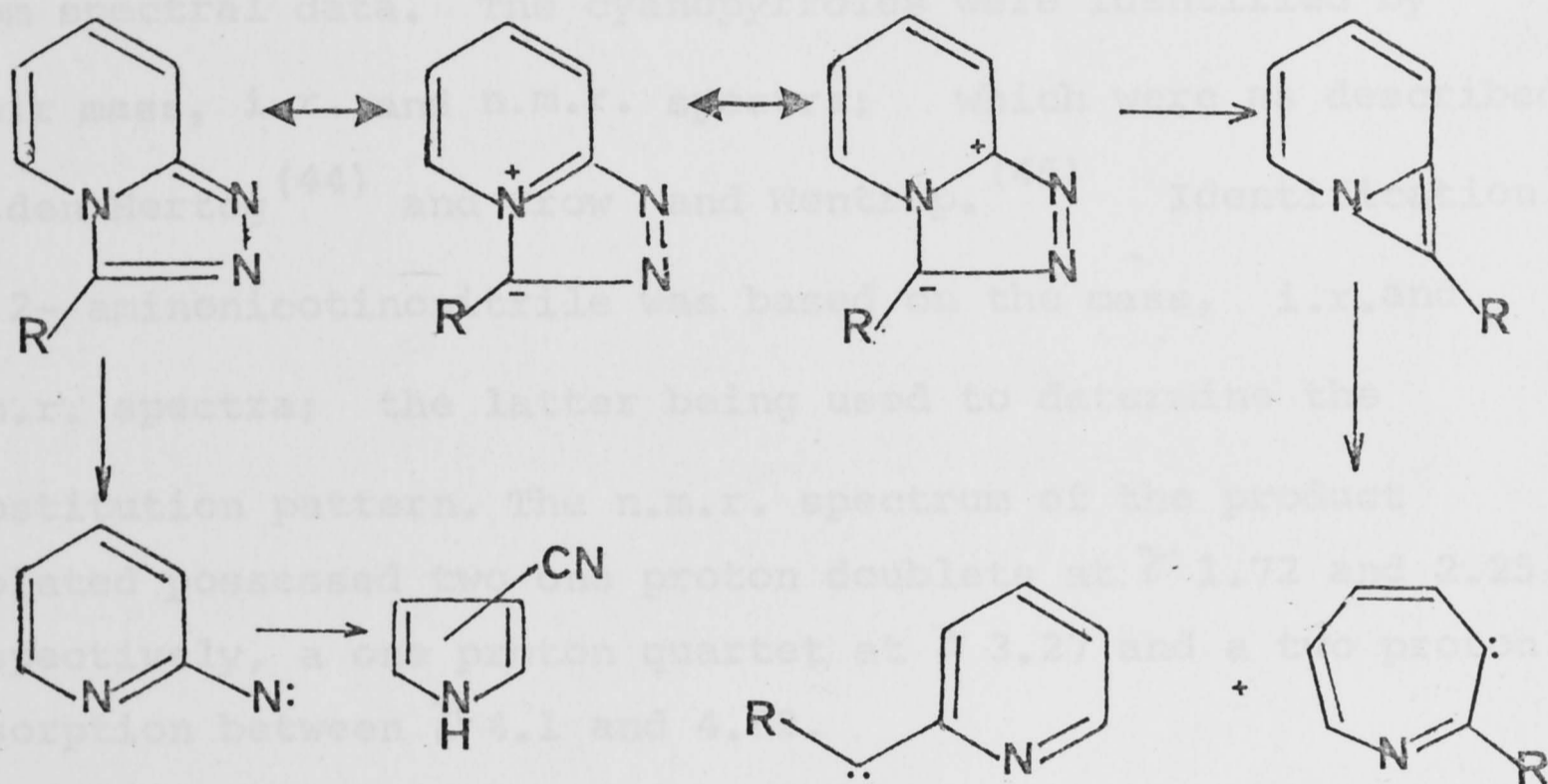
The gas phase thermolysis of s-triazolo(4,3-a)-

pyridine did show the two decomposition pathways expected, i.e.

loss of nitrile to give the ring contraction products of

2-pyridylnitrene, and loss of nitrogen to give products of

the C_6H_5N energy surface. By way of contrast to the substituted

s-triazolo(4,3-a)pyridines, pyrolysis of s-triazolo(4,3-a)pyridine

itself gave only small yields of products arising from

these two pathways, but gave 2-aminonicotinonitrile in

fair yield. The products and yields for these pyrolyses at 800°C are given in Table 1.

The products from these pyrolyses were (in general) purified by preparative g.l.c. and structures were assigned from spectral data. The cyanopyrroles were identified by their mass, i.r. and n.m.r. spectra; which were as described by den Hertog[44] and Crow and Wentrup.[45] Identification of 2- aminonicotinonitrile was based on the mass, i.r.and n.m.r. spectra; the latter being used to determine the substitution pattern. The n.m.r. spectrum of the product isolated possessed two one proton doublets at τ 1.72 and 2.25 respectively, a one proton quartet at τ 3.27 and a two proton absorption between τ 4.1 and 4.82.

The four isomers A - D are those which appear mechanistically possible; of these A can be dismissed as having no 2-proton to correspond with the signal at τ 1.72. Structure B can likewise be eliminated on the basis of the simplicity of the coupling (a singlet α , doublet β and γ) to be expected of its n.m.r. signals. The N.M.R. data is consistent only with structures C and D which could only be resolved by the preparation of 2- aminonicotinamide[47] from the material obtained by pyrolysis.

TABLE 1   800°C pyrolysis of s-triazolo(4,3-a)pyridines.

Product	Parent Compound	3-methyl derivative	3-phenyl derivative
2-aminonicotinontrile	53%	3%	–
2-cyanopyrrole	trace	16%	6%
3-cyanopyrrole	trace	19%	12%
benzonitrile	–	4%	43%
2-vinylpyridine	–	1%	–
3-vinylpyridine	–	32%	–
carbazole	–	–	3%
4-azafluorene	–	–	16%

3-vinylpyridine was identified by comparison of the mass, i.r. and n.m.r. spectra with those obtained from an authentic specimen, which was prepared by Wittig reaction on pyridine-3-aldehyde.   The trace quantities of 2-vinyl-pyridine were identified by g.l.c./m.s. with the characteristic mass spectrum being used as the primary evidence[12] for its identification. [M⁺ 105 (100%), (M-26)⁺ 67%.]

    Carbazole was identified by g.l.c./m.s. and further verified by submitting the effluent from the gas chromatograph to thin layer chromatography. 4-Azafluorene (5H-indeno (1,2b)pyridine) was tentatively identified by g.l.c./m.s., i.r. and n.m.r. but could only be differentiated from the other possibility 1-azafluorene (5H-indeno (1,2b)pyridine) by comparison with the authentic material. The melting point[30] and u.v. spectrum[51] of the material obtained from pyroly-

A

B

C

D

3-Vinylpyridine was identified by comparison of the

mass, i.r. and n.m.r. spectra with those obtained from an

authentic specimen, which was prepared by Wittig reaction on

pyridine-3-aldehyde. The trace quantities of 2-vinyl-

pyridine were identified by g.l.c./m.s. with the characteristic

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verified by submitting the effluent from the gas chromatograph

to thin layer chromatography. 4-Azafluorene (5H-indeno

(1, 2b)pyridine) was tentatively identified by g.l.c./m.s.,i.r.

and n.m.r.but could only be differentiated from the other

possibility 1- azafluorene (9H - indeno (2, 1b)pyridine) by

comparison with the authentic material. The melting point [50]

and u.v. spectrum [51] of the material obtained from pyrolysis

agrees with the recorded data for 4-azafluorene but the
melting point and u.v. spectrum for 1-azafluorene are not
recorded.

The mechanism proposed for formation of products from
the C_6H_5N energy surface involves a (1,5) sigmatropic shift
to 3aH-pyrazolo(3, 4b)pyridine 58 followed by further
sigmatropic hydrogen shifts and loss of nitrogen as indicated
below to give the presumed generators of the observed products.
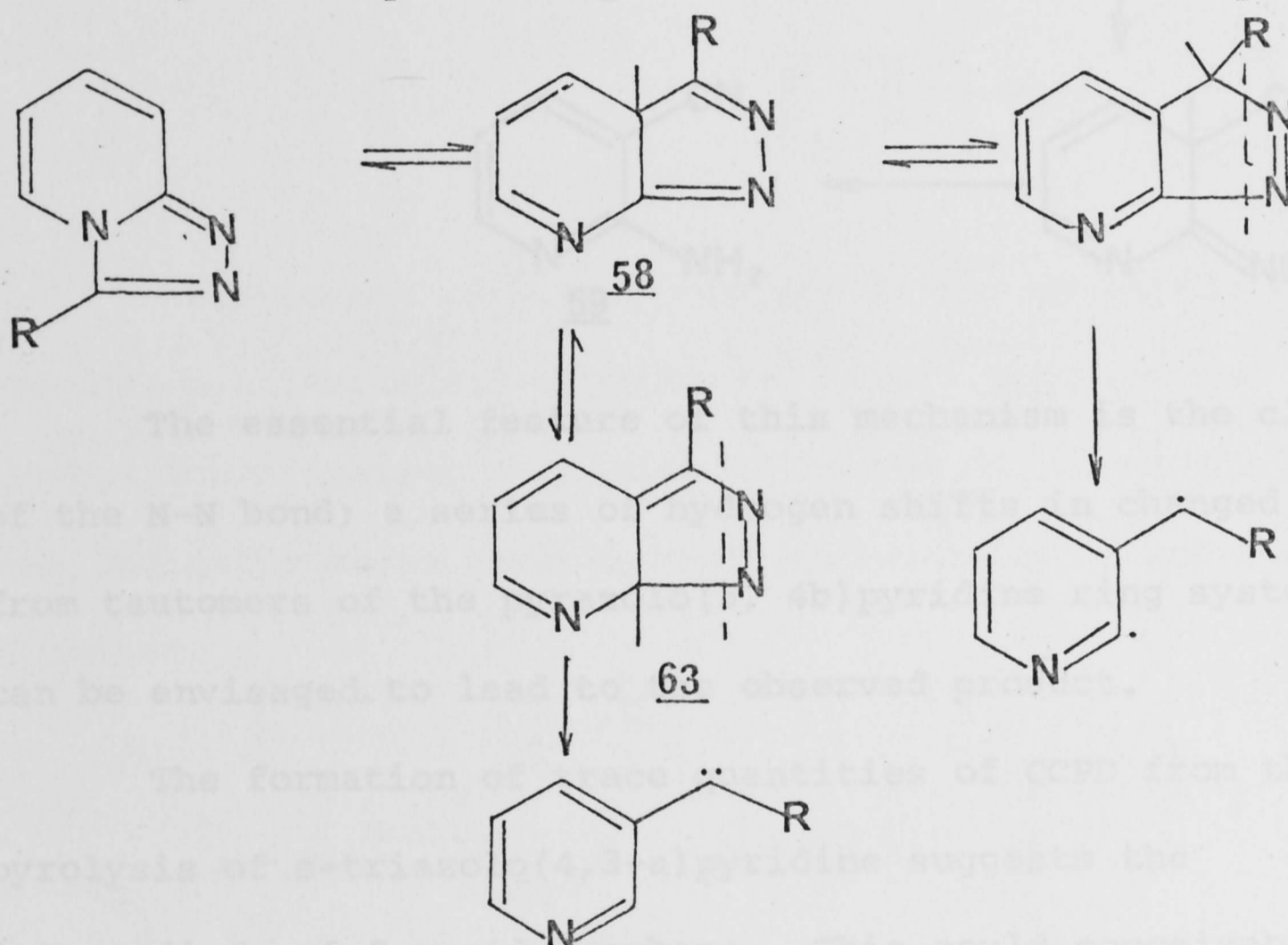
The observation of the formation of 2-aminonicotinonitrile
59 from the thermolysis of s-triazolo(4,3-a)pyridine 60 was
initially the reason for selecting this mechanism, since other
possible mechanisms (to be discussed at a later point in this
chapter), do not predict its formation. 2-Aminonicotinonitrile
can arise directly from 61, by radical cleavage of the N-N bond
to give the diradical 62. Rotation could then occur (as shown)

about the C-C bond which is followed by radical abstraction of a hydrogen atom and 1,3 hydrogen shift to give 59.
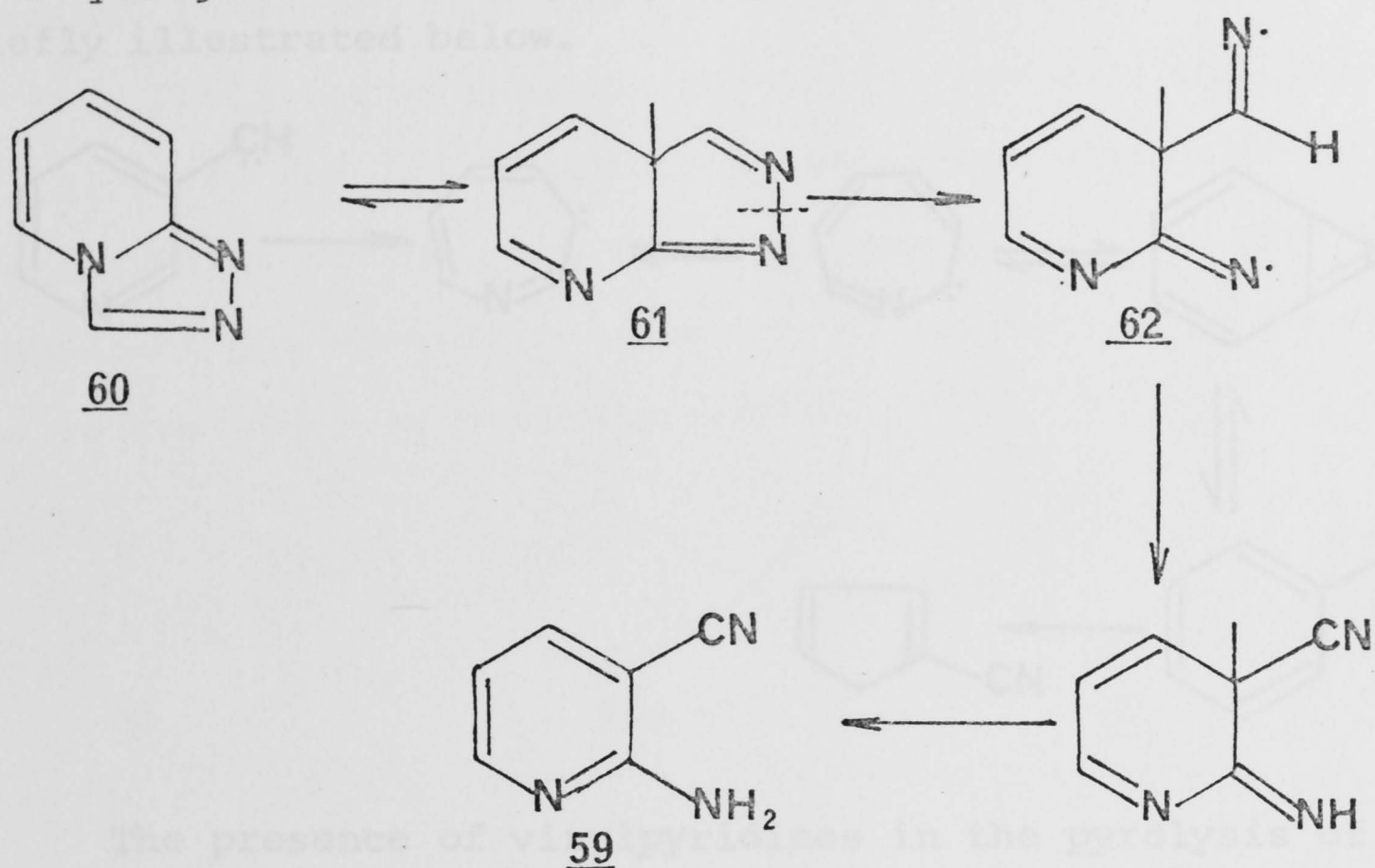
The essential feature of this mechanism is the cleavage of the N-N bond; a series of hydrogen shifts in changed order from tautomers of the pyrazolo(3, 4b)pyridine ring system can be envisaged to lead to the observed product.

The formation of trace quantities of CCPD from the pyrolysis of s-triazolo(4,3-a)pyridine suggests the intermediacy of 3-pyridylcarbene. This could conceivably arise by a (1,5) sigmatropic hydrogen shift to the 7aH-pyrazolo(3, 4b)pyridine and subsequent nitrogen loss.

The selection of 63 and 3-pyridylcarbene as intermediates, in the formation of CCPD, arose from the results obtained for the thermolysis of lH-pyrazolo(3, 4b)pyridine (see section 2.1).

The reaction sequence for the conversion of 3-pyridylcarbene
to CCPD is discussed in further detail in section 2.1, but is
briefly illustrated below.
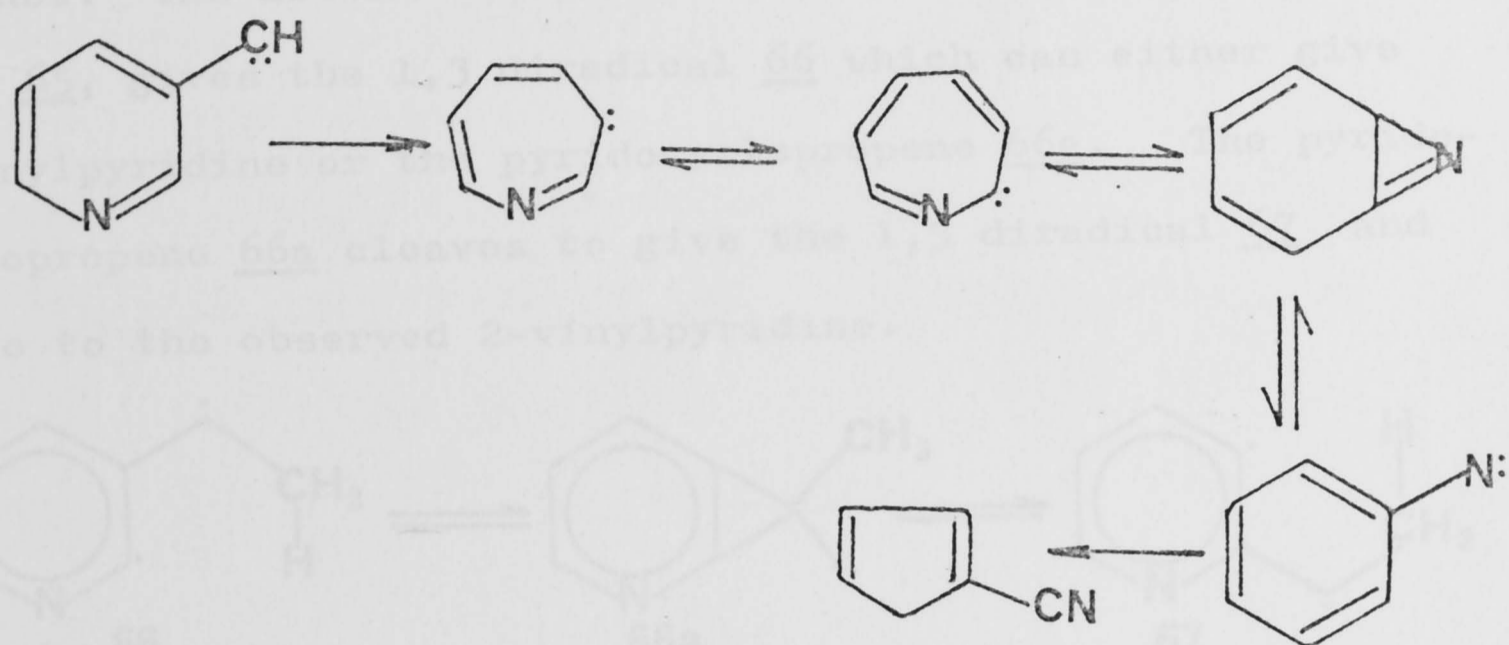
The presence of vinylpyridines in the pyrolysis of
3-methyl-s-triazolo(4,3-a)pyridine, offers good support to the
general isomerisation mechanism to 64 and 65, since they must
most logically arise from a methylpyridylcarbene or a 1,3
diradical.
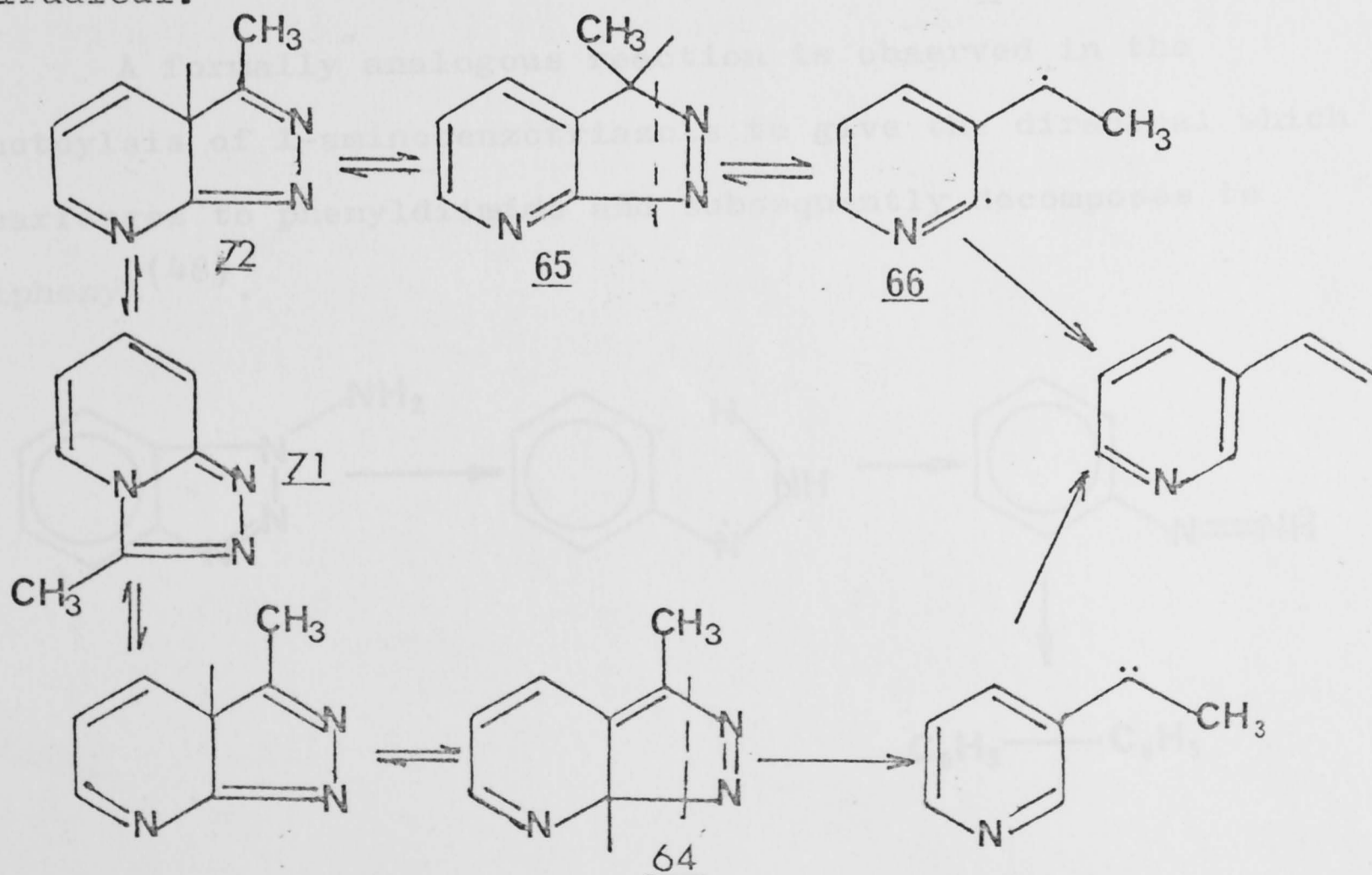
3-Vinylpyridine can be formed _via_ the (1,5) sigmatropic hydrogen shift to 64 followed by nitrogen loss to the carbene. The normal insertion into the C-H bond then gives the observed product. The alternate route, resulting from nitrogen loss from 65, gives the 1,3 diradical 66 which can either give 3-vinylpyridine or the pyridocyclopropene 66a. The pyrido-cyclopropene 66a cleaves to give the 1,3 diradical 67 and hence to the observed 2-vinylpyridine.
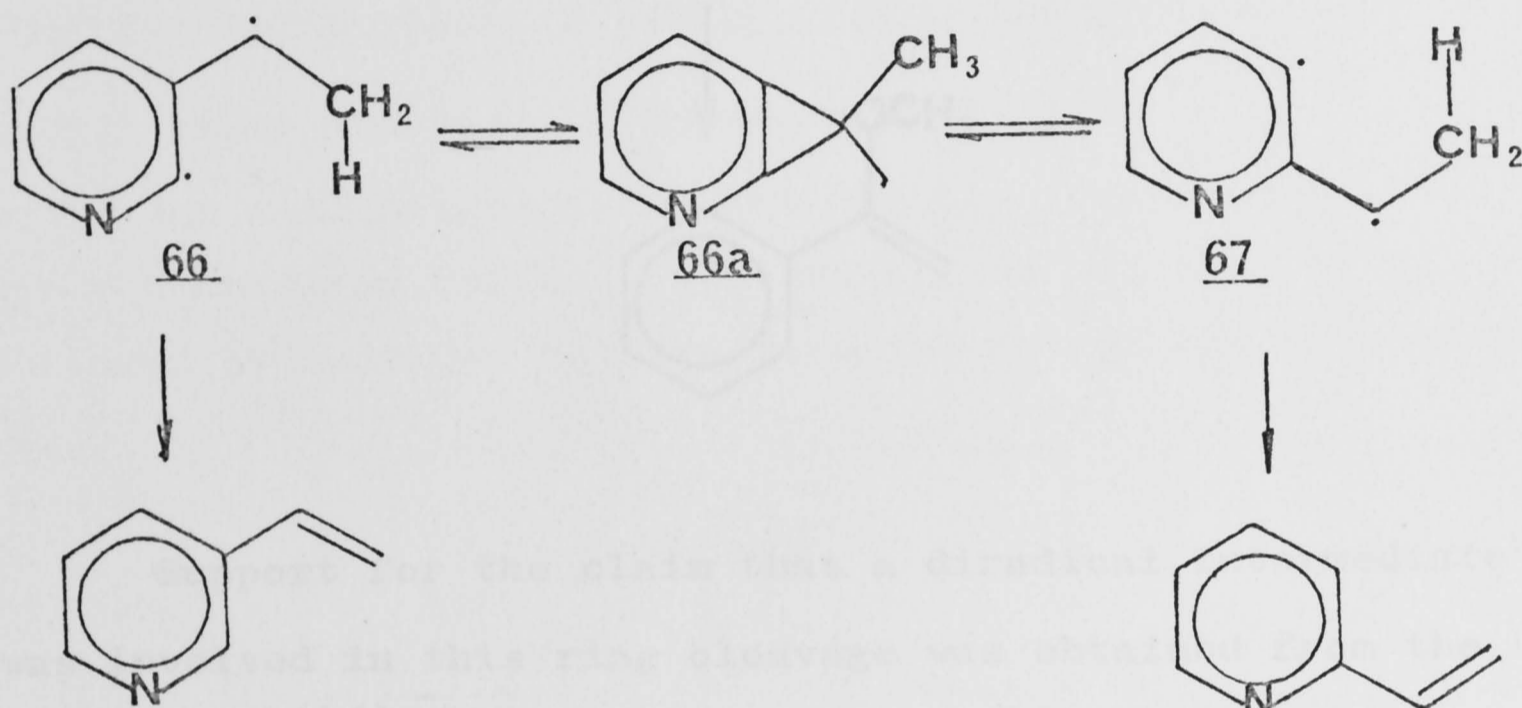
A formally analogous reaction is observed in the photoylsis of 1-aminobenzotriazole to give the diradical which rearranges to phenyldiimide and subsequently decomposes to biphenyl[48].
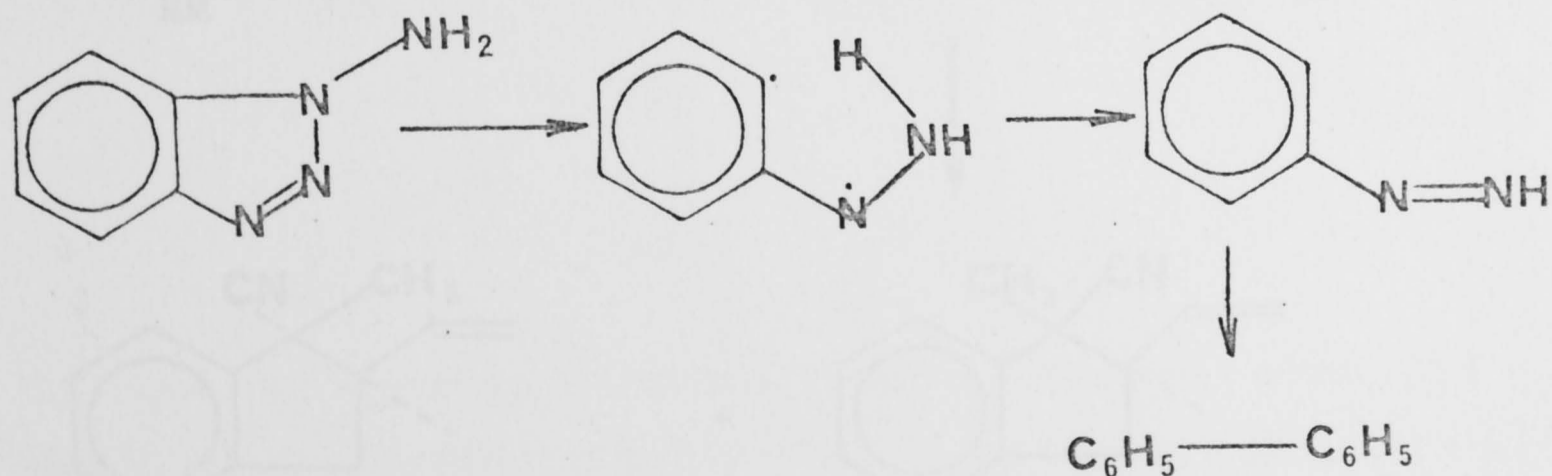
Thermal cleavage of the highly strained cyclopropene bond to give the diradicals <u>66</u> and <u>67</u> has been previously observed for the thermal decomposition of benzocyclopropenes[46] which were obtained in the photolysis of 3, 3-disubstituted indazoles.
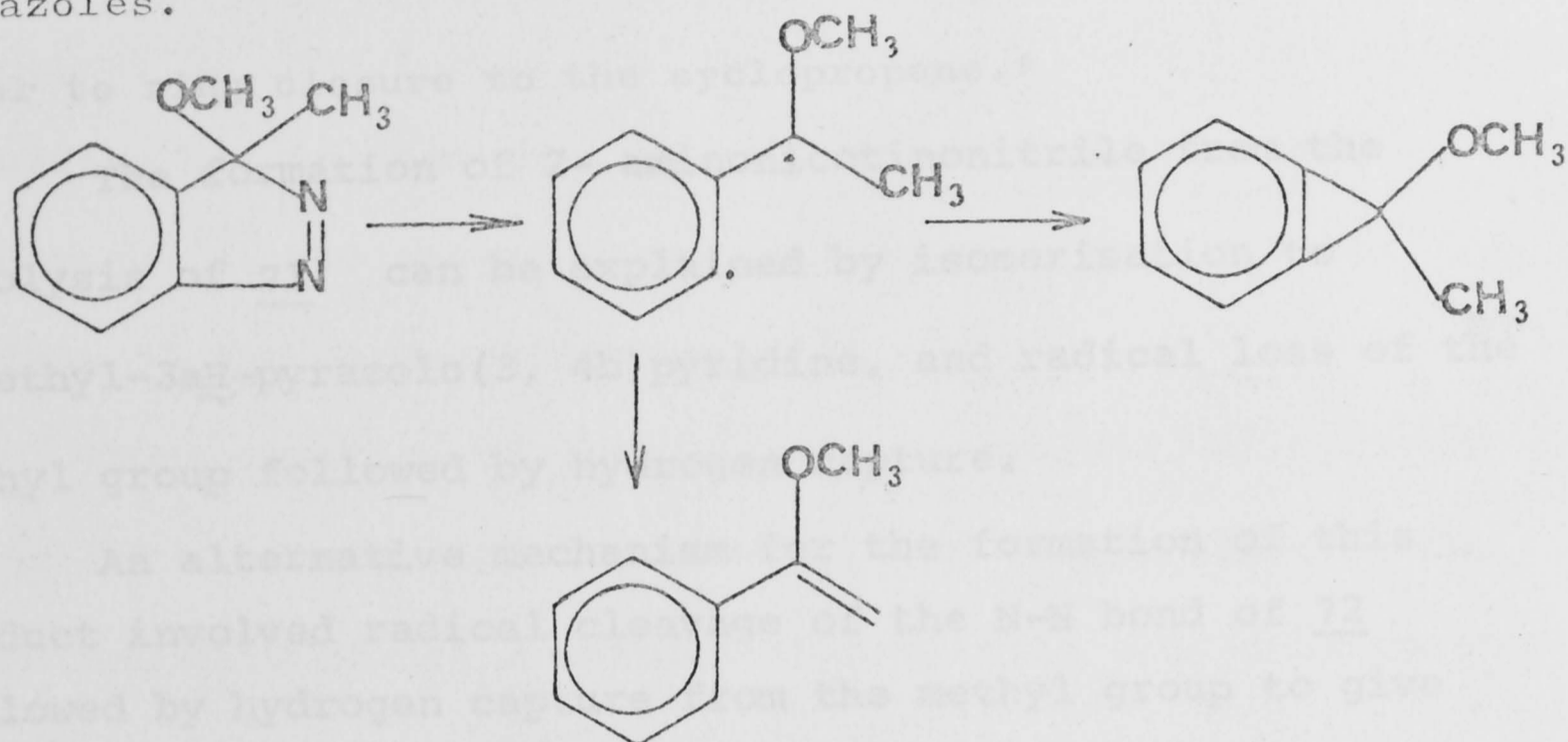
Support for the claim that a diradical intermediate was involved in this ring cleavage was obtained from the thermolysis[46] of the benzocyclopropene <u>68</u> in the presence of butadiene to give a 1:1 mixture of <u>69</u> and <u>70</u>.
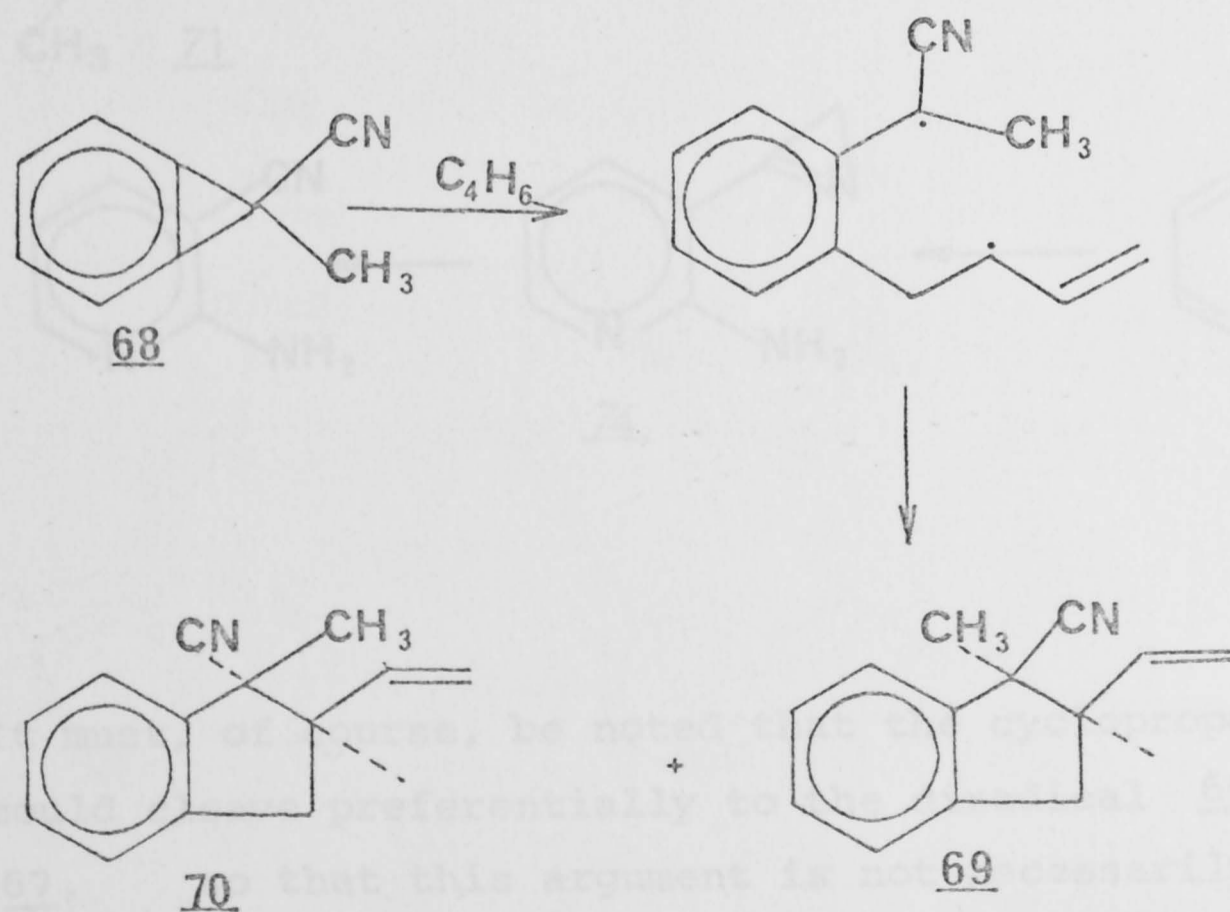
This type of mechanism also serves to explain the preponderance of the 3-vinylpyridine over the 2-isomer in the pyrolysis of 71. The radical hydrogen elimination/capture mechanism would be expected to facilitate product formation prior to ring closure to the cyclopropene.*

The formation of 2- aminonicotinonitrile from the pyrolysis of 71 can be explained by isomerisation to 3-methyl-3aH-pyrazolo(3, 4b)pyridine, and radical loss of the methyl group followed by hydrogen capture.

An alternative mechanism for the formation of this product involved radical cleavage of the N-N bond of 72 followed by hydrogen capture from the methyl group to give 73.
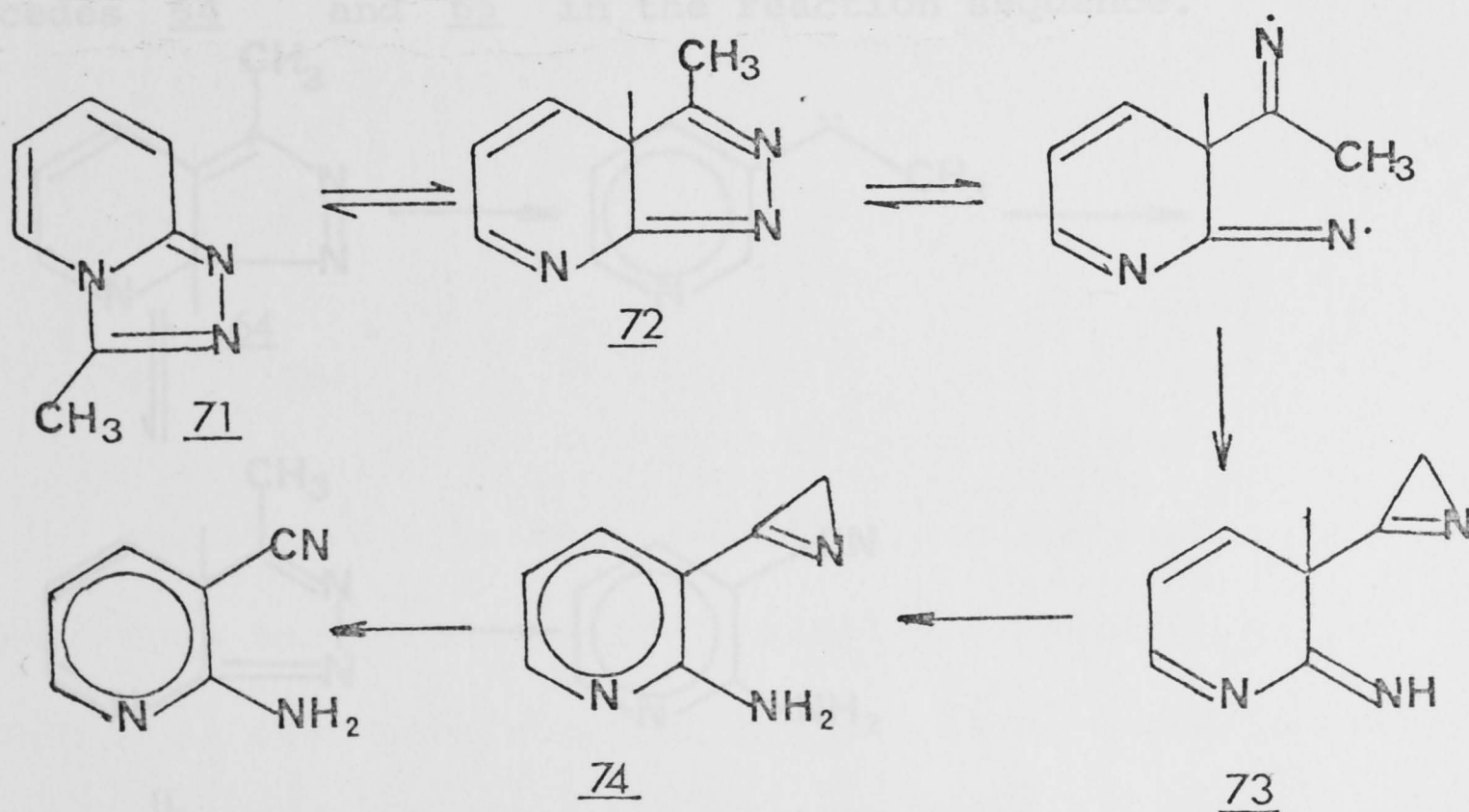
* It must, of course, be noted that the cyclopropene 66a could cleave preferentially to the diradical 66 rather than 67, so that this argument is not necessarily valid.

The iminoazirine 73 then undergoes a (1,3) hydrogen

shift to give the aminoazirine 74   which decomposes to give

methylene and the observed product.   Such a mechanism may seem

unnecessarily complicated, but this mode of thermal decomposition

of azirine has in fact been established by C.W. Rees and

co-workers[49],who showed that azirines generate carbenes by

the loss of the corresponding nitrile.

The suggestion of 3-methyl-3aH-pyrazolo(3, 4b)pyridine

as the intermediate, arising from 71 by rearrangement, does

imply that more of the 2-aminonicotinonitrile should be observed,

than was actually the case (3%),   for this intermediate

precedes 64   and 65   in the reaction sequence.

64

65
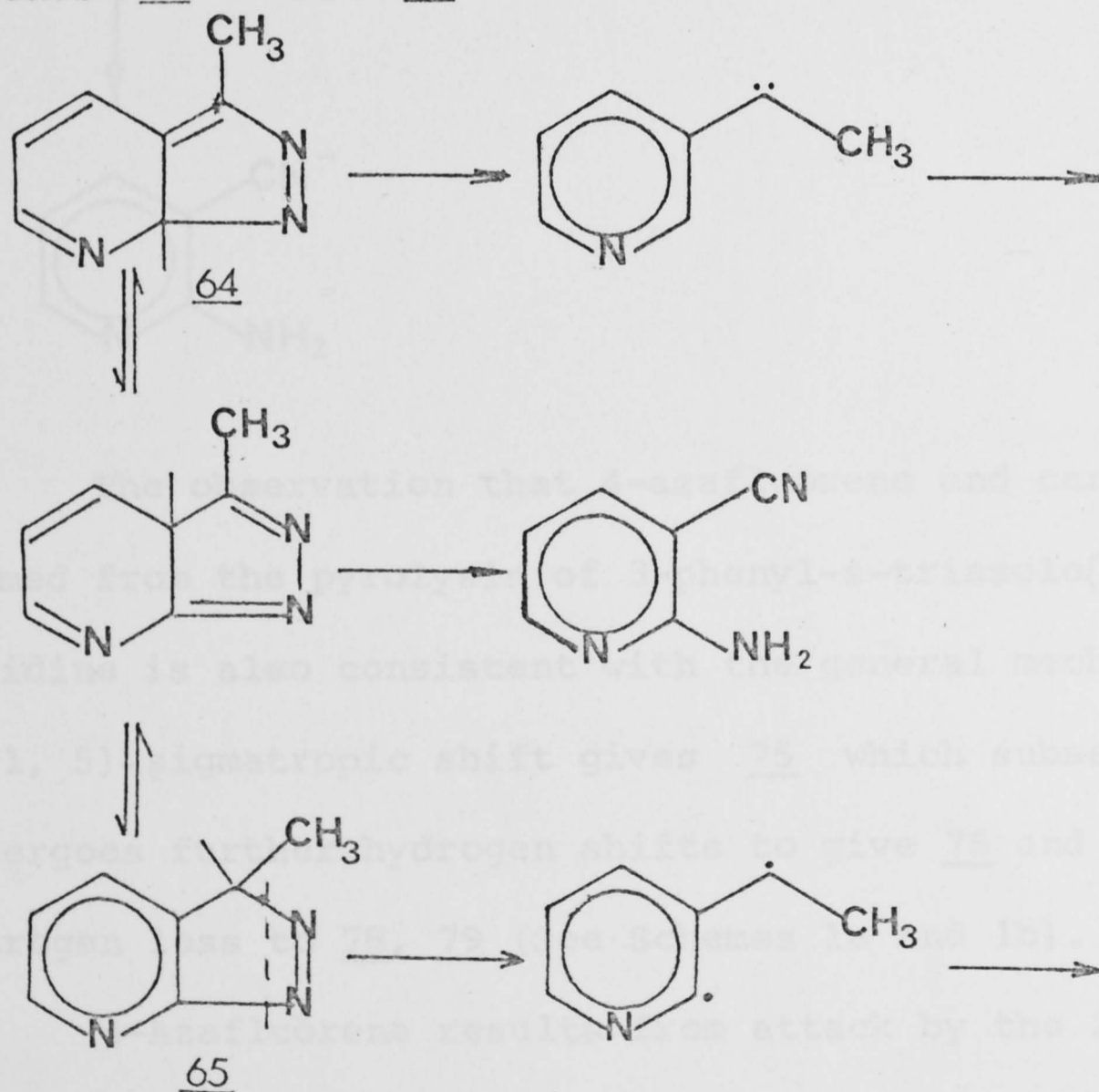
It seems clear that cleavage of the N-N bond proceeds
to a lesser extent in 71 than do the subsequent hydrogen
shifts to 64 and 65. This could in fact be due to
competing reaction paths. Concerted loss of acetonitrile
from 72 to give 2-pyridylnitrene could also compete with
the cleavage of the N-N bond. The methyl substitution could
have a tendency to increase the leaving group ability of
the nitrile and could explain the experimental findings.
(This mechanism will be discussed later in the chapter).
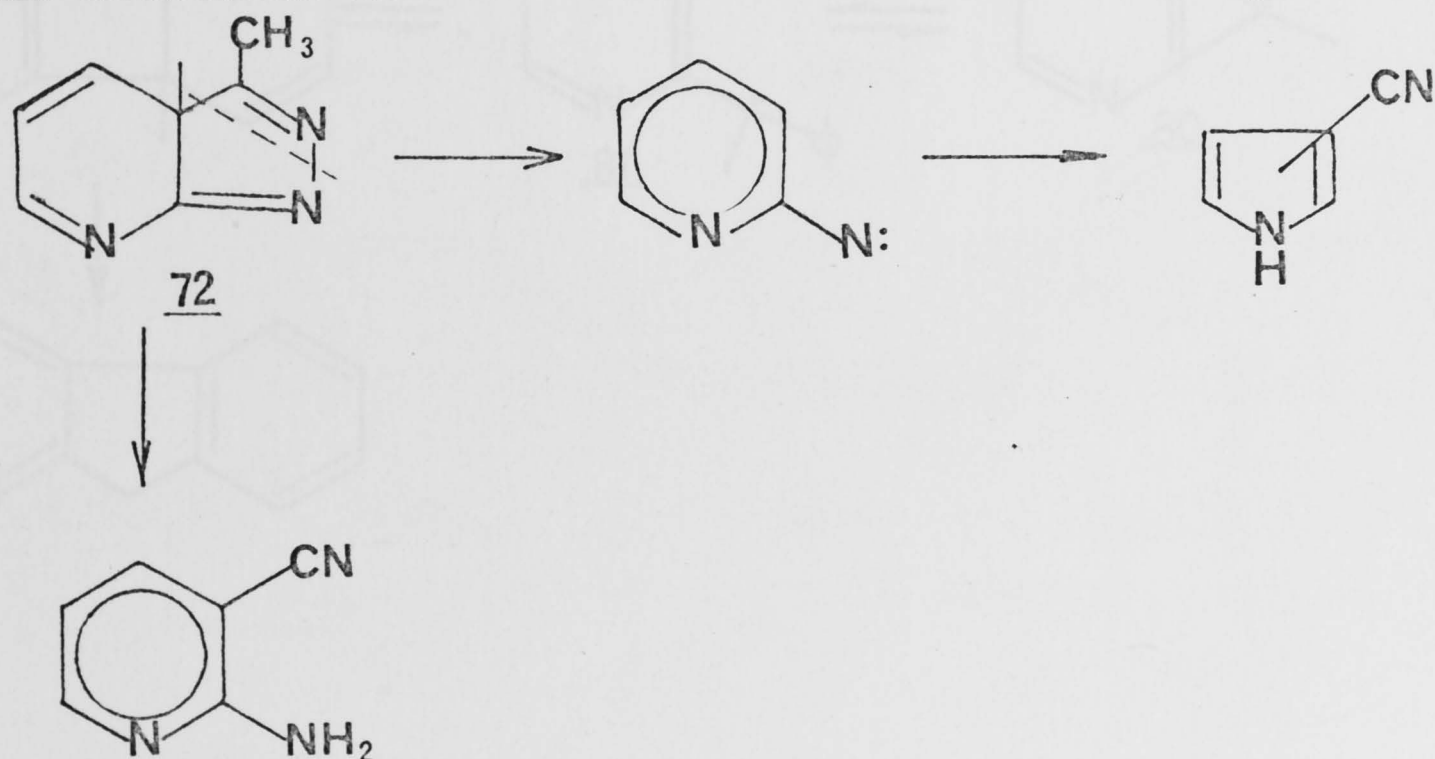
The observation that 4-azafluorene and carbazole were
formed from the pyrolysis of 3-phenyl-s-triazolo(4,3-a)-
pyridine is also consistent with the general mechanism proposed.
A (1, 5)-sigmatropic shift gives 75 which subsequently
undergoes further hydrogen shifts to give 76 and 77 with
nitrogen loss to 78, 79 (See Schemes 1a and 1b).

4-Azafluorene results from attack by the 2-pyridyl
radical site on the adjacent phenyl ring, followed by a (1,3)-
hydrogen shift.
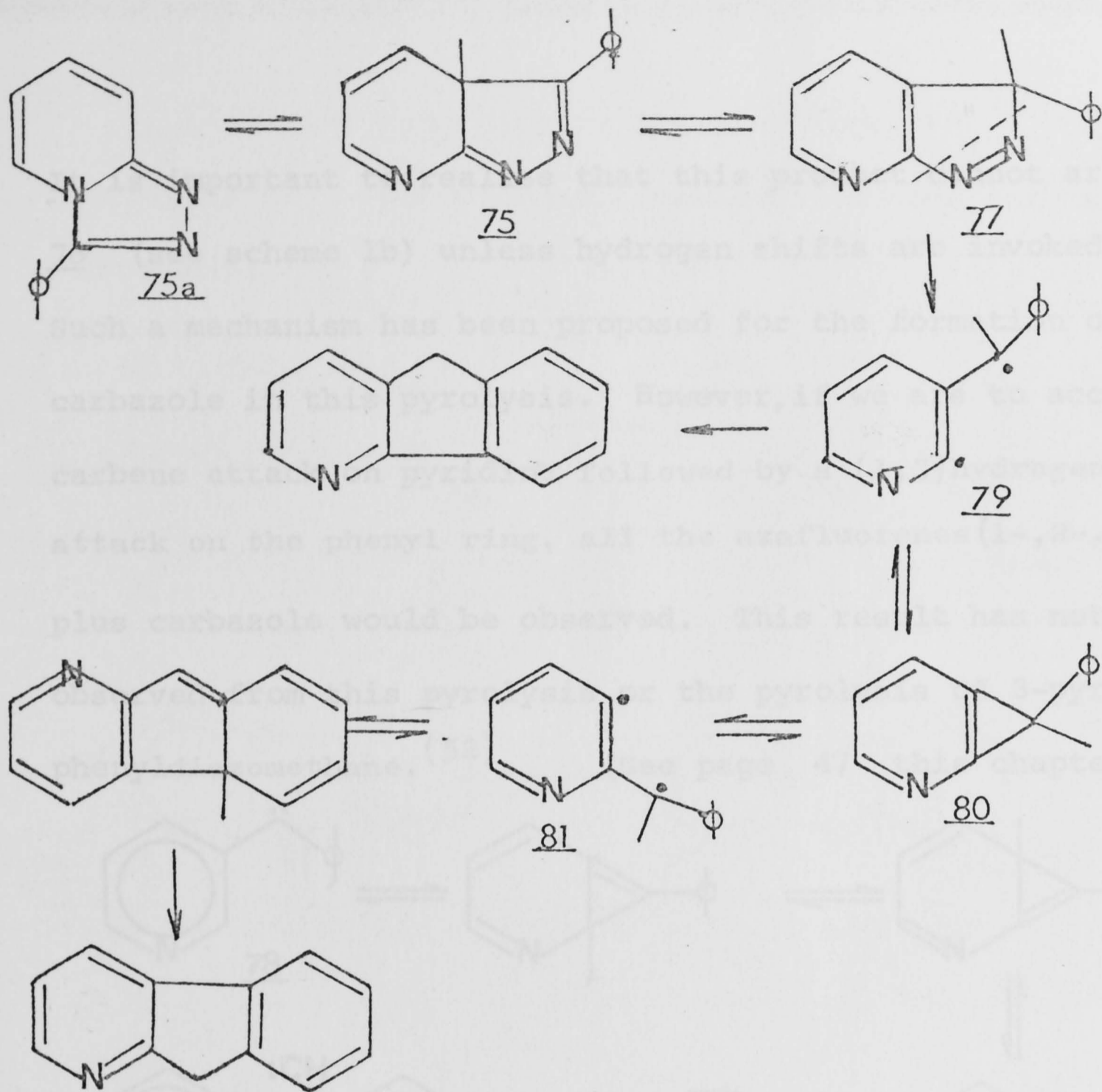
Scheme (1a)   1,3-Diradical Pathway to the Azafluorenes

It is important to realise that this product cannot arise from

78 (see scheme 1b) unless hydrogen shifts are invoked.

Such a mechanism has been proposed for the formation of

carbazole in this pyrolysis. However, if we are to accept this

carbene attack on pyridine followed by a (1,3)hydrogen shift and

attack on the phenyl ring, all the azafluorenes(1-,2-,3- and 4-)

plus carbazole would be observed. This result has not been

observed from this pyrolysis or the pyrolysis of 3-pyridyl-

phenyldiazomethane.[52]   (See page 47 this chapter).
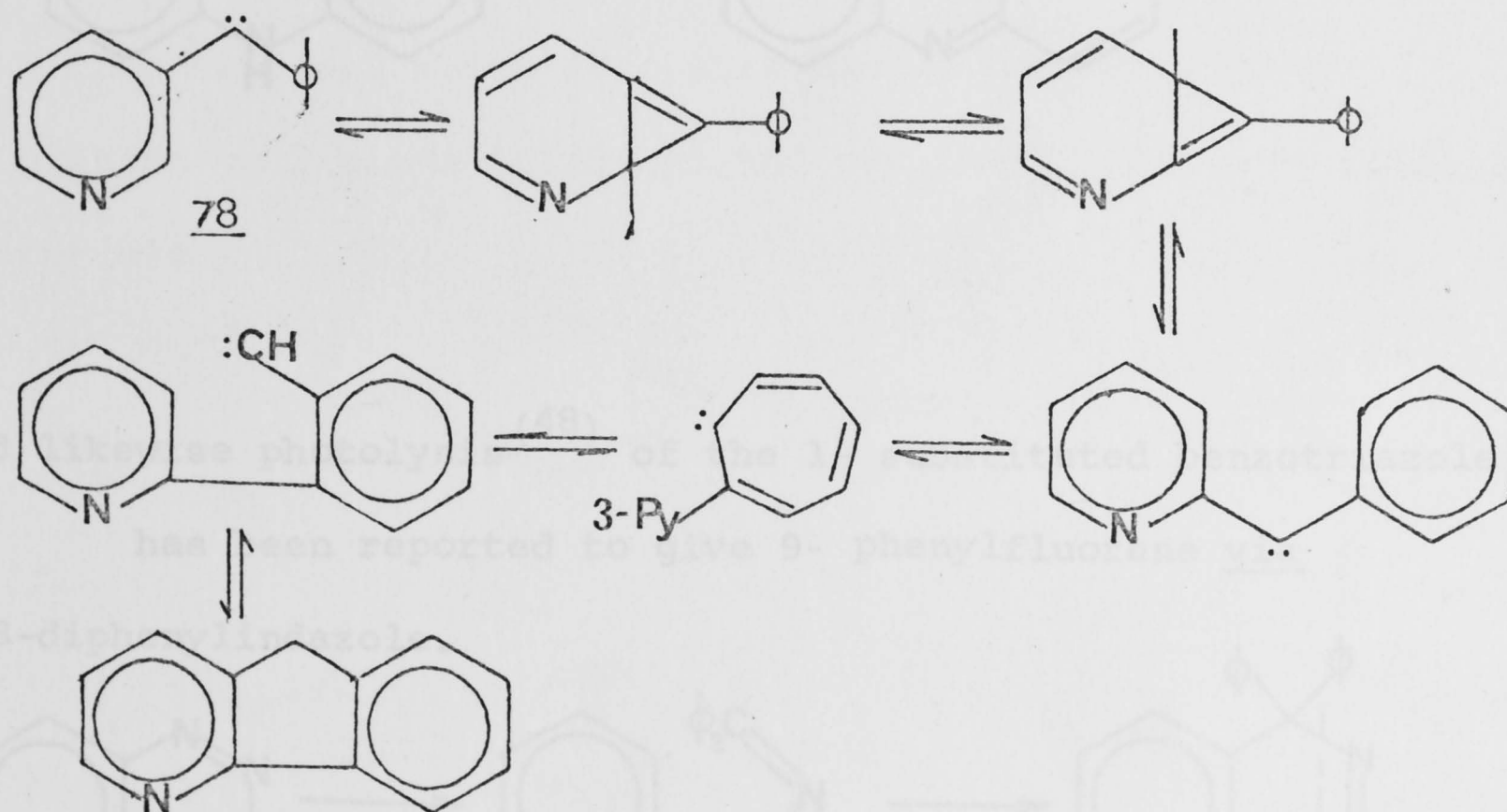
The possibility of observing 1-azafluorene (9H-indeno-

(2,1-b)pyridine exists (though not observed) via formation of

the pyridocyclopropene 80 which undergoes ring cleavage

to the diradical 81 and hence to product.

A similar ring closure has been reported[48] for the
photolysis of 1- phenylbenzotriazole which gave carbazole in
high yield,
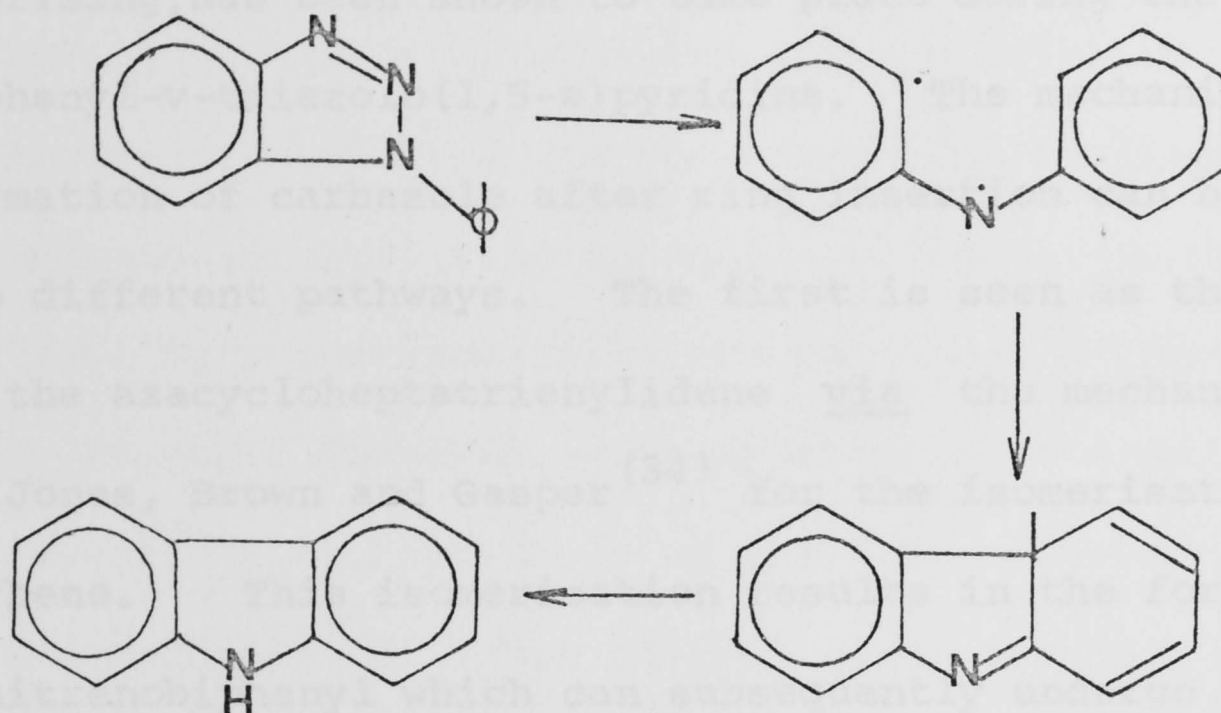
and likewise photolysis[48] of the 1- substituted benzotriazole
__82__ has been reported to give 9- phenylfluorene __via__
3,3-diphenylindazole.
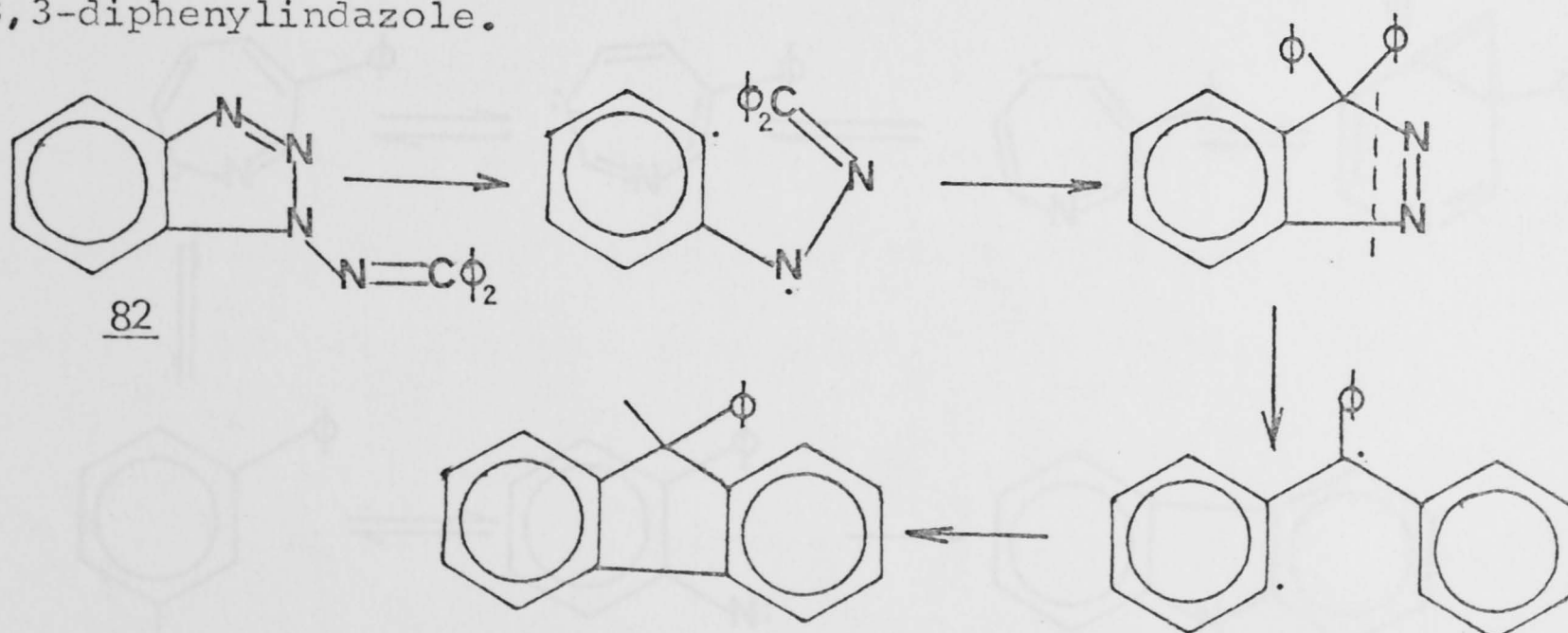
Carbazole formation is attributed to the generation of
phenyl-3-pyridylcarbene (from 75a); the carbene then inserts
into the pyridine ring, a result which, though theoretically
surprising,has been shown to take place during the pyrolysis of
3-phenyl-v-triazolo(1,5-a)pyridine. The mechanism for the
formation of carbazole after ring insertion can be divided into
two different pathways. The first is seen as the isomerisation
of the azacycloheptatrienylidene via the mechanism proposed
by Jones, Brown and Gasper[34] for the isomerisation of phenyl-
carbene. This isomerisation results in the formation of
3-nitrenobiphenyl which can subsequently undergo nitrene-
migration to 2-nitrenobiphenyl and cyclisation to give
carbazole.
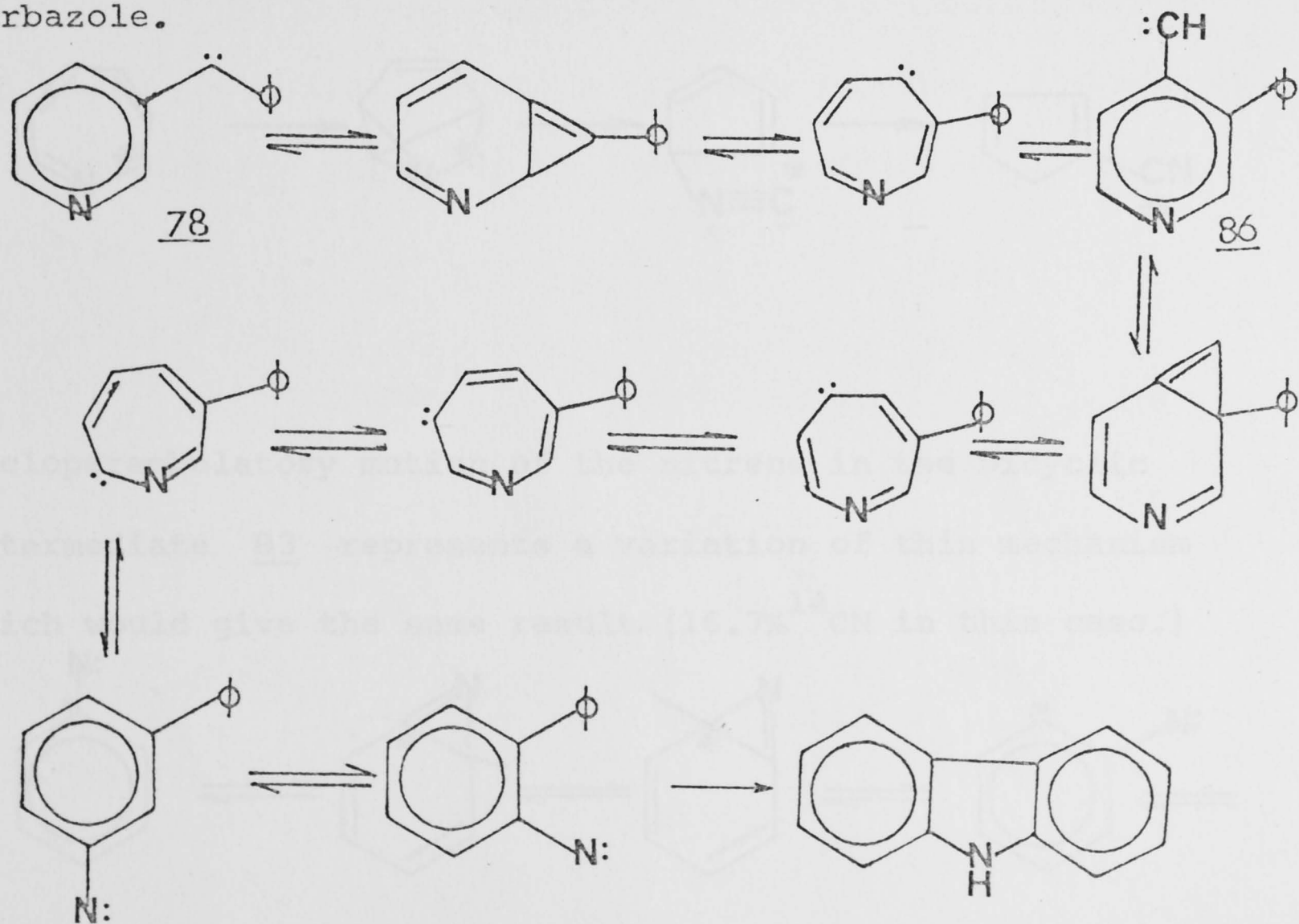
Such a nitrene migration is supported by the work of

Crow and Paddon-Row[53] on the thermolysis of $1-^{14}C$-phenyl-

azide. The results of this study were that total scrambling

throughout the product (CCPD) was observed, with 27% ^{14}C

appearing in the nitrile carbon. There exist two possible

mechanisms to explain this occurrence. The first of these

mechanisms involves ring expansion to 2-azacycloheptatrienylidene

followed by rapid isomerisations to 3-and 4-azacyclohepta-

trienylidenes, involving both hydrogen shifts and label

migration. Direct collapse of the 2-azacycloheptatrienylidenes

by the mechanism illustrated then gives a result of 16.7%

label being contained in the nitrile carbon.
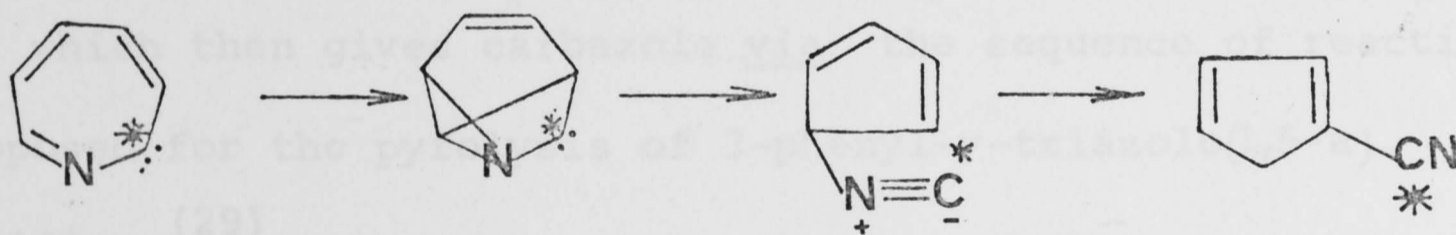
Cycloperambulatory motion of the nitrene in the bicyclic

intermediate 83 represents a variation of this mechanism

which would give the same result. (16.7% ^{14}CN in this case.)
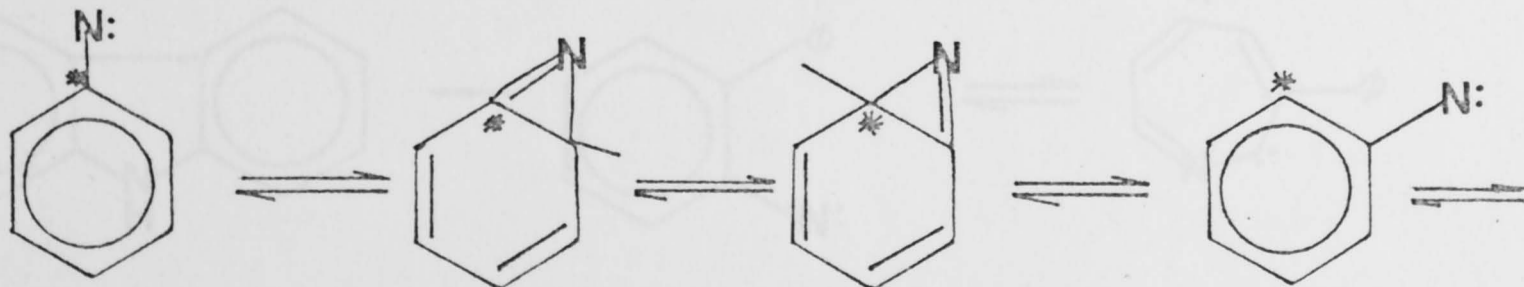
The second mechanism does not involve hydrogen-shifts but involves the removal of the restrictions on the direct ring contraction mechanism. The result of this relaxation of the contraction mechanism is that the α or C_2- of 3-azacycloheptatrienylidene is allowed to appear as the nitrile carbon; this results in 25% ^{14}C appearing in the cyano group. This mechanism was not preferred by the authors[53] as it required the three modes of ring collapse to proceed with equal ease; a result which would indeed be fortuitous.

The second mechanism for the formation of carbazole involves hydrogen shifts from the bicyclo-intermediate 84 to give the phenyl-2-pyridylcarbene insertion intermediate 85, which then gives carbazole via the sequence of reactions proposed for the pyrolysis of 3-phenyl-v-triazolo(1,5-a)-pyridine.[29]
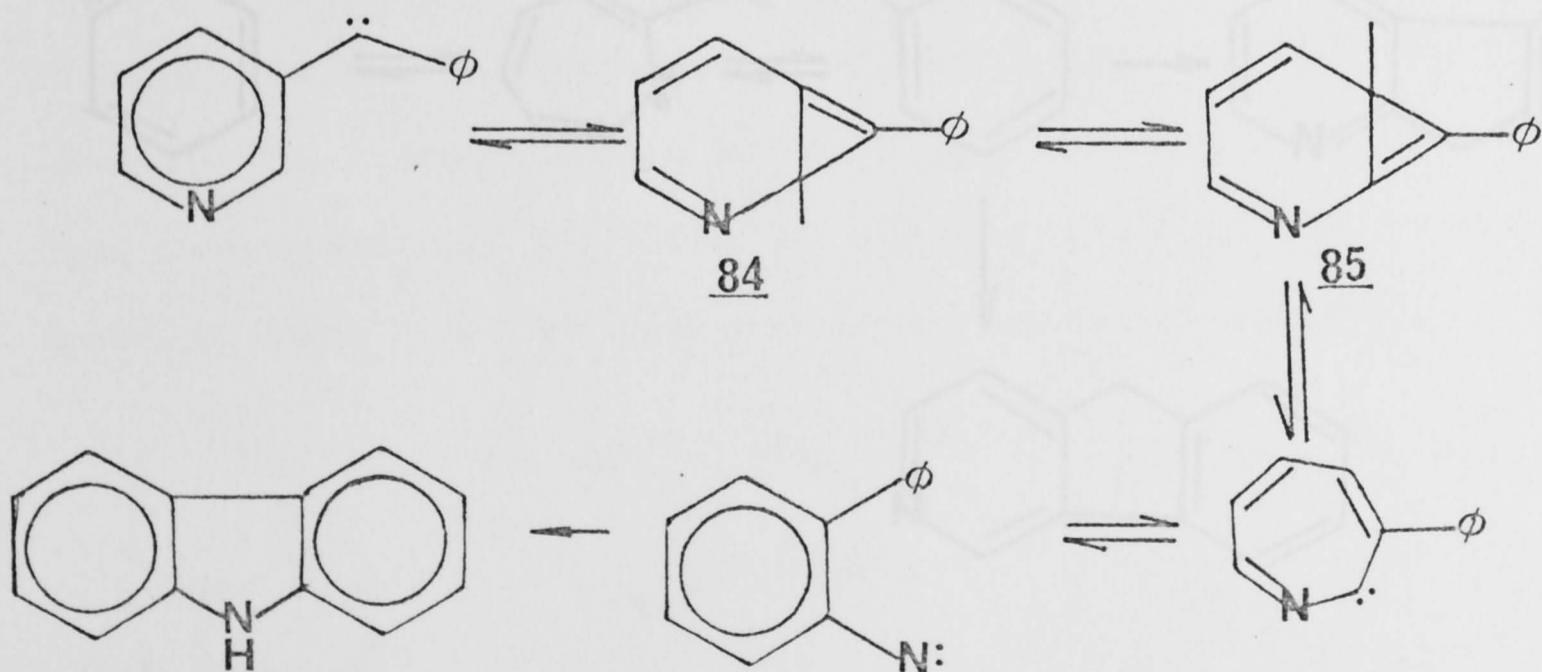
Scheme 1b
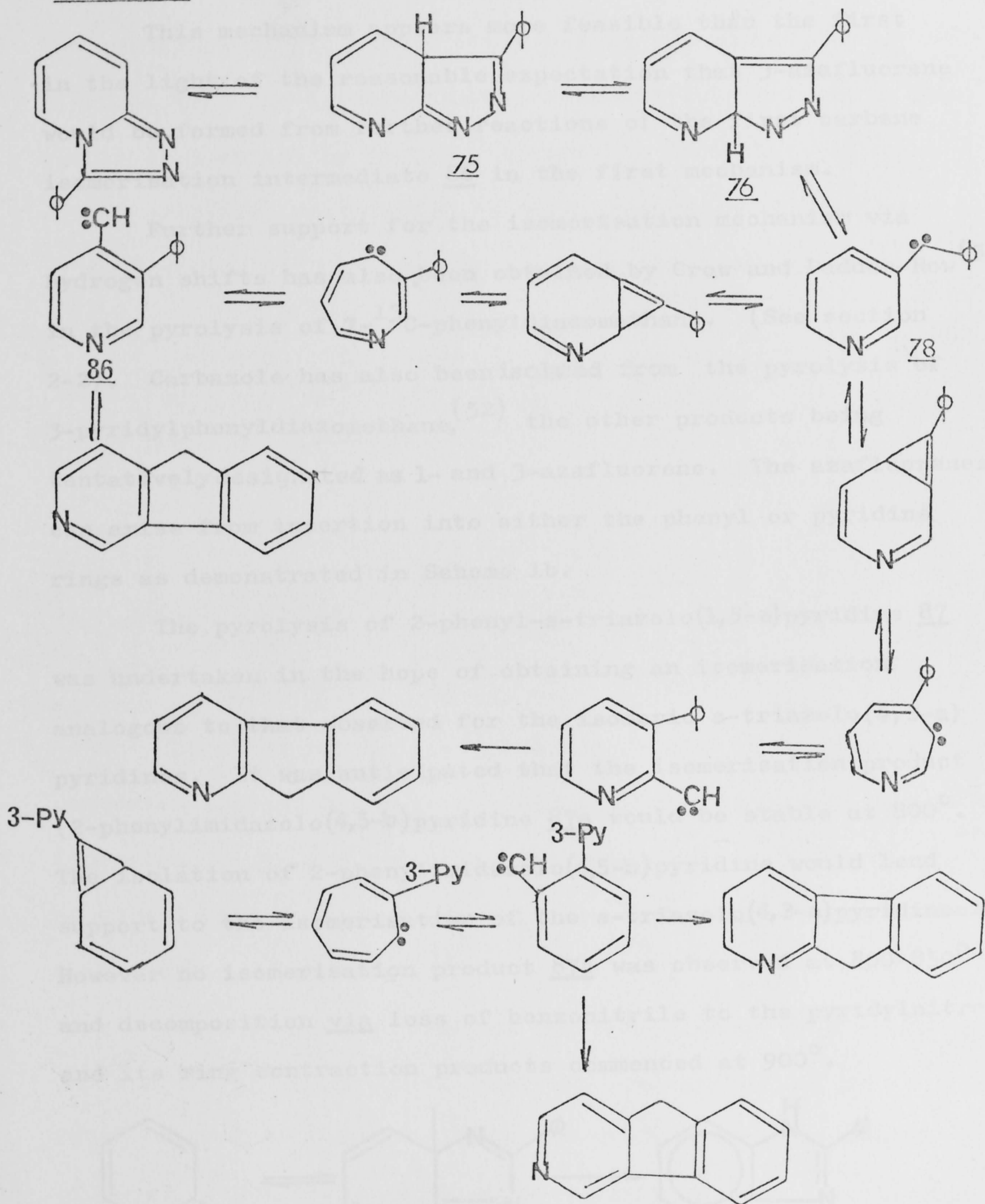
Carbene pathways to 1- and 3-azafluorene

This mechanism appears more feasible than the first in the light of the reasonable expectation that 3-azafluorene would be formed from further reactions of the first carbene isomerisation intermediate 86 in the first mechanism.

Further support for the isomerisation mechanism via hydrogen shifts has also been obtained by Crow and Paddon-Row[54] in the pyrolysis of $7-^{13}C$-phenyldiazomethane. (See section 2-2). Carbazole has also been isolated from the pyrolysis of 3-pyridylphenyldiazomethane,[52] the other products being tentatively designated as 1- and 3-azafluorene. The azafluorenes can arise from insertion into either the phenyl or pyridine rings as demonstrated in Scheme 1b.

The pyrolysis of 2-phenyl-s-triazolo(1,5-a)pyridine 87 was undertaken in the hope of obtaining an isomerisation analogous to that observed for the isomeric s-triazolo(4,3-a) pyridines. It was anticipated that the isomerisation product (2-phenylimidazolo(4,5-b)pyridine 87a would be stable at 800^c. The isolation of 2-phenylimidazolo(4,5-b)pyridine would lend support to the isomerisation of the s-triazolo(4,3-a)pyridines. However no isomerisation product 87a was observed at 800-850° and decomposition via loss of benzonitrile to the pyridylnitrene and its ring contraction products commenced at 900°.
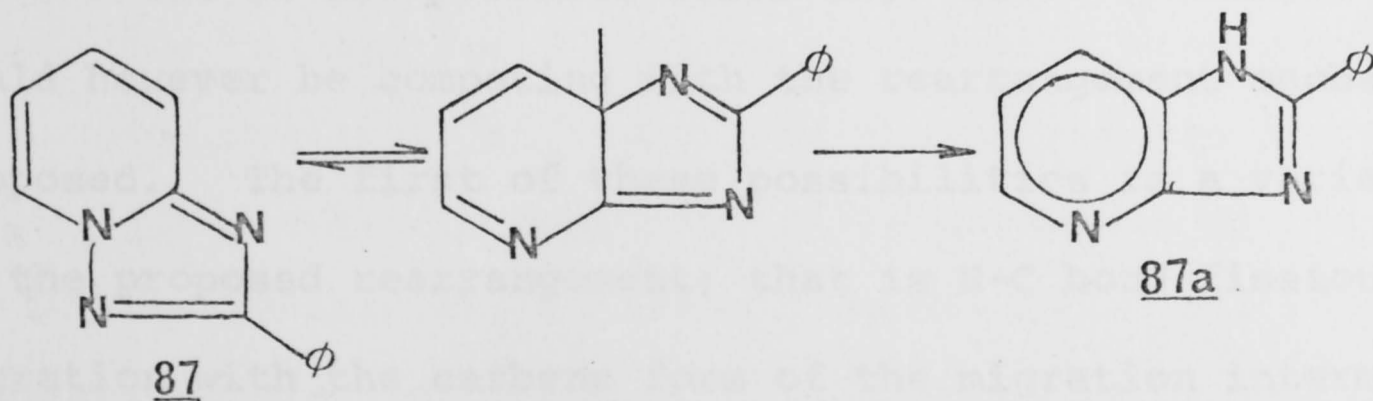
The absence of the isomerisation product 87a from

the pyrolysis of <u>87</u> can be explained in two ways. The

first is that the isomerisation intermediate is not stabilised

to the same extent as is the intermediate from the s-triazolo-

(4,3-a)pyridines, which would achieve enhanced stabilisation

by interaction with the nitrogen atom's lone pair electrons.
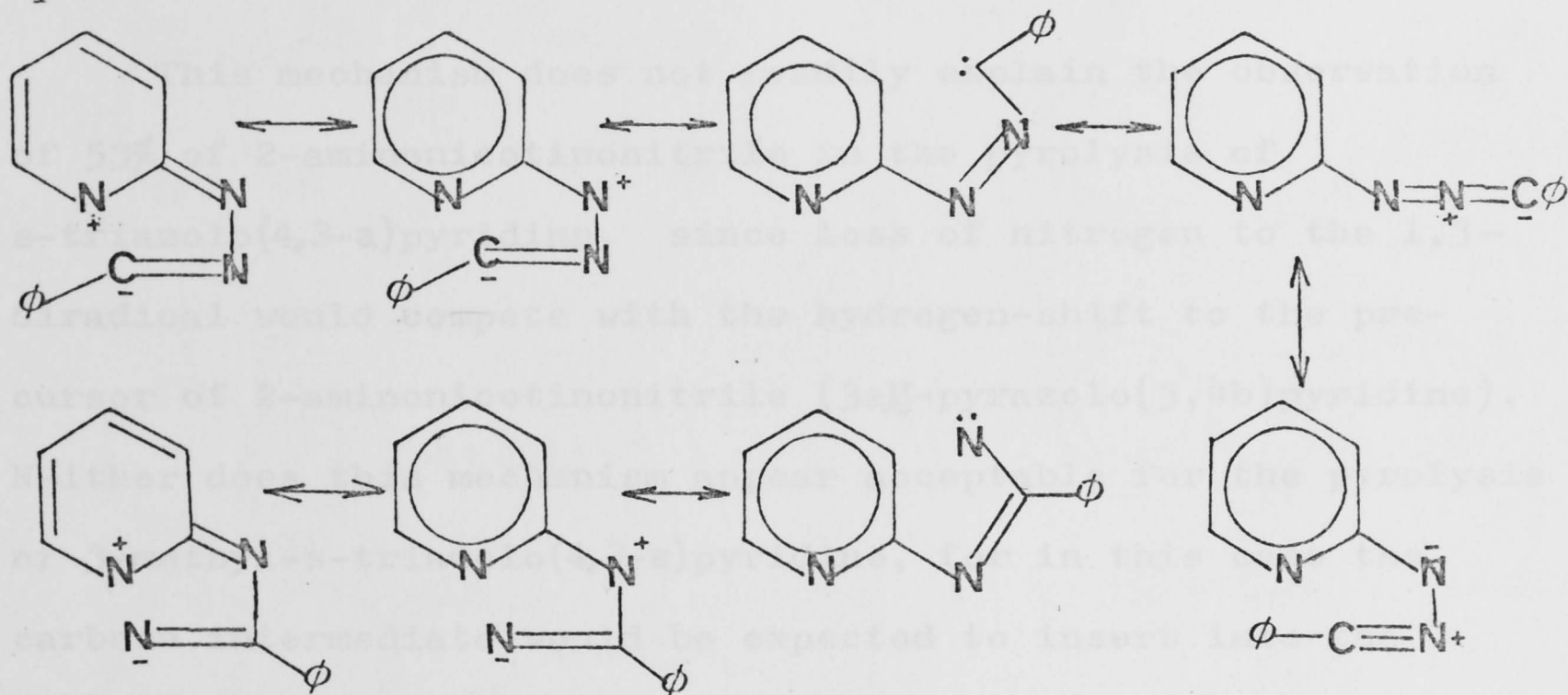
The other possible explanation is that <u>87</u> undergoes

concerted loss of benzonitrile and this competes with the

isomerisation, or the isomerisation product loses benzonitrile

to give 2- and 3-cyanopyrrole <u>via</u> the mechanism proposed for

triazolo(4,5-b)pyridine.[37]

Other mechanisms explain the formation of only some,

and not all of the products observed. These mechanisms

could however be competing with the rearrangement mechanism

proposed. The first of these possibilities is a variation

on the proposed rearrangement; that is N-C bond fission and

migration with the carbene form of the migration intermediate

inserting into the C-H bond to give the corresponding

(3H-pyrazolo(3,4b)pyridine.

$\underline{66}\left(R=CH_3\right)$
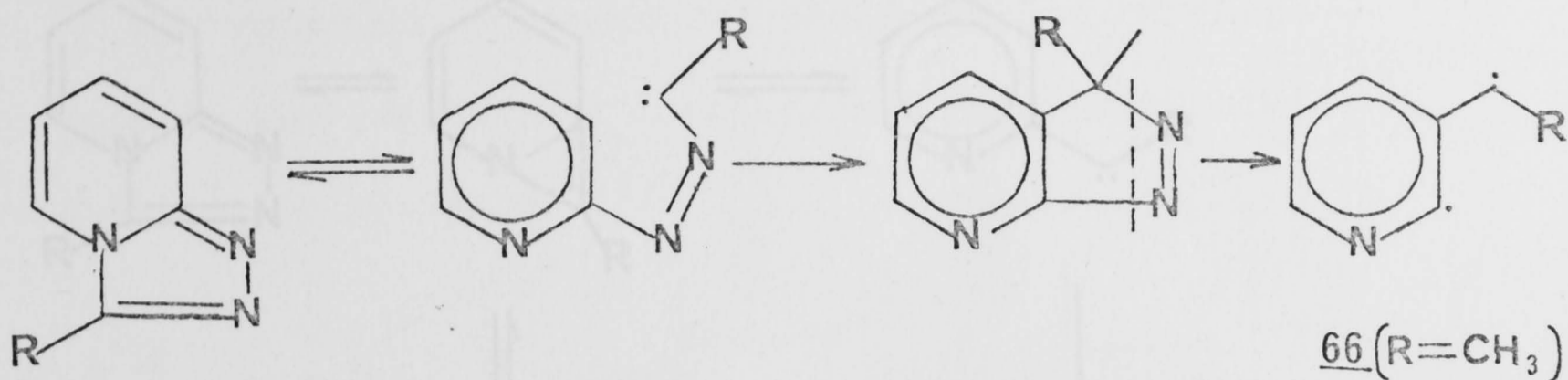
This mechanism does not readily explain the observation of 53% of 2-aminonicotinonitrile in the pyrolysis of s-triazolo(4,3-a)pyridine, since loss of nitrogen to the 1,3-diradical would compete with the hydrogen-shift to the precursor of 2-aminonicotinonitrile (3aH-pyrazolo(3,4b)pyridine). Neither does this mechanism appear acceptable for the pyrolysis of 3-methyl-s-triazolo(4,3-a)pyridine, for in this case the carbene intermediate would be expected to insert into the aliphatic C-H bond, rather than the aromatic C-H bond. In the related case of the 3-phenyl s-triazolo(4,3-a)pyridine the phenyl substitution could stabilise the carbene by inter-action with the aromatic sextet of electrons of the phenyl substituent and could thereby enhance its lifetime.

The intially sought mechanism which incorporated the 1-2 bond insertion pathway detailed on p 28, does quite adequately explain the results for 3-phenyl-s-triazolo(4,3-a)pyridine and, by assuming preferential radical cleavage from the pyridocyclo-butene 110 to give a majority of the diradical 66 it is possible to predict the relative proportions of the vinyl-pyridines obtained from the methyl substituted triazole.
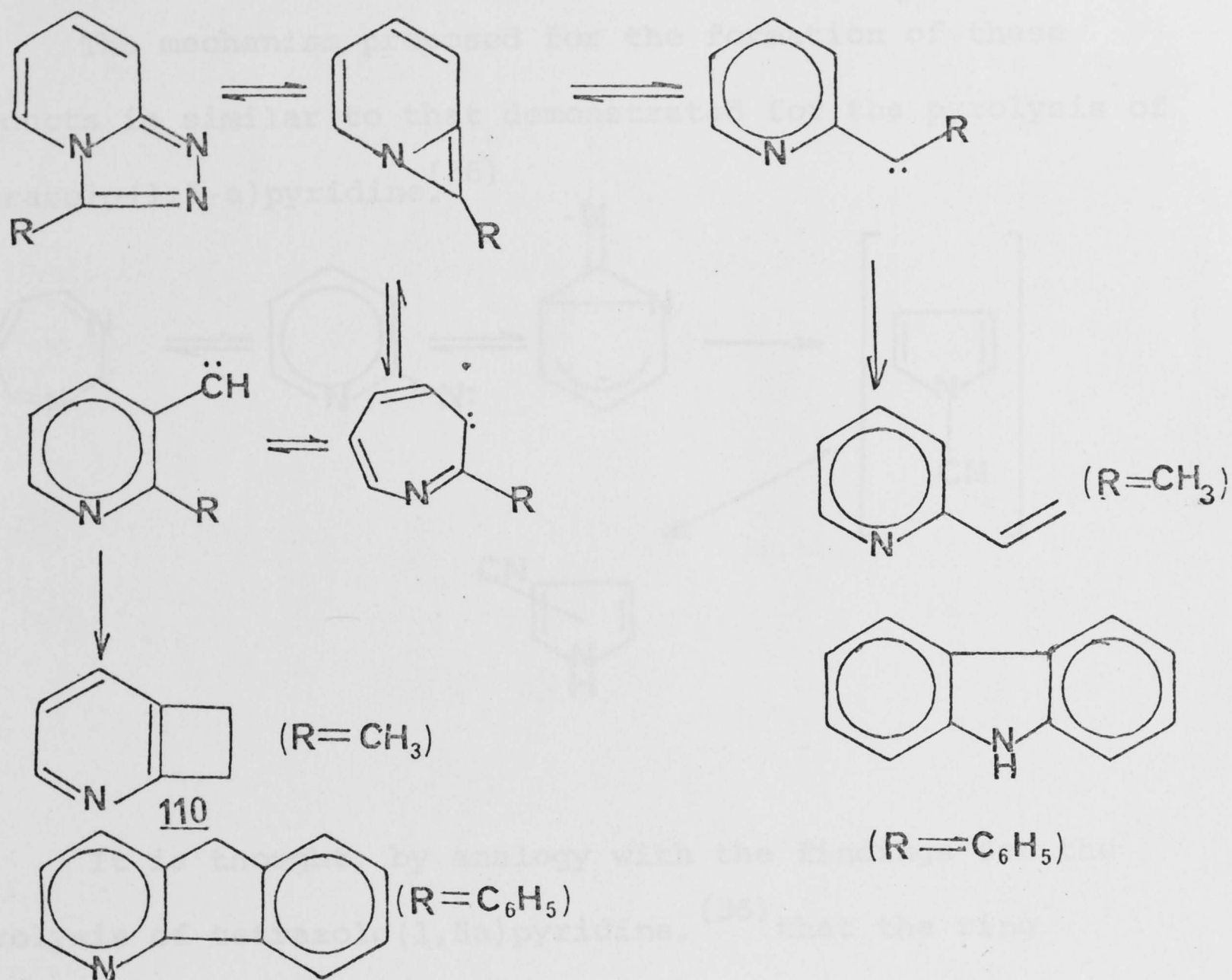
The products observed from the loss of nitrile can arise by two mechanisms. The first of these mechanisms involves the loss of nitrile from the s-triazolo(4,3-a)pyridine itself, or loss of nitrile from the isomerisation intermediate 3aH-pyrazole-(3,4b)pyridine to give 2-pyridylnitrene.
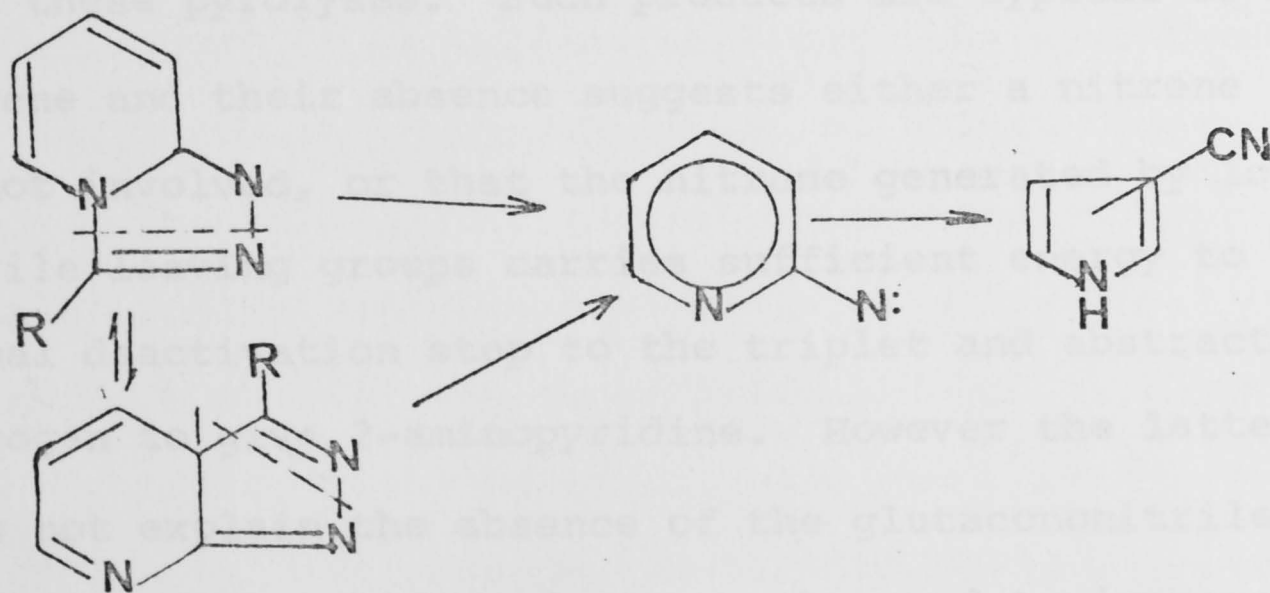
The mechanism proposed for the formation of these

products is similar to that demonstrated for the pyrolysis of

tetrazolo(1,5-a)pyridine.[36]
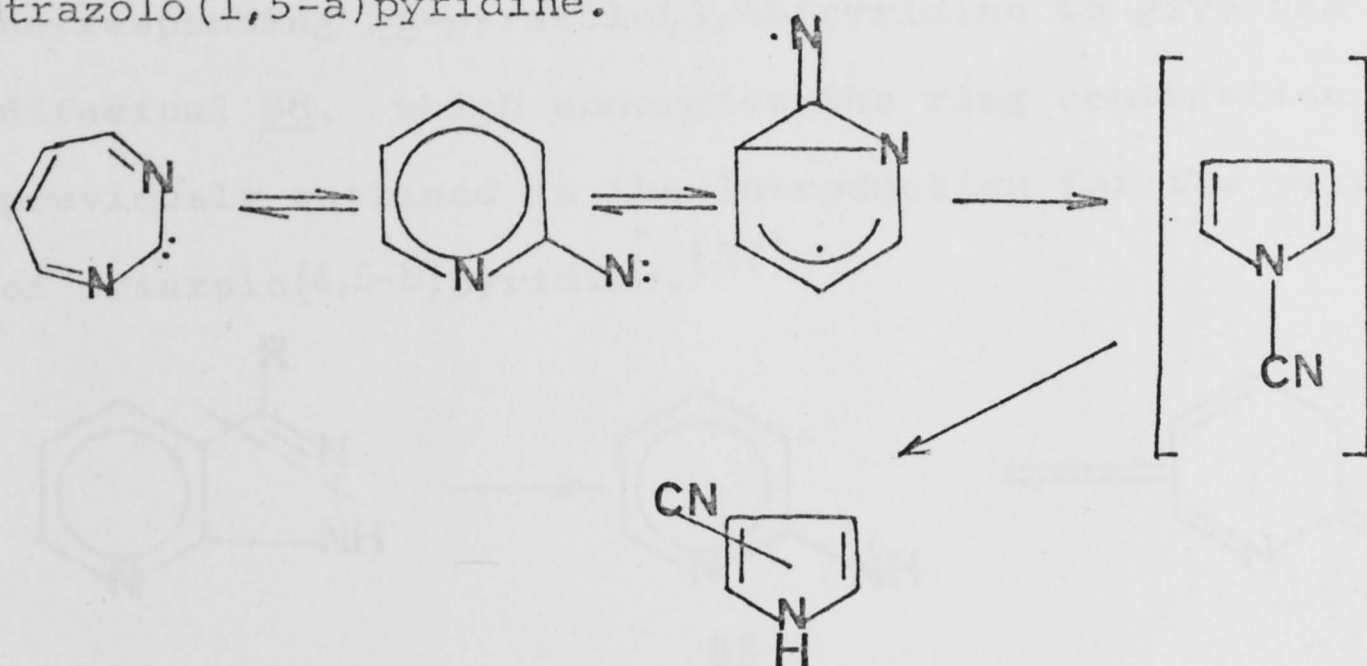
It is thought, by analogy with the findings for the

pyrolysis of tetrazolo(1,5a)pyridine,[36] that the ring

expansion/contraction cycle involving 2,7-diazacyclohepta-

trienylidene is taking place,although no direct evidence has

been obtained from this work to verify the supposition in this

case.

No glutacononitrile or 2-aminopyridine were obtained

from these pyrolyses. Such products are typical of 2-pyridyl-

nitrene and their absence suggests either a nitrene intermediate

is not involved, or that the nitrene generated by loss of the

nitrile leaving groups carries sufficient energy to escape the

normal deactivation step to the triplet and abstraction of

hydrogen to give 2-aminopyridine. However the latter consideration

does not explain the absence of the glutacononitrile,

particularly as this product was observed to increase with

temperature in the pyrolysis of tetrazolo(1,5-a)pyridine.[36]

The other mechanism possible for the formation of
these products is the radical loss of nitrile from the
corresponding 1H-pyrazolo(3,4b)pyridine to give the 1,3-
diradical <u>88</u>, which undergoes the ring contraction
previously outlined in the introduction for the pyrolysis
of triazolo(4,5-b)pyridine.[37]

<u>88</u>
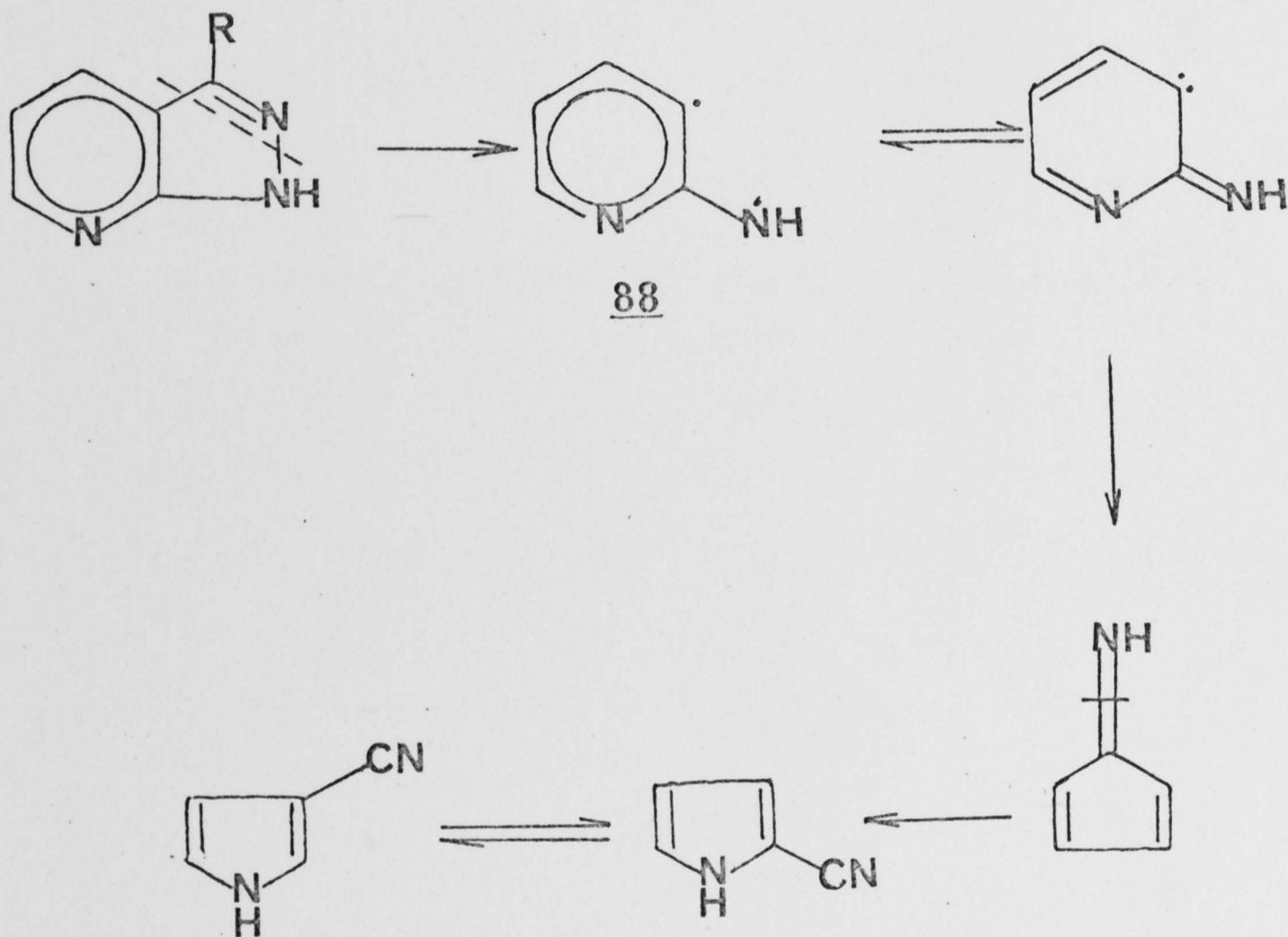
The thermal isomerisation of cyanopyrroles has been
established[12] as taking place with the equilibrium between
2- and 3- isomers being found to be 2:1 in favour of the
2-isomer at 800°. The separate pyrolyses of 1H-pyrazolo
(3,4b)pyridine and benzoimidazolo establish that hydrogen
cyanide loss will not occur below 900-950°. However this is
in accordance with the result obtained from s-triazolo(4,3-a)
pyridine. Until the 3- substituted pyrazolo(3,4b)pyridines
are thermolysed, no conclusions can be drawn relating to
this mechanism.

Whatever the mechanism involved, the results
demonstrate that acetonitrile and benzonitrile are better
leaving groups than hydrogen cyanide.

Gas phase pyrolysis of fused ring pyrazoles.

Section 2.1.   Gas Phase Pyrolysis of 1H-pyrazolo(3,4b) Pyridine

The pyrolysis of the s-triazolo(4,3-a)pyridines showed the possible rearrangement of these compounds to the pyrazolo(3,4b)-pyridine ring system, with the products observed being derived from intermediates attained by hydrogen shifts in this ring system.
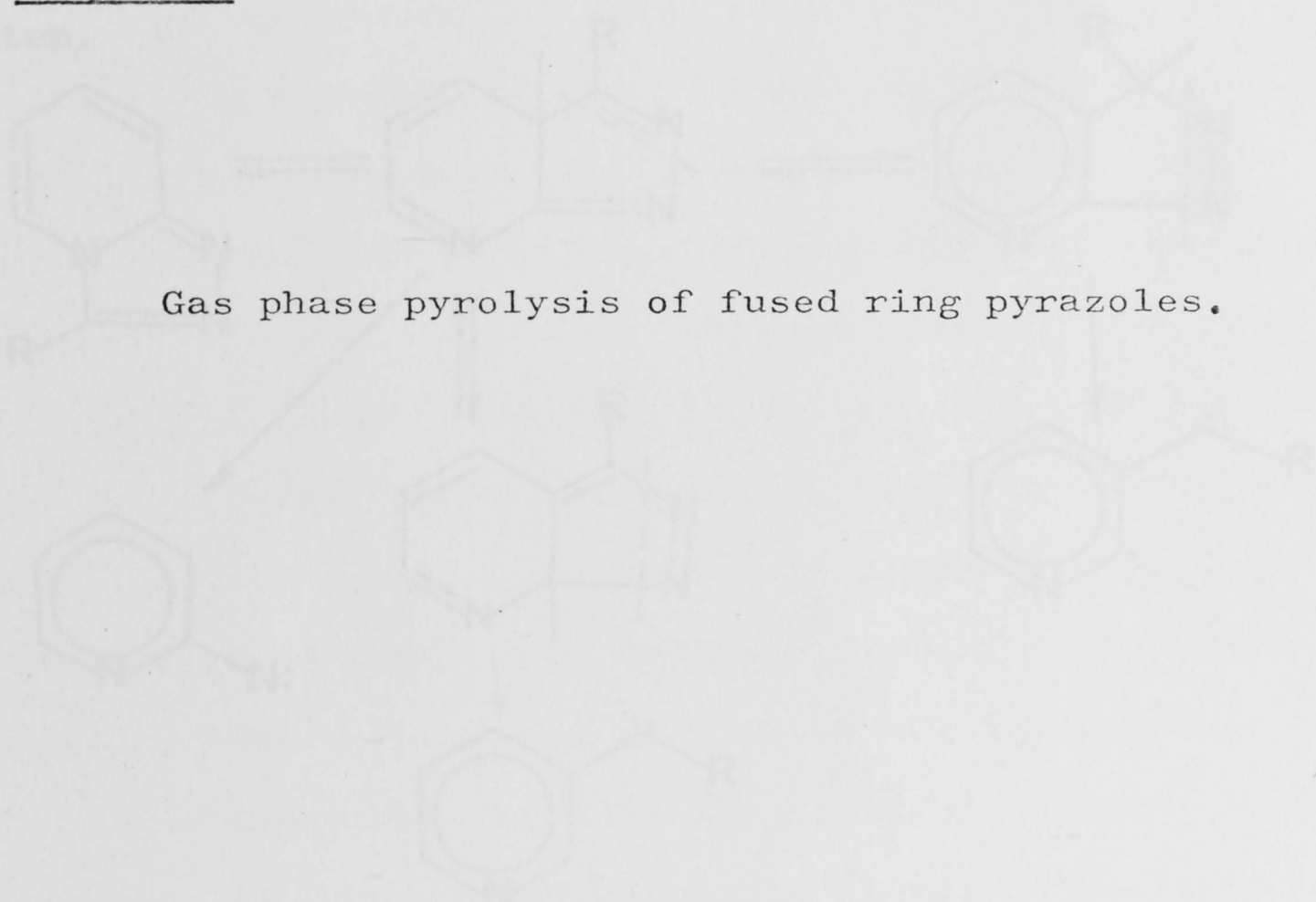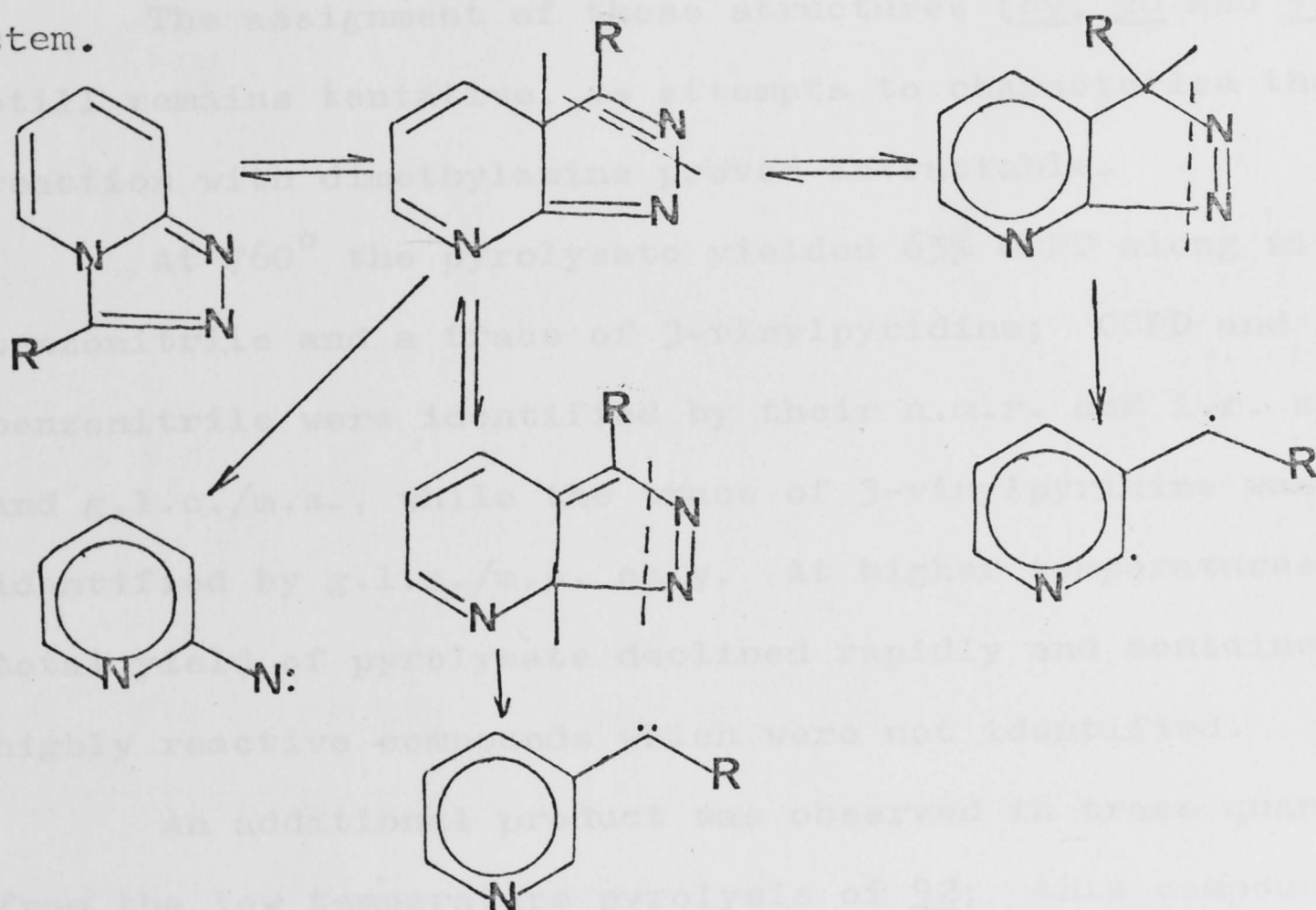
To investigate the generality of these hydrogen shifts and subsequent decomposition from the tautomers so obtained, the pyrolysis of 1H-pyrazolo(3,4b)pyridine was undertaken.

The pyrolysis of 1H-pyrazolo(3,4b)pyridine showed a strong temperature dependency, with the low temperature pyrolysis (650°) leading to a mixture containing 55% CCPD; the remainder of the pyrolysate contained three other compounds which were tentatively assigned structures 89, 90 and 91 from their spectral data.

n.m.r. (τ CCl$_4$) 6.97(s) C≡C-H; 4.92(s) 4.80(s)

=C=CH$_2$; 3.03(m), 3.33(m), 3.85(m), 3.53(m) (ring protons)

i.r. (cm^{-1} CCl$_4$); 3460(NH)(s); 3300(s) - C≡C-H;

2170(m) - C≡C; 1940(s), 1974(s) =C=CH$_2$.

The above data relates to the mixture of azafulvenallenes

and ethynylpyrroles.

The assignment of these structures (89, 90 and 91)

still remains tentative, as attempts to characterise them by

reaction with dimethylamine proved intractable.

At 760° the pyrolysate yielded 65% CCPD along with 9%

benzonitrile and a trace of 3-vinylpyridine; CCPD and

benzonitrile were identified by their n.m.r. and i.r. spectra

and g.l.c./m.s., while the trace of 3-vinylpyridine was

identified by g.l.c./m.s. only. At higher temperatures the

total yield of pyrolysate declined rapidly and contained

highly reactive compounds which were not identified.

An additional product was observed in trace quantities

from the low temperature pyrolysis of 92; this compound

was identified as 2-aminonicotinonitrile by i.r. and g.l.c.

retention times.

The mechanism proposed for the formation of these

products involves hydrogen shifts to the tautomers 93,

and 98 followed by collapse of these intermediates to give

the products observed.
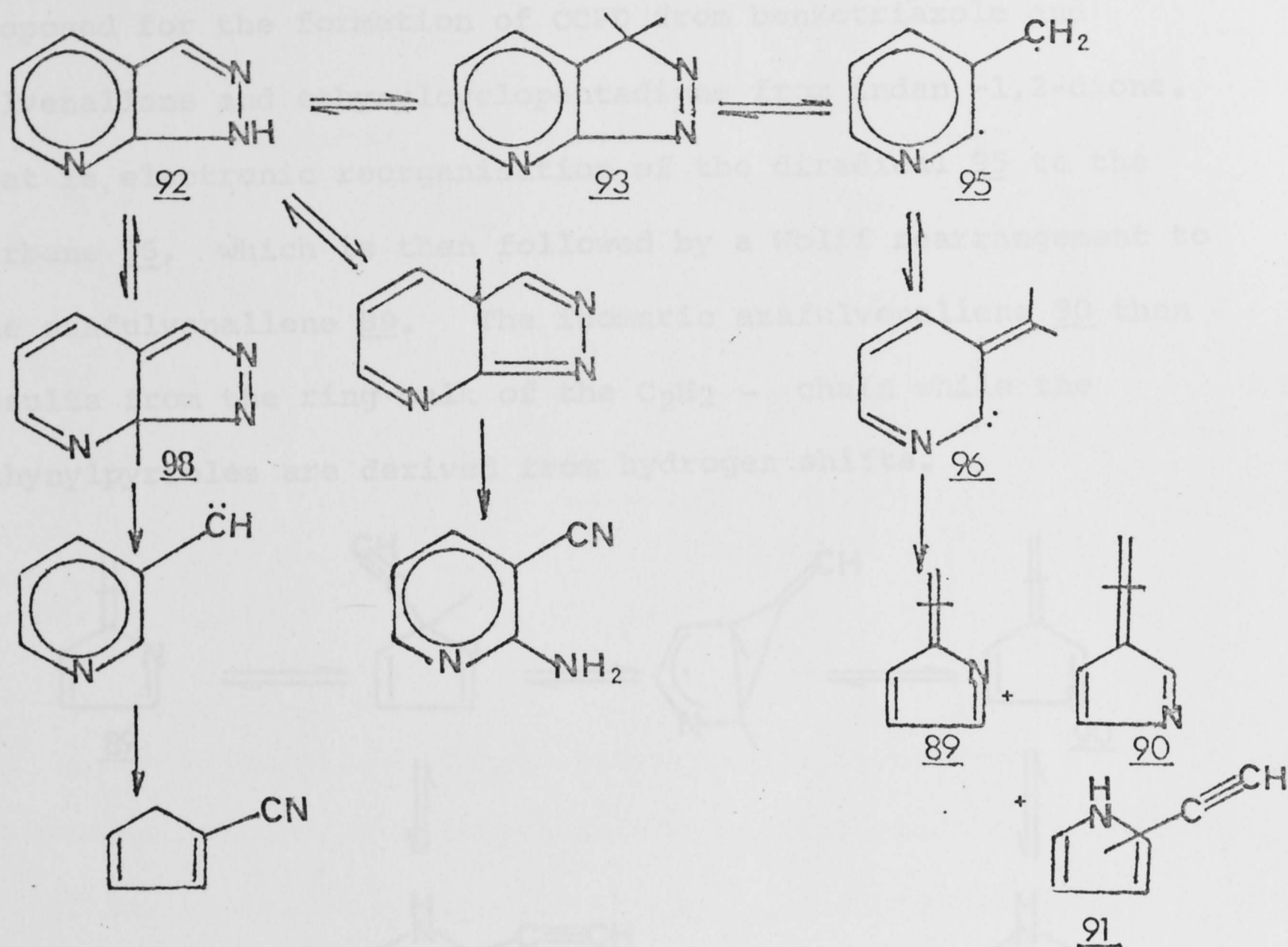
The formation of 2-aminonicotinonitrile   from 92

is attributed to the formation of 3aH-pyrazolo(3,4b)pyridine

followed by N-N bond cleavage to the diradical 94. The

diradical 94 then undergoes intramolecular hydrogen shifts to

give the product
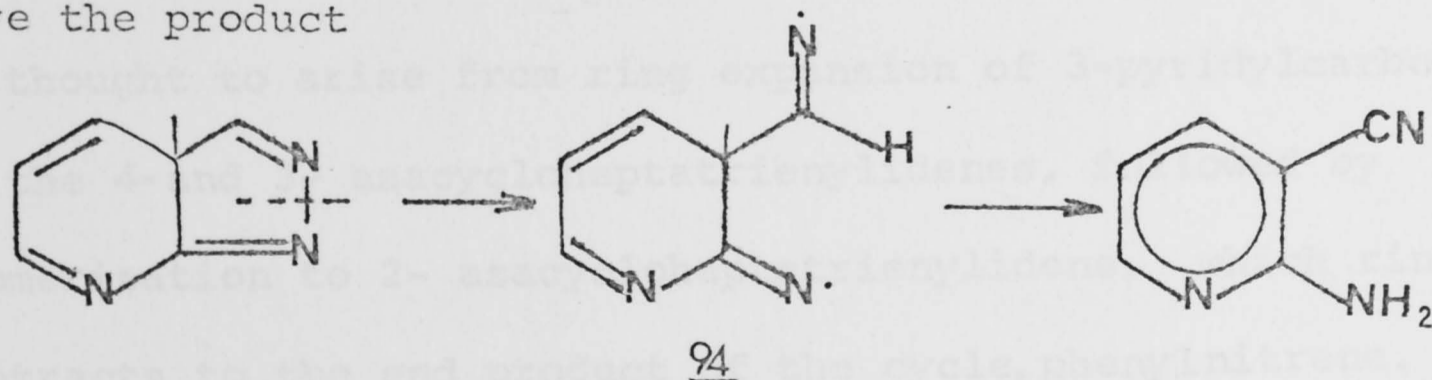
The mechanism proposed for the formation of the

ethynylpyrroles 91 and azafulvenallenes 89 , 90 is that

proposed for the formation of CCPD from benzotriazole and
fulvenallene and ethynylcyclopentadiene from indan -1,2-dione.
That is, electronic reorganisation of the diradical 95 to the
carbene 96, which is then followed by a Wolff rearrangement to
the azafulvenallene 89. The isomeric azafulvenallene 90 then
results from the ring walk of the C_2H_2 - chain while the
ethynylpyrroles are derived from hydrogen shifts.
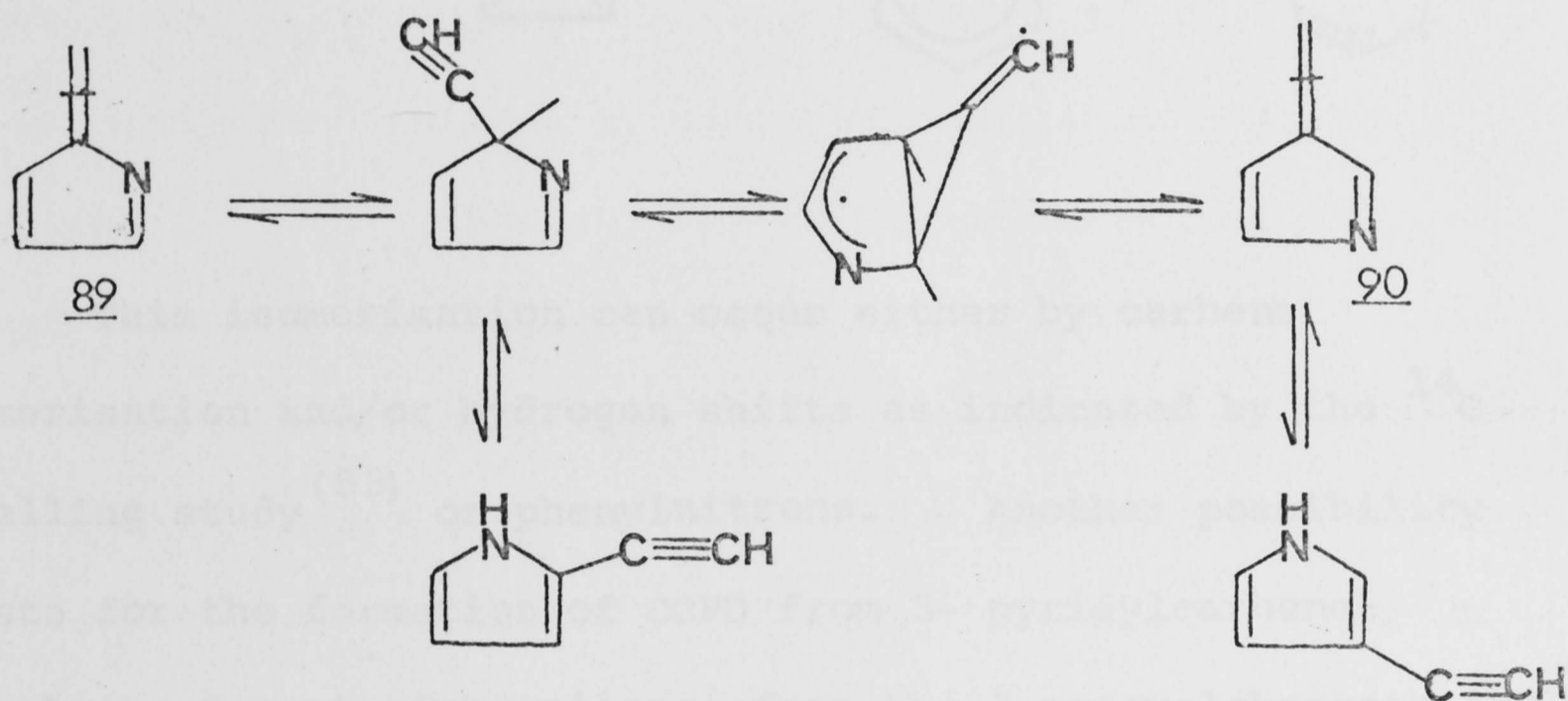
The formation of CCPD from the pyrolysis of 92
is thought to arise from ring expansion of 3-pyridylcarbene
to the 4-and 3- azacycloheptatrienylidenes, followed by
isomerisation to 2- azacycloheptatrienylidene, which ring
contracts to the end product of the cycle, phenylnitrene.
Phenylnitrene then undergoes the ring contraction to CCPD
by one of the mechanisms previously outlined.
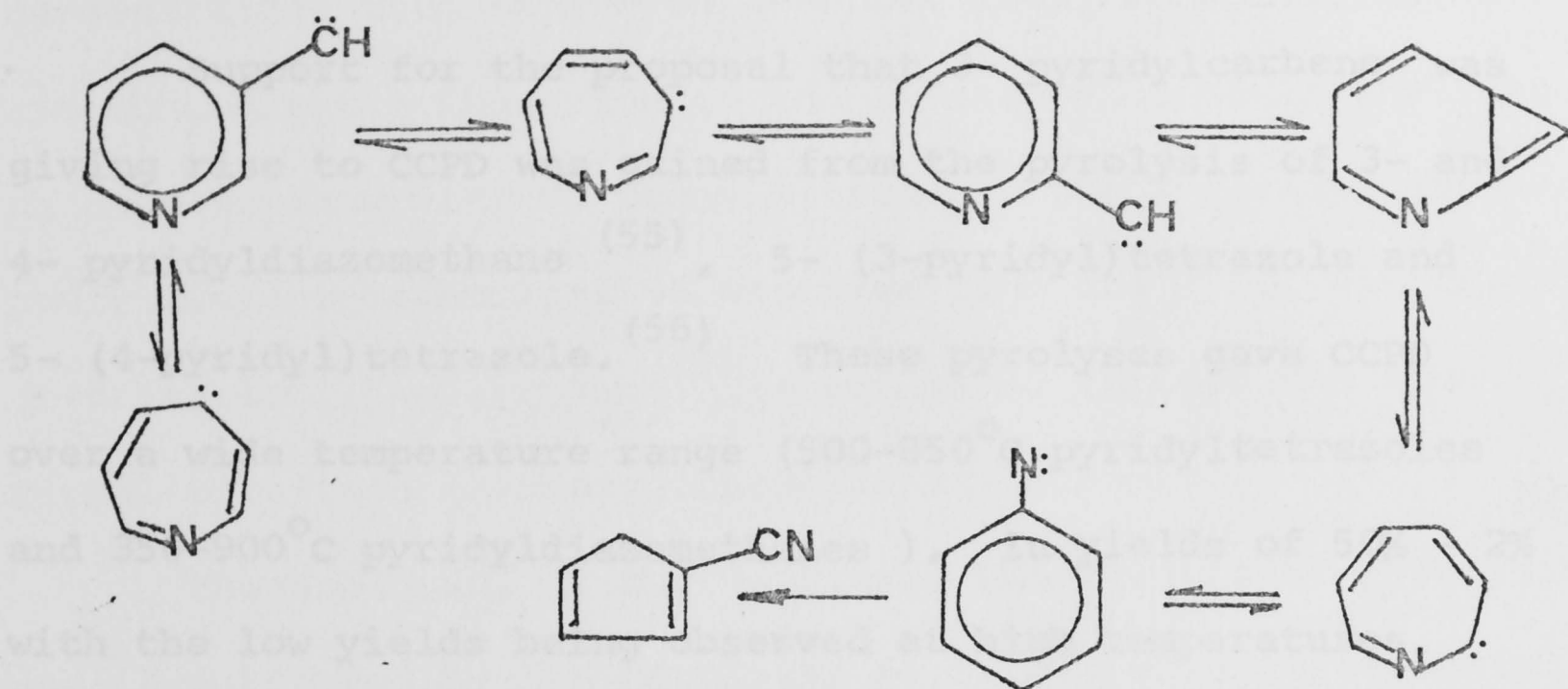
This isomerisation can occur either by carbene

isomerisation and/or hydrogen shifts as indicated by the ^{14}C

labelling study[53] on phenylnitrene.   Another possibility

exists for the formation of CCPD from 3- pyridylcarbene:

this being direct ring collapse from the 3-azacycloheptatrienyl-

idene to give the observed product.
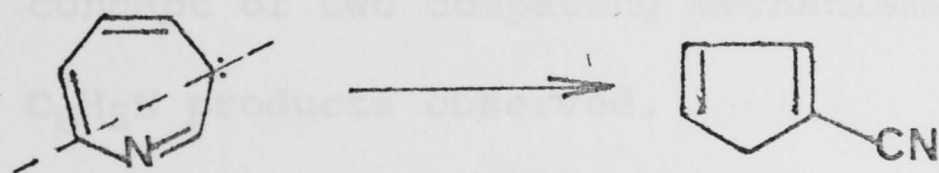
The labelling studies of   phenylnitrene[53] and

phenylcarbene[54] both establish a rapid isomerisation of the

corresponding cycloheptatrienylidenes prior to ring contraction.

This evidence indicates that direct collapse from

3-azacycloheptatrienylidene would be unlikely to be operating

as the only mechanism.

Support for the proposal that 3- pyridylcarbene was giving rise to CCPD was gained from the pyrolysis of 3- and 4- pyridyldiazomethane [55], 5- (3-pyridyl)tetrazole and 5- (4-pyridyl)tetrazole. [56] These pyrolyses gave CCPD over a wide temperature range (500-850°C pyridyltetrazoles and 350-900°C pyridyldiazomethanes), in yields of 50% - 2% with the low yields being observed at high temperatures. The occurrence of aniline in minor quantities from these pyrolyses [56] [55] lends support to the intermediacy of phenylnitrene as the precursor to CCPD.

It is significant that no azafulvenallenes and ethynylpyrroles were obtained from either of these generations of 3- and 4-pyridylcarbene, [55][56] as these results confirm the proposal that these products do not arise from the pyridylcarbene/phenylnitrene cycle. These findings strengthen the concept of two competing mechanisms being responsible for the C_6H_5N products observed.

The results obtained from the pyrolyses of v-triazolo (1,5-a)pyridine [29] and the sodium salt of tropone tosylhydrazone [31] (where no ring contraction products were observed) led to the conclusion [29,31] that the ring contraction and ring expansion pathways were independent, competing mechanisms. The results obtained from 1H-pyrazolo(3,4b)pyridine and 3- and 4-pyridylcarbene [55][56] contradict this conclusion as the

carbenes first ring expand to 3- or 4- azacycloheptatrienylidene and subsequently isomerise to the 2- azacycloheptatrienylidene which ring contracts to phenylnitrene. The 2-pyridylcarbene/ phenylnitrene isomerisation observed from the pyrolysis of v-triazolo(1,5-a)pyridine[29] also passed through the same formal structure (2-azacycloheptatrienylidene).

The ambiguity of the v-triazolo(1,5-a)pyridine pyrolysis[29] was investigated by the pyrolysis of 5- (2-pyridyl)tetrazole[56] 97 which yielded 44-3.5% of CCPD over a temperature range of of 500-850°C. (Maximum yield at 600°C).
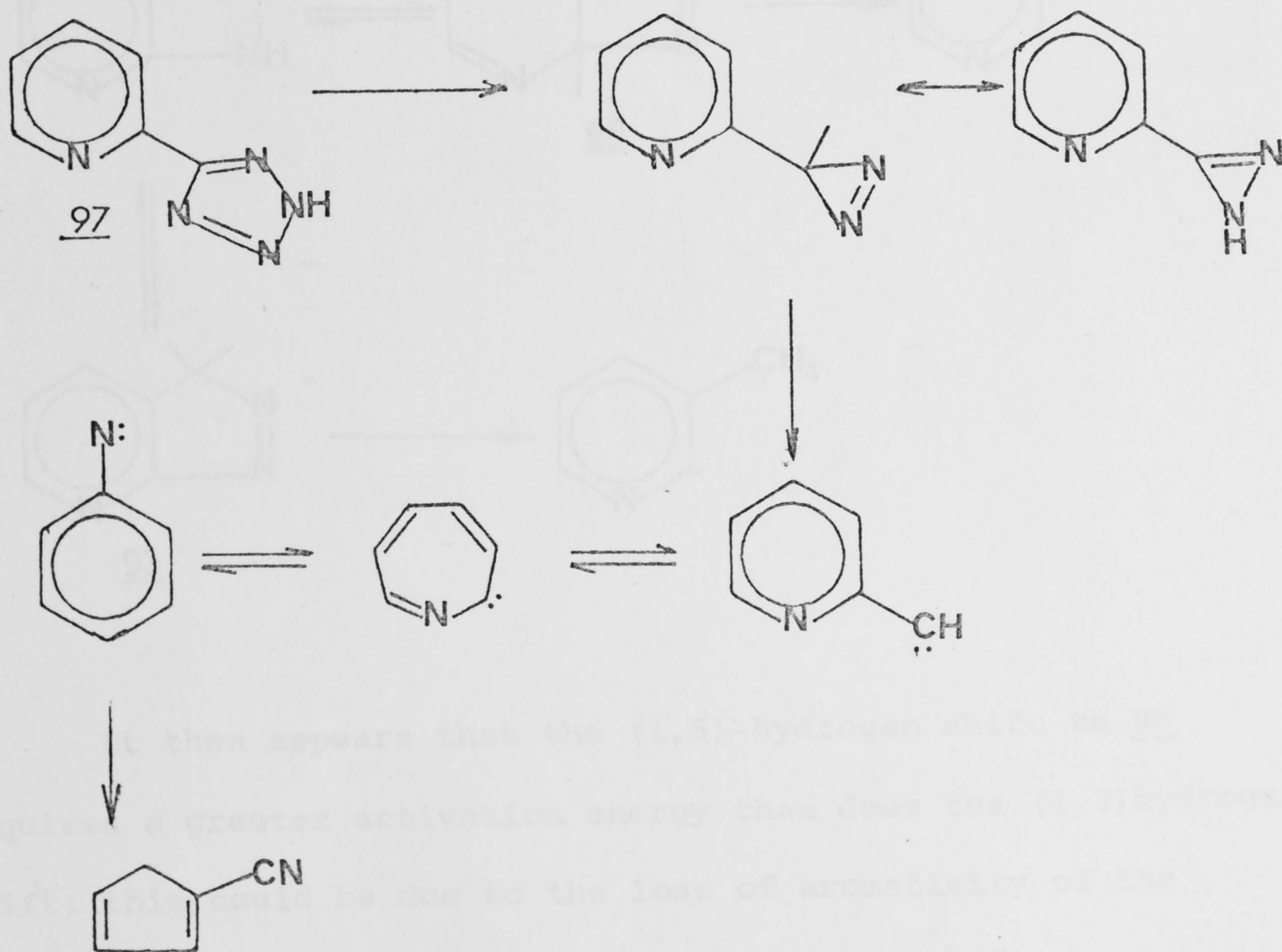
The authors[56] then concluded that the 2-pyridyl

carbene generated from v-triazolo(1,5-a)pyridine[29] was

obtained _via_ a non-concerted process to give the triplet state

2-pyridylcarbene.

The temperature dependency of the pyrolysis of 92

appears to be a function of the activation energy required for

the hydrogen shifts to occur. On this basis it appears that

at "low" temperature (600-650°C) the (1,3)-hydrogen shift to

give 93 is competing with the (1,5)-hydrogen shift to give 98.

98

93
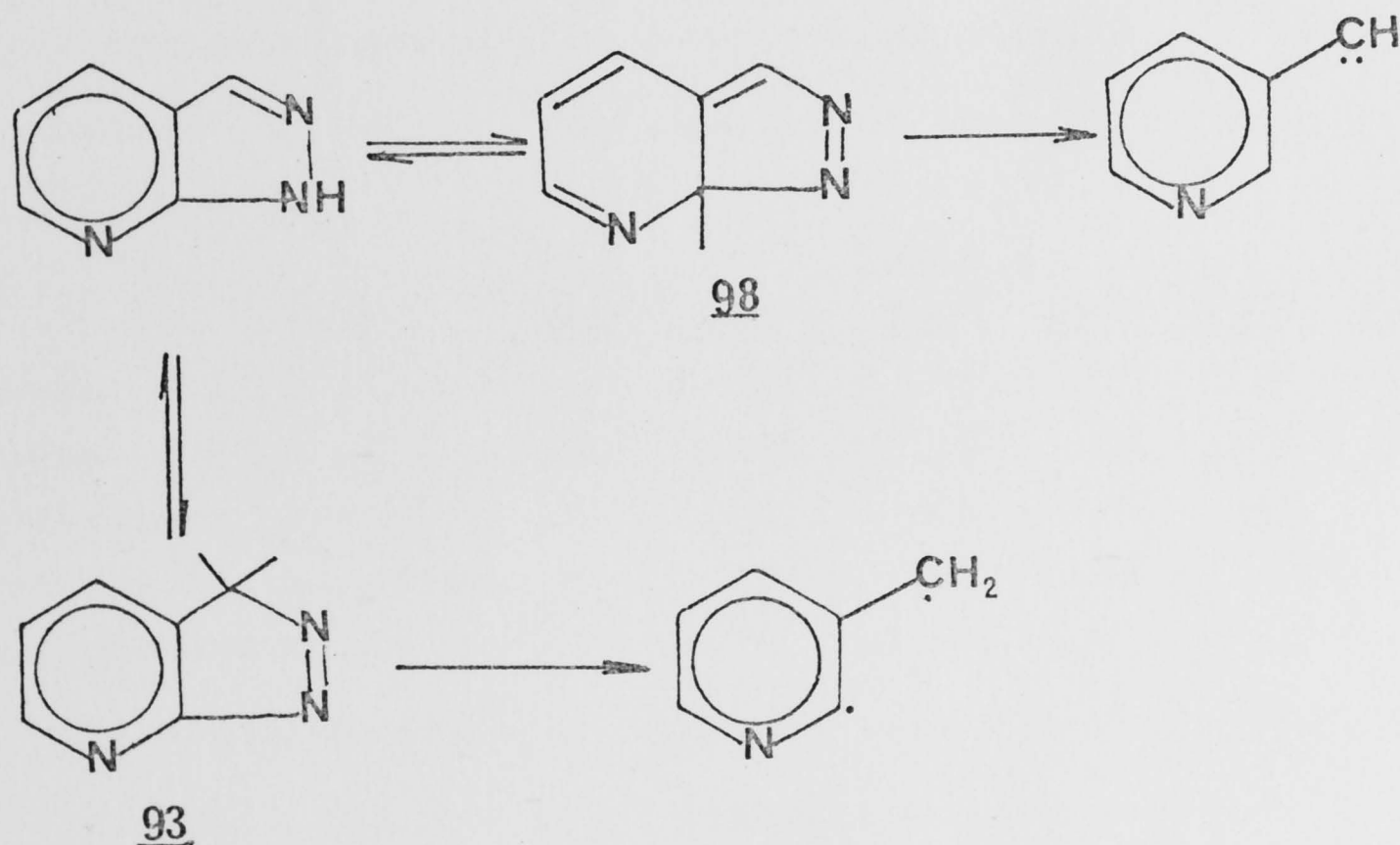
It then appears that the (1,5)-hydrogen shift to 98

requires a greater activation energy than does the (1,3)hydrogen

shift; this could be due to the loss of aromaticity of the

pyridine ring, brought about by this hydrogen shift.

So, as the temperatures rise, the conditions become more

favourable for the (1,5)-hydrogen shift to take place; to
explain the actual complete dominance of the (1,5)-hydrogen
shift one must assume that the reaction rate for the (1,5)
must be greater than that for the (1,3)-hydrogen shift.

Section 2.2 Gas Phase Pyrolysis of 1H-Indazole

The gas phase pyrolysis of 1H-pyrazolo(3,4b)pyridine
gave CCPD in good yield at 760°, and gave a mixture of aza-
fulvenallenes, ethynylpyrroles and CCPD at temperature ≤ 650°.
It is proposed that these products are derived from carbene and
1,3-diradical intermediates (see section 2.1). The pyrolysis
of 1H-indazole was attempted as a test for   the generality of
these reaction pathways,although it was appreciated that the
products obtained from either carbene or 1,3 diradical would
in this case be the same. Pyrolysis of 1H-indazole gave the
phenylcarbene[30] ring contraction products fulvenallene and
ethynylcyclopentadiene plus o-aminobenzonitrile (at low
temperature < 700°). The results of these pyrolyses are
given in Table 2.

Table 2

	600°	700°	760°	800°	850°	950°
Benzene	-	6%	4%	12%	17%	-
Toluene	-	12%	6%	12%	18%	7%
Fulvenallene	-	45%	50%	43%	-	-
Ethynylcyclopentadiene	-	15%	18%	14%	-	-
o-aminobenzonitrile	3%	-	-	-	-	-

No heptafulvalene or stilbene were detected from these
pyrolyses although traces of anthracene were detected in the
mass spectrometer for the high temperature pyrolyses
(anthracene has been suggested[31] as a high temperature re-
arrangement product of heptafulvalene). The o-aminobenzonitrile
was identified by comparison of the spectral data with that of
the authentic compound. The products 47 and 48 were identified
by their n.m.r., mass and i.r. spectral data which were in
accordance with the data reported by Hedaya and co-workers
for their pyrolyses of benzyl fluoride, phenyldiazomethane[30]

and indan-1,2-dione.[38] The ring contraction products 47 and

48 were further characterised by an essentially quantitative

reaction with dimethylamine to give 6-methyl -6-dimethylamino-

fulvene.[59] This reaction was explored further by n.m.r.

which showed that the dimethylamine was a sufficiently strong

base to facilitate the tautomerisation of ethynylcyclopentadiene

to fulvenallene prior to reaction with dimethylamine.

As in the case of 1H-pyrazolo(3,4b)pyridine, it is

apparent that hydrogen shifts must be considered in the

possible mechanisms for the formation of these products, and

that the same carbene/biradical duality could exist. A 1,3-

hydrogen shift would lead to the tautomer 99 which would undergo

radical loss of nitrogen to give the diradical 100. The

diradical 100 could then undergo ring contractions analogous to

those proposed for the triazaloarenes[37] and indan -1,2-dione.[38]
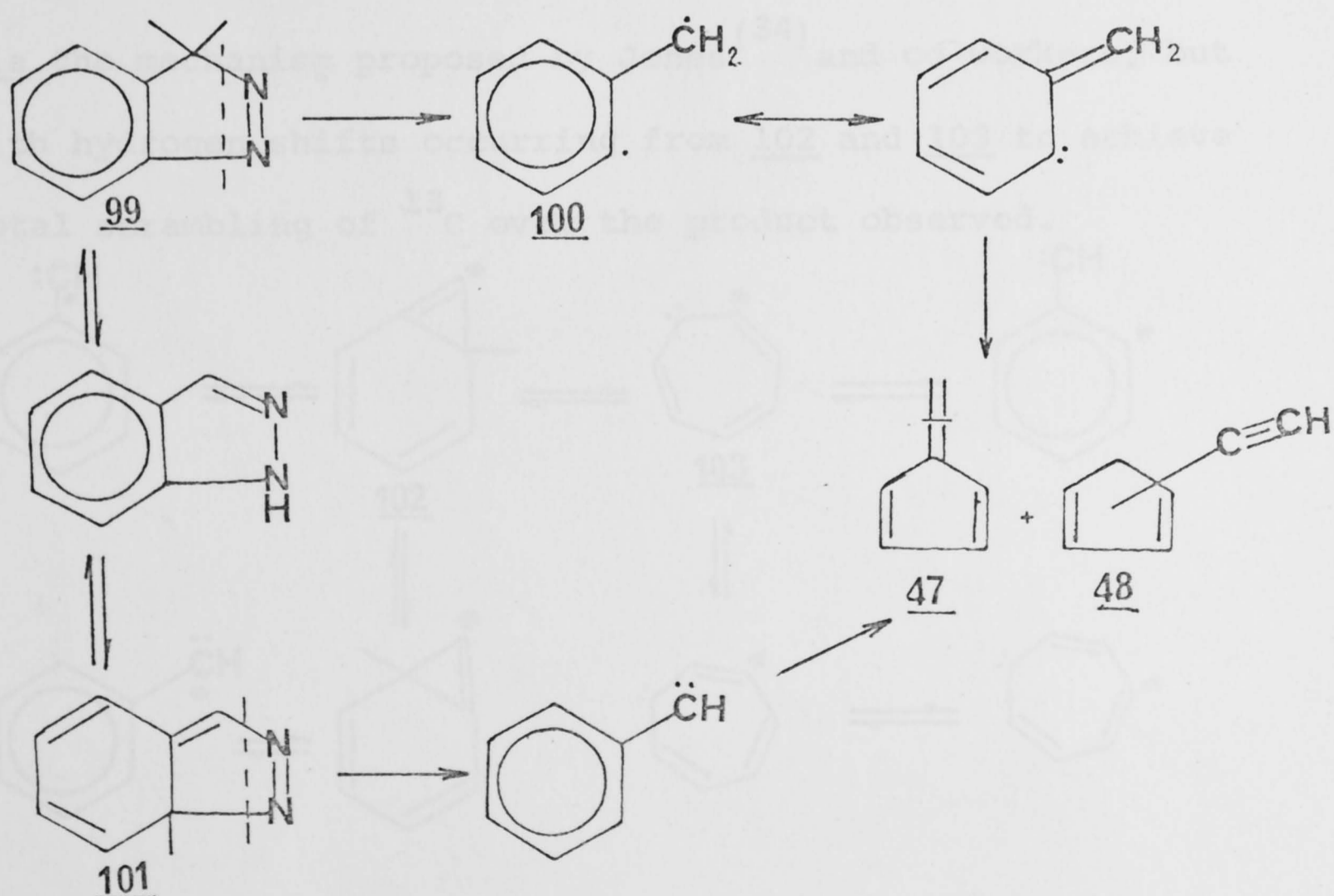
The possibility also exists for a 1,5- hydrogen shift to <u>101</u> which undergoes nitrogen loss to given phenylcarbene. Phenylcarbene would also give the same ring contraction products as the diradical mechanism.   The gas phase pyrolysis of 1H-pyrazolo(3,4b)pyridine indicated that both these mechanisms were operative, with the carbene mechanism becoming the dominant pathway from 700°C upwards.   These results imply that indazole is a possible generator of phenylcarbene, giving yields of ring contraction products up to 68%.

The mechanism for the ring contraction of phenylcarbene has been recently established by Crow and Paddon-Row[54] who showed by the pyrolysis of 7-^{13}C-phenyldiazomethane,   that phenylcarbene ring expands to cycloheptatrienylidene <u>via</u> the bicyclic intermediate <u>102</u>, prior to ring contraction. It was demonstrated that the phenylcarbene underwent isomerisation <u>via</u> the mechanism proposed by Jones[34] and co-workers, but with hydrogen shifts occurring from <u>102</u> and <u>103</u> to achieve total scrambling of ^{13}C over the product observed.
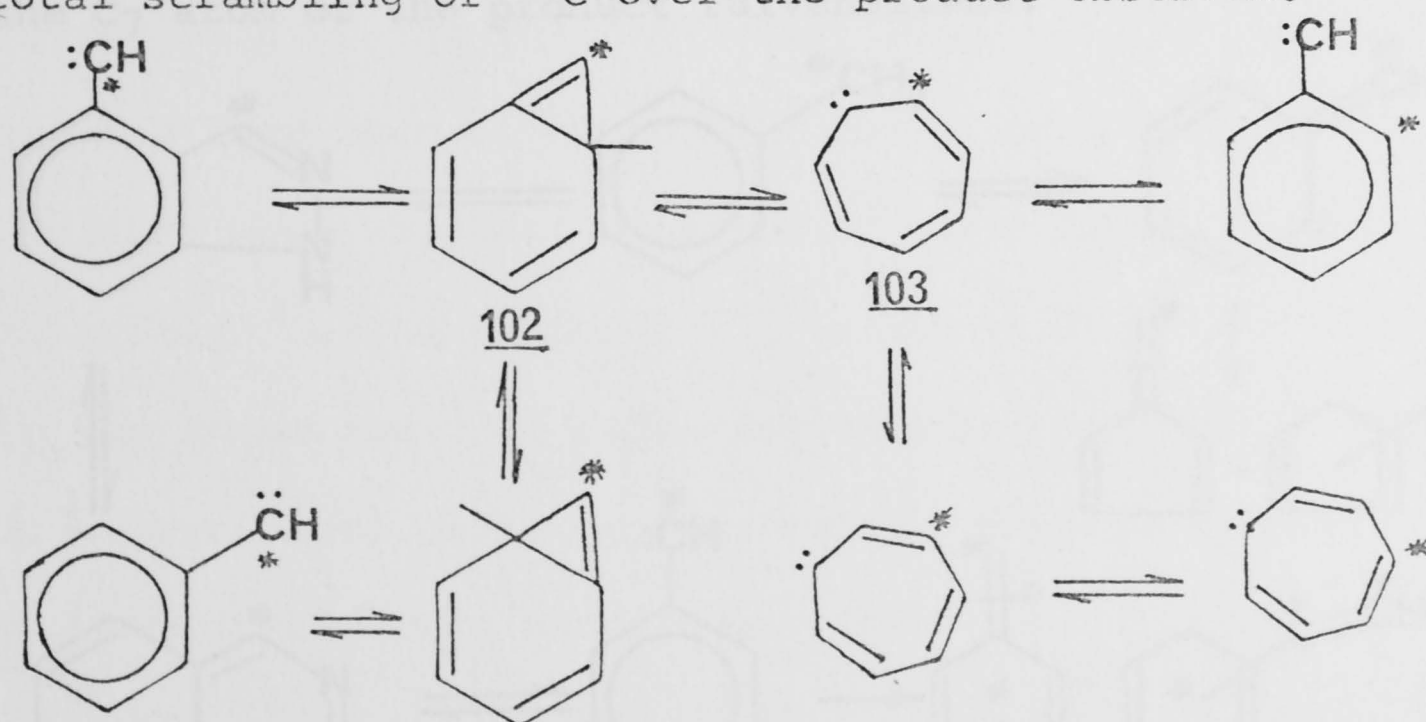
These findings are at variance with the results
observed by Wentrup and Wilczek[31] for the generation of
cycloheptatrienylidene from which no ring contraction products
were observed.   It was then concluded [54] that the
cycloheptatrienylidene was possibly generated in a spin state
different from that of the system obtained via phenylcarbene.
The results of Hedaya and Kent[54] for the labelled tolylcarbene,
where no hydrogen shifts were observed, can be explained by
asserting that the cycloheptatrienylidene isomerisation and
intramolecular trapping are very much faster than the hydrogen
shift mechanism.

The findings of Crow and Paddon-Row[54] show that the
possibility exists for the removal of the ambiguity in the
indazole pyrolysis by the thermolysis of 3-^{13}C-indazole as,
if the carbene mechanism is operative, scrambling of the label
should be observed, while if the 1,3-diradical mechanism is
operating total retention of the label should be observed in
the C_7 atom of the product fulvenallene.
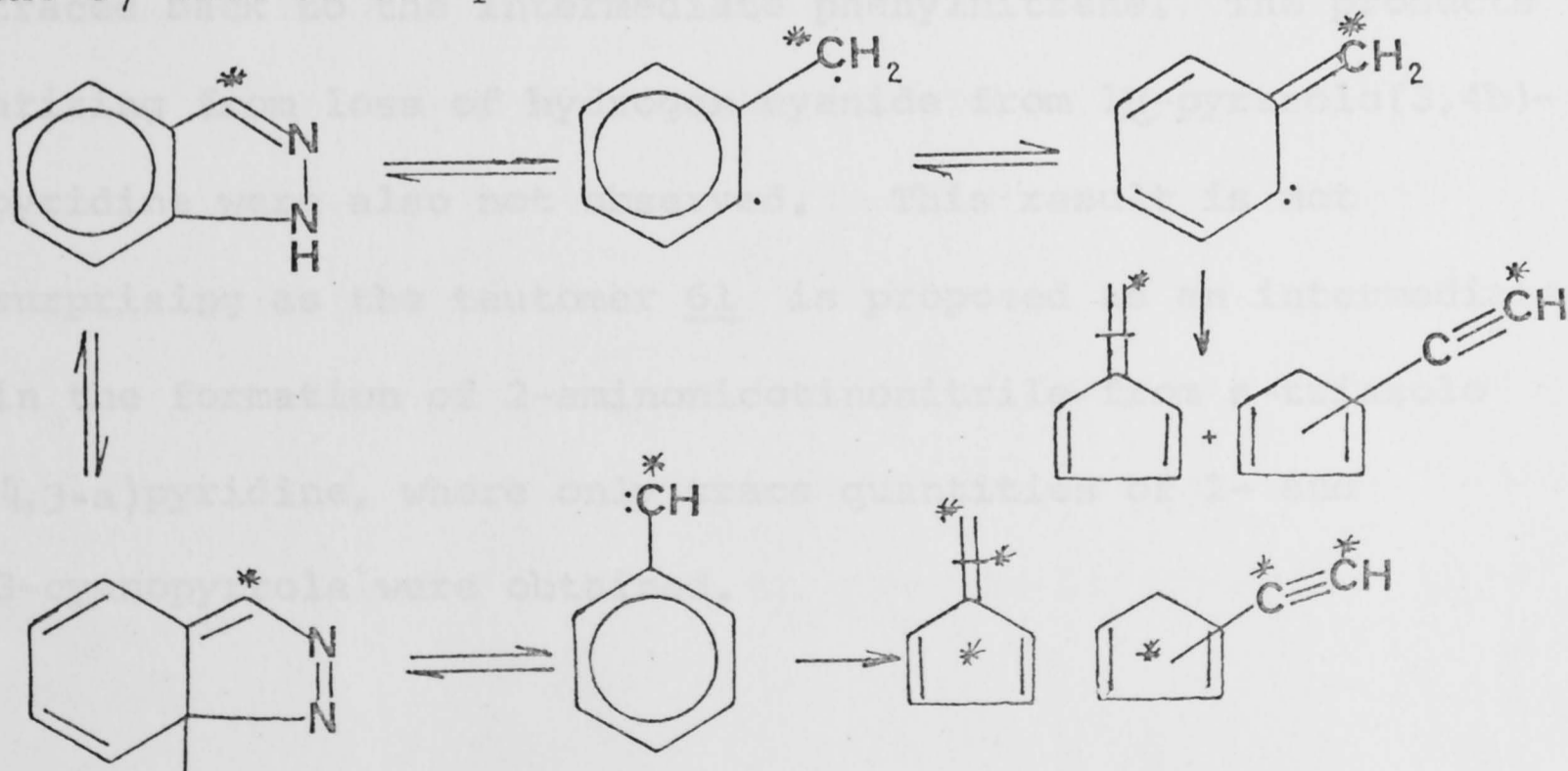
If the analogy is to be drawn from the pyrolysis

of 1H-pyrazolo(3,4b)pyridine at low temperatures ($\leqslant 700^{\circ}$C),

the two mechanisms will be competing, while at higher

temperature the carbene mechanism appears predominant and

scrambling of the label would occur.

The formation of o-aminobenzonitrile from 1H-indazole

is analogous to the formation of 2-aminonicotinonitrile from

1H-pyrazolo(3,4b)pyridine, i.e. N-N cleavage in the

tautomeric 3aH-isomer 104 followed by intramolecular hydrogen

shifts.
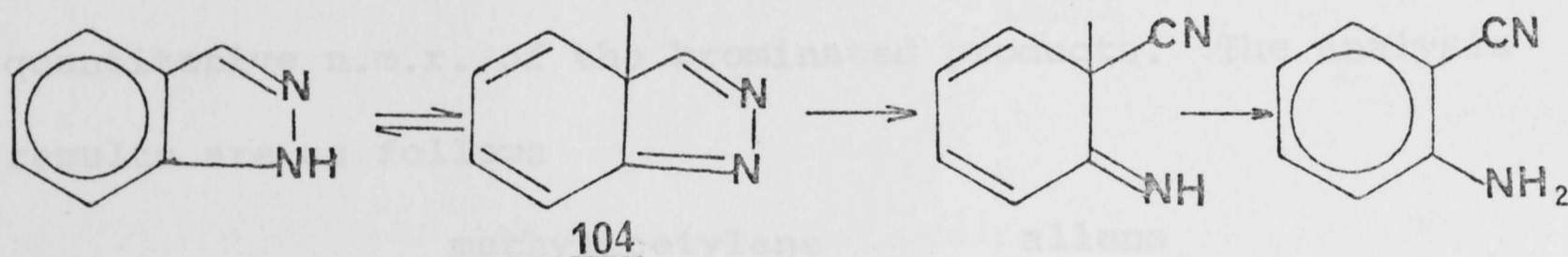
Although it is possible for 104 to lose hydrogen

cyanide, no products were observed whose formation could be

traced back to the intermediate phenylnitrene. The products

arising from loss of hydrogen cyanide from 1H-pyrazolo(3,4b)-

pyridine were also not observed. This result is not

surprising as the tautomer 61 is proposed as an intermediate

in the formation of 2-aminonicotinonitrile from s-triazolo

(4,3-a)pyridine, where only trace quantities of 2- and

3-cyanopyrrole were obtained.

Section 2.3   Gas Phase pyrolysis of Pyrazole

The results of the 1H-pyrazolo(3,4b)pyridine and

indazole pyrolyses indicate that these ring systems undergo

a series of hydrogen shifts to give a dual mechanism for

nitrogen loss, resulting in both carbene and diradical

pathways. The pyrolysis of pyrazole was undertaken to

investigate the generality of these decompositions.

The products obtained (methylacetylene and allene)

were identified by mass and n.m.r. spectral data, with these

compounds being further characterised by their bromination

products. The analysis of these pyrolyses was achieved by

quantitative n.m.r. of the brominated products. The analysis

results are as follows

	methylacetylene	allene
700°C	40%	13.5%
850°C	52%	38%.

At 850°C methylacetylene gas was pyrolysed and shown

to convert to allene (19%), however the residence time of

the gas in the furnace would be extremely low and would not be

likely to account for the isomerisation observed in the

pyrolysis of pyrazole.

The mechanism proposed for the formation of the products

involves a 1,3 or 1,5-hydrogen shift to give 106 which is then

followed by loss of nitrogen to give the intermediates 107
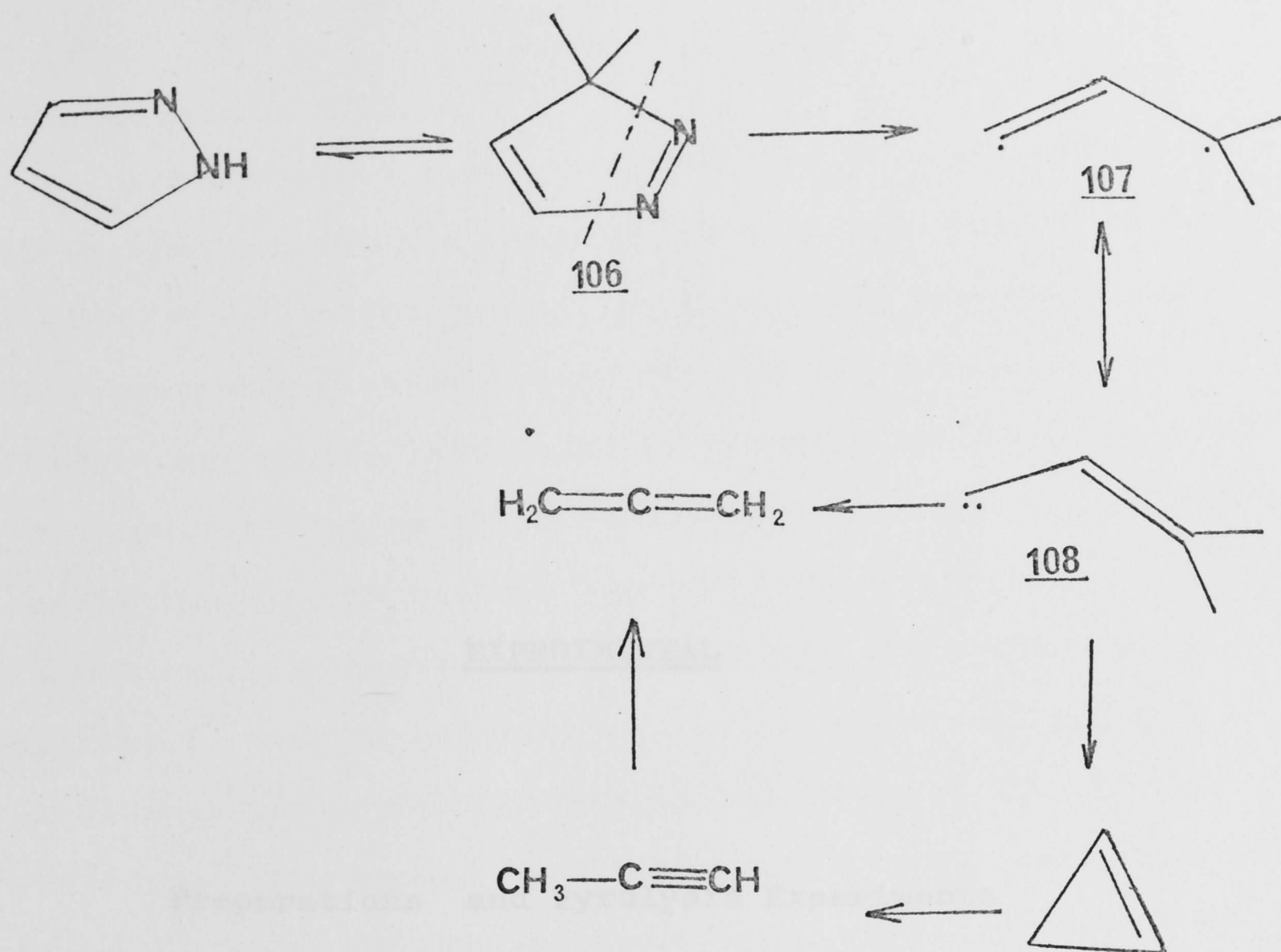
and 108.

The carbene and diradical intermediates 107 and 108
would then result in the formation of cyclopropene which would
be unstable under these conditions and has been shown[58] to
isomerise to methylacetylene at 400°C. Allene would then arise
from the isomerisation of methylacetylene. Allene can
also be obtained by carbene C-H bond insertion.

Similar products have been observed for the pyrolysis
of 1-cyanopyrazole and 1-methylpyrazole[42] (see introduction),
where the authors propose 1,3-migration of the cyano-or
methyl group prior to decomposition via loss of molecular
nitrogen. However the yields of the products observed are
extremely low when compared with the yields from pyrazole.

EXPERIMENTAL

Preparations and Pyrolysis Experiments

Experimental - General

The pyrolysis apparatus consisted of a silica tube
(30cm x 2cm) which was packed with 5 to 10mm pieces of 4mm
silica tubing. The 4mm silica tubing was used to prevent
the occurrence of streamlined flow in the furnace. The
furnace was heated externally by three 30 ohm heaters which
were connected up as three independent circuits. All three
heating zones were used at the one temperature in the
following experiments. The furnace was calibrated (voltage
applied to heating circuits against temperature) using a
platinum-iridium thermocouple in the range of 200° - 1100°.
The furnace was backed by a high capacity two stage Dynavac
Eight oil pump with the pressure being recorded on a
Vacustat gauge after the traps.

The volatile materials were collected in liquid nitrogen
cooled traps and were dissolved in chloroform for the
s-triazolo(4,3-a)pyridine pyrolysates and in carbon tetra-
chloride for the fused ring pyrazole pyrolysates. The
products were examined and analysed by g.l.c. using a 5750
Hewlett-Packard gas chromatograph equipped with dual flame
ionisation detectors and a comparison column.
The two columns used were Column A (10% Carbowax 20M on
80/100 mesh varaport 30) and Column B (5% Carbowax 20M on
80/100 mesh varaport 30). When preparative g.l.c. was
required an Aerograph 705 was used.

An Unicam SP200G spectrophotometer was used for the
measurement of i.r. spectra and all i.r. spectra were run
in carbon tetrachloride unless otherwise stated. The i.r.

.spectra are reported in cm^{-1} with (s), (m) and (w) indicating absorption intensities. ((s) = strong absorption; (m) = medium absorption; (w) = weak absorption). Carbon tetrachloride with tetramethylsilane as internal standard was used as solvent for the measurement of n.m.r. spectra. 60MHz n.m.r. spectra were recorded with a Perkin-Elmer R-10 spectrometer. The mass spectra were recorded with either an AEI MS10C2 spectrometer or an Atlas CH7 spectrometer. The ion abundances are expressed as percentages of the base peak with the exception of 3-methyl-s-triazolo(4,3-a)pyridine where the spectrum given is only schematic as the ion abundances are not known accurately. The u.v. spectra were recorded on a Pye-Unicam SP 1800 spectrophotometer and all spectra were run in 96% ethanol. Known compounds were identified by comparison with authentic specimens.

Preparations

<u>2-Pyridylhydrazine</u>[60] was prepared by the method of K.T.

Potts and H.R. Burton[60] by refluxing 2-bromopyridine in

hydrazine hydrate for 7 hours.

<u>s-Triazolo(4,3-a)pyridine</u>

A mixture of 7.8g 2-pyridylhydrazine and 18.3g 98%

formic acid was refluxed for 4 hours. The solution was

cooled and poured into 200 ml of water. The aqueous solution

was then made slightly basic by the addition of 40% sodium

hydroxide. The alkaline aqueous solution was extracted

with 2 x 100 ml and 1 x 60 ml of chloroform and the chloroform

extracts were combined and dried over Na_2SO_4. The

chloroform was distilled off to yield a crude brown oil

which deposited a white crystalline solid from benzene/hexane.

The white crystals obtained were dried under vacuum and

sublimed (bath temperature 80°) to yield 3.88g of white

hygroscopic crystals m.p. 72° lit.[61] 78°.

i.r. spectrum 1630(m), 1530(w), 1500(s), 1315(m), 1120(s),

1015(m), 785(s), 775(m), 760(s), 705(s) cm^{-1}

m.s. see page 96.

n.m.r. spectrum$(CDCl_3/TMS)$.[62]

1.10 (1H) singlet, 1.75 (1H) doublet, J 7c.p.s.,

2.08 (1H) doublet, J 8c.p.s., 2.5-3.25 (2H) pair of
quartets.

<u>3-Methyl-s-triazolo(4,3-a)pyridine</u> was prepared by refluxing

2-pyridylhydrazine with glacial acetic acid for 4 hours as

directed by the method of K.T. Potts and H.R. Burton[60].

The yield obtained was 82% and the melting point was 128°

while the literature[61] value was $128-129^o$.

i.r. 1635(m), 1545(w), 1500(m), 1150(m), 755(s), 740(s),

725(m)   nujol cm^{-1}.

m.s.   see page 98

n.m.r. spectrum$^{(62)}$ (CDCl$_3$/TMS).

      7.21 (3H) singlet - CH$_3$, 1.83 (1H) doublet, 7c.p.s.,

      2.08 (1H) doublet, 2.40-3.10 (2H) pair of quartets.

<u>2-Benzoyl-1-(2-pyridyl)hydrazine</u> was prepared by two methods

both of which are outlined by K.T. Potts and H.R. Burton.$^{(60)}$

(1)   2-Benzoyl-1-(2-pyridyl)hydrazine was prepared by the

addition of benzoyl chloride to 2-pyridylhydrazine in dry

pyridine at 0°. The yield obtained was 52% and the melting

point was 192°. Lit.$^{(67)}$ m.p. 193°.

(2)   2-Pyridylhydrazine and benzoic acid were heated in

a melt at 170° for four hours. This method yielded no

3-phenyl-s-triazolo(4,3-a)pyridine which is contrary to results

obtained previously$^{(60)}$. The yield of 2-benzoyl-1-(2-pyridyl)

hydrazine was 7%.

<u>3-Phenyl-s-triazolo(4,3-a)pyridine</u>$^{(60)}$ was prepared by reacting

2-benzoyl-1-(2-pyridyl)hydrazine with phosphorus oxychloride.

The white crystalline product was obtained in 37% yield,

m.p. 172° (lit$^{(60)}$ m.p.172°)

i.r. spectrum 1630(m), 1545(m), 1310(w), 1110(s), 1010(m),

770(m), 760(w), 750(s), 720(w), 700(m) nujol cm^{-1}.

m.s.   see page 97.

n.m.r. spectrum$^{(62)}$ (CDCl$_3$/TMS).

      1.61 (1H) doublet, J 6c.p.s., 1.90-2.45 (6H) complex
      multiplet,

      2.45-2.72 (1H) quartet, 3.00 (1H) quartet, J 6c.p.s.

<u>N-(2-pyridyl)benzamidine</u>[63] was prepared by the method out-
lined by K.T. Potts and Co-workers[63] in 37%.   The white
crystalline product had a melting point of 91°,   while the
literature[63] value was 92°.

<u>2-Phenyl-s-triazolo(1,5-a)pyridine</u>[63]

This compound was prepared in 55% yield by the method
detailed by K.T. Potts and Co-workers[63].

m.p. 137°, lit[63] m.p. 138°.

i.r. spectrum

3075(w), 3050(w), 1640(m), 1460(m), 1440(s),

1395(w), 1335(s).

m.s.   see page 97.

n.m.r. spectrum (CDCl$_3$/TMS).

1.38(1H) doublet,3c.p.s., 1.70 (2H) quartet,

2.21 (1H) doublet,6c.p.s., 2.52 (5H) multiplet,

3.01 (1H) quartet.

Nicotinamide-1-oxide

To 100g nicotinamide,   which was dissolved in 850ml
glacial acetic acid, was added 200ml 30% hydrogen peroxide.
The resulting solution was then warmed with stirring on a
water bath for two hours.   The solution was concentrated to
one quarter of its original volume, and the product crystall-
ised out on the addition of ethanol.   The product was then
washed with anhydrous ether and then dried at 80° to yield 69g
of white crystals.

m.p. 292°, lit[47] m.p. 291-293°.

2-Chloronicotinonitrile

A 45% yield of this compound was obtained by following
the method of E.C. Taylor Jr. and A.J. Crovetti[47] who

reacted nicotinamide-1-oxide with phosphorus oxychloride
and phosphorus pentachloride m.p. 98-99° lit.[47] m.p. 106-107°.

3-Amino-1H-pyrazolo(3,4b)pyridine

2.76g 2-chloronicotinonitrile (0.02M) and 1.6ml
hydrazine hydrate in 10ml isopropyl alcohol were refluxed
for 70 hours. The solution was then cooled and the isopropyl
alcohol was removed under reduced pressure. The product was
then treated with aqueous sodium bicarbonate and extracted
with chloroform. The chloroform was then dried (Na_2SO_4)
and the chloroform removed to yield 2.1g of a yellow crystalline
compound.

m.p. 182°, lit[64] m.p. 184-185°.

i.r. spectrum (nujol),3320, 3180(NH_2), 3150(NH) cm^{-1}.

1H-Pyrazolo(3,4b)pyridine

(1)   2.0G 3-amino-1H-pyrazolo(3,4b)pyridine and 1.02g
sodium nitrite were stirred for 30 minutes at -5°C in 19ml
borofluoric acid. The yellow solid formed was filtered off
and washed with cold ether/acetone.

The solid was added to a solution of 0.8g sodium in
80ml dry methanol; this addition resulted in a very vigorous
reaction with gas being evolved. The solution was then
refluxed for 20 minutes. The alcoholic solution was
concentrated to approximately half its original volume and
was then poured in water. The aqueous solution was extracted
(6x100ml) ether; the ether was dried (Na_2SO_4) and was

distilled off under reduced pressure to yield a golden oil
which still contained water. The oil was dried under a
vacuum and became solid; this solid was sublimed to give a
white hydroscopic solid, m.p. 90°, lit.[64] 98°.

m.s.   see page 96.

n.m.r. spectrum $(CDCl_3/TMS)$

1.26(1H) singlet, 1.80(1H) doublet, 1.93(1H) doublet,
2.80(1H) quartet.

i.r. spectrum 3460(m), 3200(s), 3150(s), 3035(s), 2960(m),
2920(s), 1607(s), 1520(s), 1395(s), 1310(s) cm^{-1}.

(2)   To 2.7g 3-amino-1H-pyrazolo(3,4b)pyridine in 5ml
concentrated hydrochloric acid and 5ml of water, was added
1.68g sodium nitrite in 10ml of water. The temperature
throughout the addition was kept below -5° and the reaction
stirred. The diazotisation was monitored with starch-
iodide paper to the appropriate end point. 30ml of benzene
was added to the reaction mixture; this was then followed
by the addition of 5.8ml 5M sodium hydroxide. A dark
emulsion formed and a further 3ml 5M sodium hydroxide was
added. The benzene layer was separated off and the aqueous
phase extracted (2x200ml) chloroform. The benzene and
chloroform layers were combined and dried (Na_2SO_4). The
solvent was distilled off under reduced pressure to give a
dark oil which when vacuum dried and sublimed yielded 100mg
of 1H-pyrazolo(3,4b)pyridine.

The small quantity of residue remaining after the
sublimation contained unreacted 3-amino-1H-pyrazolo(3,4b)-
pyridine,while a trace of 3-phenyl-1H-pyrazolo(3,4b)pyridine
was detected in the mass spectrometer M⁺ 195; (M-92); (M-103).

3-Vinylpyridine

Methyl triphenylphosphonium bromide (10.8g) was dissolved in ether (40ml) and dimethylformanide (20ml). Sodium methoxide (1.62g) was added and the mixture stirred at room temperature for 1 hour, under a stream of dry nitrogen. Pyridine-3-aldehyde(3.0g), which was dissolved in 5ml ether, was added dropwise over a period of five minutes and the reaction mixture stirred for a further 10 minutes. The reaction mixture was poured into water and the ether layer was separated. The aqueous layer was then extracted with a further portion (100ml) ether. The ethereal solutions were combined and dried (Na_2SO_4) and the ether removed. The small amount of material obtained was distilled at 0.1mm and 40° to a colourless oil which amounted to 40mg.

n.m.r. 1.40 (1H) singlet, 1.5 (1H) doublet, 2.3 (1H) multiplet, 2.8 (1H) quartet,

Vinylic protons ABX pattern

X 3.3, A 4.23, B 4.65,

J_{AX} 18 c.p.s., J_{BX} 11 c.p.s.

2-Aminonicotinamide

Crude 2-aminonicotinonitrile (100mg) which was obtained from the pyrolysis of s-triazolo(4,3-a)pyridine, was treated with 30% hydrogen peroxide in alcoholic potassium hydroxide according to the method of E.C. Taylor and A.J. Crovetti[47]. The product amounted to 0.062g and the melting point was 197°, lit.[47] 199°.

Pyrolysis Experiments

Pyrolysis of s-triazolo(4,3-a)pyridine

(a)   s-Triazolo(4,3-a)pyridine (322mg) was pyrolysed at

800° and 0.25mm with the sample being sublimed into the

furnace at approximately 80°.   The small amount of volatile

compound produced was dissolved in carbon tetrachloride.

The i.r. spectrum of the solution had prominent bonds at

3460, 3300, 2960, 2235, 2220 cm^{-1}.   The solution was

examined by g.l.c. (Column A isothermal 150°, Helium 60ml/min).

The g.l.c. indicated trace quantities of CCPD and benzonitrile.

The solid residue was dissolved in chloroform and g.l.c.

(Column B isothermal 200°, helium 60ml/min), showed only one

compound.   172 Mg (53% of solid product was obtained and

tentatively identified as 2-aminonicotinonitrile,   on the

basis of the spectral data and the m.p. of the product (m.p.

129-130°, lit.[47] 130-131°).

i.r. spectrum (-NH$_2$), 3500(w), 3460(s), 3400(s), 3300(broad).

        (-CN) 2220cm^{-1}.

n.m.r. spectrum(CDCl$_3$/TMS) 1.72 doublet (1H), 2.25 doublet

        (1H), 3.27 quartet (1H), 4.1 - 4.82 (2H).

m.s. M$^+$ 119 100%, (M-27)$^+$ 66% (see spectrum p. 96).

(b)   The triazole (259mg) was pyrolysed at 900° and 0.2mm

with the sample being introduced at around 80°.   The volatile

fraction was distilled to a second trap and the volatiles

were then allowed to warm up to room temperature under an

atmosphere of nitrogen.   These products, which were brilliant

green, yellow and red in colour, formed a black oil which

was not soluble in carbon tetrachloride and no spectra could

be obtained for these compounds.   114 Mg (44%) of

2-aminonicotinonitrile was isolated.

Pyrolysis of 3-methyl-s-triazolo(4,3-a)pyridine

(a)   The triazole (500mg) was pyrolysed at 800° and 1mm

with the sample being sublimed in at 130°. The volatile

fraction of the pyrolysate was distilled into a second trap

(distillation conditions 50° and 0.01mm).   This fraction

was separated by g.l.c. (Column A, $50-210^{\circ}$ at 6°/min.) into

seven compounds, two of which were only extremely minor and

were not identified.   The other five were identified as

acetonitrile (major), pyridine, 2-vinylpyridine, 3-vinyl-

pyridine (major) and benzonitrile.   The 3-vinylpyridine

was isolated by evaporating the acetonitrile, and dissolving

the residue in petroleum ether b.p. $40-60^{\circ}$ and chromato-

graphing down an alumina column.

n.m.r. spectrum 1.4 (1H) singlet, 1.5 (1H) doublet,

2.3 (1H) complex multiplet, 2.8 (1H) quartet,

Vinylic protons ABX pattern.

X   3.3,   A 4.23,   B 4.65

J_{AX} 18 c.p.s., J_{BX} 11 c.p.s.

m.s. $M^{+}105$, $(M-27)^{+}$ first loss.

The non-volatile fraction was chromatographed on

(Column B, 210°, isothermal, helium 60ml/min.) to show eight

fractions;   the first of which was identified as 3-vinylpyridine

which had remained despite the distillation separation. The

other three major compounds were separated by preparative

g.l.c. (using the same column as above) and were shown to be

2-cyanopyrrole, 3-cyanopyrrole and unchanged starting

material.

2-cyanopyrrole

i.r. spectrum (NH free) 3470, 3300 (hydrogen bonded)

2230 (CN).

n.m.r. spectrum 3.17 (2H) multiplet, 3.82 (1H)

-0.2(NH).

m.s.   M.$^+$ 100%;(M-27).$^+$ 23%.

3-cyanopyrrole

i.r. spectrum   3480 (free NH), 3300 (hydrogen bonded)

2240 (CN).

n.m.r. spectrum 2.68 (1H) multiplet, 3.20 (1H) multiplet

3.55 (1H),   0.4 broad (1H).

m.s.   identical to the m.s. of 2-cyanopyrrole.

The remainder of the mixture contained a trace of

2-aminonicotinonitrile and three other unidentified compounds,

one of which gave rise to a molecular ion at m/e 133 which

lost 27 mass units for its first loss.

(b)   The triazole (500mg) was pyrolysed at 800° and 0.01mm

with the sample being introduced at 150°.   Weight of

residue recovered 0.272g;   g.l.c. analysis gave the following

yields:

	% pyrolysate	% yield
3-vinylpyridine	46	32
2-cyanopyrrole	20	16
2-vinylpyridine	2	1
3-cyanopyrrole	24	19
benzonitrile	1.7	4
2-aminonicotinonitrile	11	3.

81.

(c)   3-Methyl-s-triazolo(4,3-a)pyridine (498mg) was

pyrolysed at 750° and 0.02mm with the sample being introduced

at 125-135°.   0.368G of material was recovered after

pyrolysis and g.l.c. analysis gave the following results:-

Weight of 3-methyl-s-triazolo(4,3-a)pyridine recovered =

0.245g or 49% which represents 66% of the pyrolysate.

	%pyrolysate	%yield
3-vinylpyridine	11	21
2-vinylpyridine	1	1
Benzonitrile	1	2
2-aminonicotinonitrile	–	trace
2-cyanopyrrole	9	20
3-cyanopyrrole	11	23.

(d)   The triazole was pyrolysed at 1,000° and 0.25mm with

the sample being sublimed in at 150°.   The pyrolysate was

dissolved in chloroform and g.l.c. (Column A) showed two main

components, these being benzene and benzonitrile with

numerous minor compounds. No further results were obtained

for 3-methyl-s-triazolo(4,3-a)pyridine at this temperature.

3-Phenyl-s-triazolo(4,3-a)pyridine

(a)   The triazole (1.00g) was pyrolysed at 800° and 0.1mm

with the sample being introduced into the furnace by

sublimation at 170°.   The pyrolysate was dissolved in

chloroform and separated by g.l.c. (Column B, isothermal 200°,

helium 60ml/min.)   The separation achieved showed four

major components which were collected by preparative g.l.c.

using the same column and the conditions cited above. These

compounds were shown to be 2- and 3-cyanopyrrole and

benzonitrile by comparison of the spectra of these compounds with the data reported.

The fourth major constituent of the mixture did not entirely separate from the 2-cyanopyrrole and the mixture was separated on preparative t.l.c. plates twice, using 70% ether/40-60° petroleum ether as developing solvent. This compound was tentatively identified as 5H-indeno(1,2b)-pyridine (4-azafluorene) from the spectral data and the melting point (m.p. 92°, lit,[50] m.p. 93°).

5H-indeno(1,2b)pyridine

i.r. spectrum 3040(m), 2900(m), 1600(s), 1480(m),
$\qquad$ 1420(s), 1400(s).

n.m.r. spectrum $CDCl_3$/TMS.

$\qquad$ 1.28(1H) doublet, 1.75(1H) complex quartet,

$\qquad$ 2.08 (doublet), 2.25-2.80 (4H), 6.08 singlet(2H).

m.s. M^+ 167 (100%); $(M-1)^+$ (24%); $(M-27)^+$ (14%);

$\qquad$ $(M-28)^+$ (16%); M^{++} 88.5; for a more detailed spectrum, see page 97. u.v. spectrum[51] λ_{max}. 307m , ε 16,000; λ_{max}. 282.5m , ε 8,600; λ_{max}. 250m , ε 9,900.

(b) 3-Phenyl-s-triazolo(4,3-a)pyridine (1.00g) was pyrolysed at 800° and 0.01mm with sample being introduced by sublimation at 180°. A dark red oil resulted (505mg) which was dissolved in 5ml of chloroform. The solution was analysed by g.l.c. (Column B, isothermal 200°, helium 60ml/ min) to give the following results:

product	% pyrolysate	% yield
4-azafluorene	27	16
2-cyanopyrrole	6	6
3-cyanopyrrole	13	12
benzonitrile	45	43
carbazole	5	3

(c)   The triazole (538mg) was pyrolysed at 1000° and

1.00mm pressure with the sample being introduced by sublim-

ation (180°).   The chloroform soluble residue (0.044g) was

chromatographed (Column B 200° isothermal,   helium 60ml/min) and

indicated 2- and 3-cyanopyrrole plus three other compounds,

two of which were tentatively assigned as biphenyl and

stilbene, plus one other compound which possessed a parent ion

of m/e 184.   No further pyrolyses were conducted at this

temperature.

2-Phenyl-s-triazolo(1,5-a)pyridine

(a)   2-Phenyl-s-triazolo(1,5-a)pyridine (100mg) was pyrolysed

at 800° and 0.01mm with the sample being sublimed into the

furnace at 140°.   The chloroform soluble residue (100mg) was

shown to be starting material.

(b)   2-Phenyl-s-triazolo(1,5-a)pyridine (186mg) was

pyrolysed at 850° and 0.01mm pressure,   with the sample being

introduced by sublimation at 140°.   The pyrolysate was

shown to be predominantly starting material with traces of

2- and 3-cyanopyrrole being indicated by g.l.c.; no 2-phenyl-

imidazolo(4,5b)pyridine was observed.

(c)   2-Phenyl-s-triazolo(1,5-a)pyridine (115mg) was pyrolysed at 900° and 0.05mm with the sample being sublimed into the furnace at 140°.   The pyrolysate (101mg) was shown to contain 2- and 3-cyanopyrrole, benzonitrile and starting material by g.l.c. and i.r.   No 2-phenylimidazolo(4,5b) pyridine was detected.

1H-Pyrazolo(3,4b)Pyridine

(a)   1H-Pyrazolo(3,4b)pyridine (50mg) was pyrolysed at 600° and 0.1mm;   the sample was introduced by sublimation at 95°.   A white solid (43mg) collected in the delivery tube before the liquid nitrogen trap.   This compound was shown to be starting material by the comparison of the spectral data obtained with that of the authentic material.   The liquid fraction which had collected in the liquid nitrogen trap was dissolved in carbon tetrachloride.

partial i.r. spectrum 3475, 3305, 2225, 2120, $1945cm^{-1}$.

The liquid fraction was separated into 4 components by g.l.c. (Column A, isothermal 150°, helium 60ml/min).   The second component possessed a similar retention time to CCPD. All four components were collected after a heated outlet for mass spectral examination.   Only one spectrum was obtained, that of CCPD, as the other three components collected as a purple polymer at the heated outlet.   The products from this pyrolysis were thought to be azafulvenallenes, ethynylpyrroles and CCPD.

(b)   1H-pyrazolo(3,4b)pyridine (60mg) was pyrolysed at 650° and 0.05mm with the sample being introduced into the furnace

by sublimation at 95°. The volatile products were collected
in a liquid nitrogen trap which, when the pyrolysis was over,
was allowed to warm up to room temperature. The volatiles
were then distilled under vacuum into a second liquid nitrogen
cooled trap. The volatile fraction was then allowed to warm
up to room temperature under an atmosphere of nitrogen and
the distillate was dissolved in carbon tetrachloride
containing tetramethylsilane as internal standard.

n.m.r. spectrum 6.97 singlet $C \equiv CH$; 4.95 singlet $=C=CH_2$;

        4.80 singlet $=C=CH_2$; 3.03 multiplet;

        3.33 multiplet (partly obscured by CCPD

                    signals)

        6.75 (singlet), 3.38 singlet, 2.45 doublet CCPD

i.r. spectrum (cm^{-1}) 3460(s) N-H; 3300(s) - $C \equiv C-H$;

                2120(m) - $C \equiv C -$;

                1940(s) $=C=CH_2$; 1974 $=C=CH_2(s)$

                2220(s) -$C \equiv N$.

The solid residue remaining after distillation of the
volatiles was shown to consist of 1H-pyrazolo(3,4b)pyridine
plus a trace of 2-aminonicotinonitrile by g.l.c. (Column A,
isothermal 200°, helium 60ml/min). The presence of
2-aminonicotinonitrile was also verified by preparative t.l.c.
(silica gel, ether/hexane = 1:1 v/v) which yielded a small
quantity of 2-aminonicotinonitrile i.r. spectrum:-NH_2 3500,
3460, 3400, 3300 (hydrogen bonded) -$C \equiv N$ $2220cm^{-1}$.

(c) 1H-Pyrazolo(3,4b)pyridine (101mg) was pyrolysed at 630°
and 0.2mm with the sample being introduced into the apparatus

by sublimation at 98°.   The pyrolysate was collected on the

liquid nitrogen trap as shown below.   This trap had been

coated with an ethanolic solution of dimethylamine by vacuum

distilling the dimethylamine solution on to the liquid

nitrogen chilled surface prior to the pyrolysis.
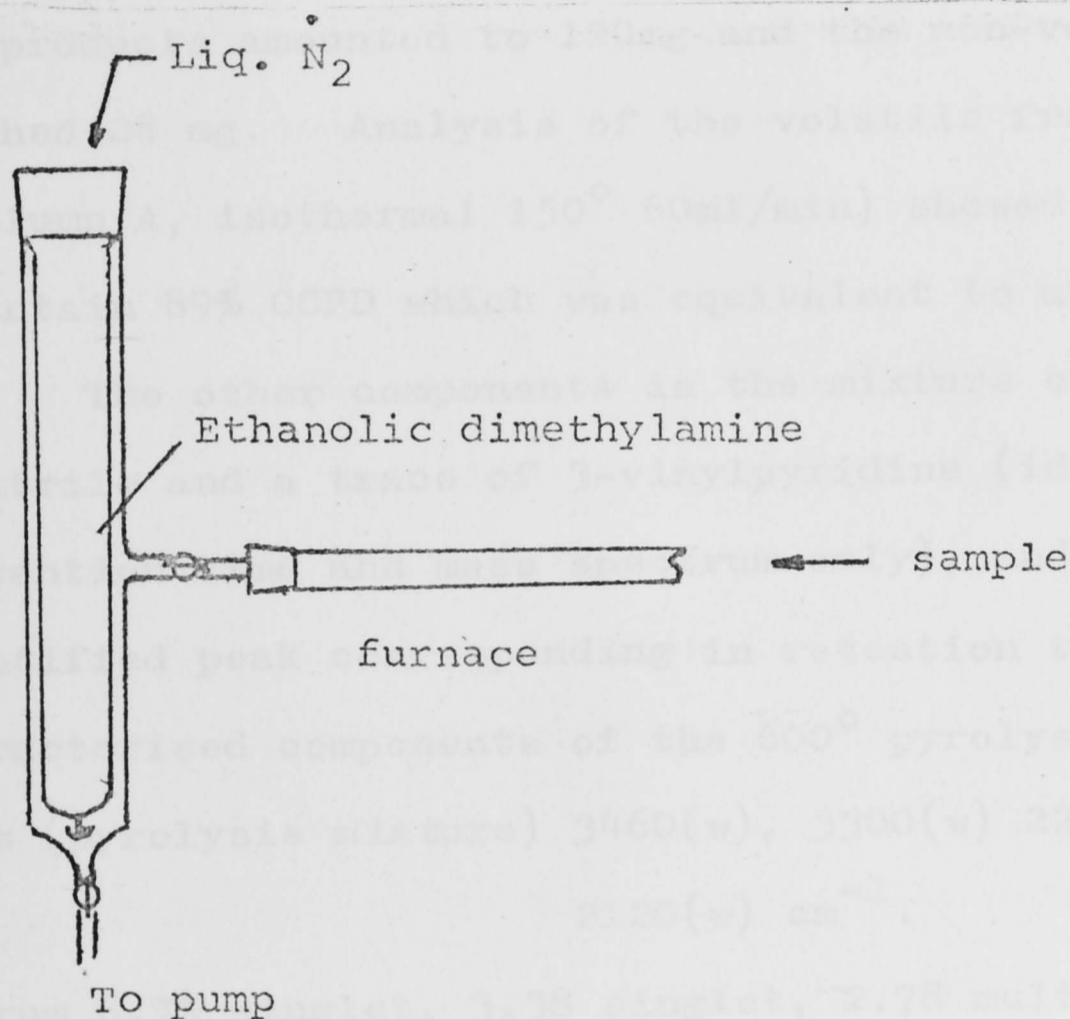
After the pyrolysis was completed the trap was

isolated from the pump and the furnace,and the liquid nitrogen

was drained from the trap. The interior of the trap was

filled with nitrogen and the trap was then allowed to warm up

slowly to room temperature.   A dark red solution resulted

with the inner tube of the trap being coated with dark red

insoluble material.   The solution was then evaporated to

dryness and the mixture chromatographed by preparative t.l.c.

(silica gel, ether/hexane = 1;1 v /v and yielded only polymeric

products plus CCPD dimer.

(d)   1H-Pyrazolo(3,4b)pyridine (220 mg) was introduced

into the apparatus at 95°,   and pyrolysed at 760° and 0.5mm

pressure.   The volatile residue which collected in the

liquid nitrogen trap was dissolved in carbon tetrachloride

and evaporated carefully to dryness at low temperature.

The volatile products amounted to 120mg and the non-volatile

fraction weighed 28 mg.   Analysis of the volatile fraction

by g.l.c. (Column A, isothermal 150° 60ml/min) showed the

mixture to contain 89% CCPD which was equivalent to an absolute

yield of 63%.   The other components in the mixture consisted

of 9% benzonitrile and a trace of 3-vinylpyridine (identified

by g.l.c. retention time and mass spectrum only), and a

fourth unidentified peak corresponding in retention time to one

of the uncharacterised components of the 600° pyrolysis.

i.r. spectrum (pyrolysis mixture) 3460(w), 3300(w) 2220(s)

$$2120(w) \ cm^{-1}.$$

n.m.r. spectrum 6.75 singlet, 3.38 singlet, 2.78 multiplet),

2.45 doublet.

The non-volatile fraction obtained from this pyrolysis

proved to be the polymer obtained from the attempted dimethyl-

amine characterisation of the azafulvenallenes and ethynyl-

pyrroles.

(e)   1H-Pyrazolo(3,4b)pyridine (100mg) was pyrolysed at

950° and 0.05mm with sample being introduced by sublimation

at 95°.   The pyrolysate was trapped as in the previous

pyrolysis and several highly coloured and reactive compounds

were obtained, similar to those obtained from the 900°

pyrolysis of s-triazolo(4,3-a)pyridine).   These products could

not be characterised.

1H-Indazole Pyrolyses

(a)   Indazole (102mg) was sublimed into the apparatus at 90° and pyrolysed at 600° and 0.01mm.   100 Mg of indazole was recovered unchanged after the pyrolysis.   A yellow compound which collected in the liquid nitrogen trap was shown to be o-aminobenzonitrile, since the infrared spectrum of a carbon tetrachloride solution of the compound had $\vee$ NH_2 bands at 3465,   3390cm^{-1} and a $\vee$ CN band at 2220cm^{-1}.

(b)   Indazole (49mg) was pyrolysed at 700°/0.02mm with conduction being used to heat the sample into the apparatus. This was achieved by using a piece of aluminium foil to conduct heat from furnace to the sample flask; the temperature reached by using this method was approximately 50°.   The volatile products were collected in a liquid nitrogen trap, which was allowed to warm up to room temperature under an atmosphere of nitrogen; and were dissolved in 0.35ml carbon tetrachloride mixed with 11mg of cyclohexane as internal standard.

n.m.r. spectrum 3.63 singlet (4H);   4.61 singlet(2H);

4.0 - 4.4 multiplet (3H); 6.7 - 7.0 multiplet (3H)

i.r. spectrum   3300(s) C $\equiv$ C-H;   3060, 3020(s)

2100(w) - C $\equiv$ C - H   1960(s) C $=$ C $=$ CH$_2$

Quantitative n.m.r.

Fulvenallene	15.6mg or	42%
Ethynylcyclopentadiene	6.4mg or	18%
Yield ring contraction products		60%
Yield aromatics		16%.

The weight of non-volatile residue was 15mg and t.l.c.

(silica gel, 20% ether/hexane) showed compounds with the

same R_F as o-aminobenzonitrile and indazole.

partial i.r. spectrum 3460, 3390 ($-NH_2$), 2220($-CN$).

Reaction of Ring Contraction Products with Dimethylamine

Indazole (202mg) was sublimed in the apparatus by the

method described above, and the sample pyrolysed at 700° and

0.03mm.   The volatile compounds were distilled into a second

trap containing 2ml of 33% ethanolic dimethylamine and

frozen with liquid nitrogen.   The reaction flask was filled

with nitrogen and the mixture allowed to warm up; a very

rapid reaction resulted to give a dark red solution.   The

solvent and unreacted dimethylamine were distilled off to

leave a red solid.   The red solid amounted to 0.129g which

was equivalent to a 57% yield of ring contraction products,

assuming that the base had catalysed the tautomeric

conversion of ethynylcyclopentadiene to fulvenallene.

n.m.r. spectrum ($CDCl_3$/TMS).

3.7 - 4.1 broad multiplet (4H), 6.85 singlet (6H)

$-N(CH_3)$; 7.78 singlet (3H) $-CH_3$.

i.r. spectrum 2950(s), 2920(m), 1700(m), 1740(m), 1665(m)

1375(s) cm^{-1}.

m.s. $M^{\ddagger}$ 135 100%, $(M-1)^+$ 50%, $(M-15)^+$ 37%

(M^+-27) 50%, $(M-44)^+$ 36%.

Preparative t.l.c. of the non-volatiles (silica gel, 45%

ether/hexane) yielded 6mg o-aminobenzonitrile.

Study of dimethylamine reaction by n.m.r.

(a)   Indazole (148mg) was pyrolysed at 700° at 0.05mm

with the sample being sublimed into the apparatus as before.

The volatile products were distilled as before and the

distillate was allowed to warm up to room temperature under

an atmosphere of nitrogen.   The pyrolysate was dissolved in

0.35ml carbon tetrachloride containing tetramethylsilane

as internal standard.   The n.m.r. spectrum showed peaks

due to benzene, toluene, fulvenallene and ethynylcyco-

pentadiene.   An anhydrous solution of dimethylamine in

carbon tetrachloride was added and a vigorous reaction

occurred.

The n.m.r. of the reaction mixture showed the dis-

appearance of the ethynylcyclopentadiene by the loss of the

6.7-7.0 τ signal.   Part of this region however was

obscured by the 6.85 τ signal of both the product and the

excess dimethylamine.

(b)   Indazole (60mg) was pyrolysed at 760° and 0.02mm

pressure with the sample being heated in by conduction as

before.   The pyrolysate was distilled as before and dissolved

in 0.35ml of carbon tetrachloride and 7.3mg cyclohexane were

added as internal standard.   Quantitative n.m.r.

Fulvenallene   22.7mg or 50%

Ethynylcyclopentadiene   8.0mg or 18%.

The following table represents results obtained from all

pyrolyses done at this temperature.

fulvenallene	Ethynylcyclopentadiene	benzene& toluene
32.3%	17.7%	10.2%
50%	18%	2%
18.4%	14.1%	18.3%
31.5%	19.7%	21%
26.5%	18.5%	26%
28.3%	23.7%	30%.

The above table shows that the yield of ethynyl-cyclopentadiene remains reasonably constant (variation ± 5%) while the yield of fulvenallene varies considerably. This illustrates that either the trapping techniques and/or the contact times through the furnace have a significant effect on the yield of fulvenallene obtained.

A supporting fact for this supposition is that the only other product obtained (other than those mentioned) was a polymeric substance for which no n.m.r. or mass spectrum could be obtained.

These yields of fulvenallene could then be improved upon by the use of an efficient trapping system and a furnace with a better vacuum system and a smaller capacity than the one used in this study.

800° Pyrolysis of Indazole

65Mg indazole was pyrolysed at 800° and 0.05mm. The volatiles were distilled as before. Quantitative n.m.r. :

Fulvenallene 16.6mg or 41.0%

Ethynylcyclopentadiene 6.2mg 17.0%.

<u>850°</u>

Indazole (650mg) was pyrolysed at 850° and 0.2mm; the products were trapped and distilled as before.   The distillate was dissolved in 0.35ml carbon tetrachloride quantitative n.m.r.

No ring contraction products observed.

Yield of benzene and toluene 39%.

<u>950°</u>

Indazole (65mg) was pyrolysed at 950°.   The sample was heated in as before with the pressure rising to 0.3mm during the pyrolysis.   The volatile fraction distilled as before.   Qualitative n.m.r. :   toluene 7.8%.   In all the high temperature (850-950°) no stilbene or heptafulvalene was observed.

<u>Pyrazole pyrolyses</u>

(a)   Pyrazole (596mg) was pyrolysed at 760° and 0.05mm with application of heat required to introduce the sample into the apparatus.   The gaseous products were collected in a liquid nitrogen trap which was allowed to warm up and the volatile products were distilled into a gas bottle (chilled in liquid nitrogen).   The non-volatile residue (44mg) remaining in the first trap was shown to be pyrazole.   A specimen of gas was introduced into the mass spectrometer with the following results:

m.s. M^{+} 100%, $(M-1)^{+}$ 86%, $(M-2)^{+}$ 39.6%

$(M-3)^{+}$ 26.2%, $(M-4)^{+}$ 11%, $(M-12)^{+}$ 8%

$(m-13)^{+}$ 11%, $(M-14)^{+}$ 7%.

93.

(b)   Pyrazole (153mg) was pyrolysed at 700° and 0.05mm
with no heat being applied for the sample introduction.
The gas evolved was first collected in a liquid nitrogen
chilled trap and then distilled into an n.m.r. tube
containing 0.35ml deutrochloroform with tetramethylsilane
as internal standard. Benzene (9.8mg) was added as
internal standard for quantitative n.m.r.   The n.m.r. tube
was filled with nitrogen and sealed, and the n.m.r.
spectrum was run at -50°.

        The n.m.r. spectrum exhibited a peak at 4.47 𝒯 due
to allenic protons and another at 7.95 𝒯 due to the methyl
and/or acetylenic protons of methylacetylene. Mass spectral
evidence confirmed the presence of these compounds.

(c)   Pyrazole (0.309g) was introduced into the apparatus
with the application of heat and was pyrolysed at 700° and
0.2mm. The gas was trapped as before and then distilled into
a gas bottle which was cooled in liquid nitrogen.   The gas
was then warmed up to -60° and dissolved in chilled
n-pentane; the solution was then treated with a pentane
solution of bromine while the temperature was kept around
-60°.   The unreacted bromine was removed by washing the
pentane solution with aqueous sodium thiosulphate. The pentane
solution was dried   (Na₂SO₄)and the solvent distilled off
under reduced pressure.   The brominated product weighed .500g.

n.m.r. spectrum 5.70 singlet (4H)   BrH₂C - CBr₂- CH₂Br
                 3.55 doublet (1H)   Br\   /CH₃
                                        C==C
                 7.65 doublet (3H)   H /   \Br.

3.90 singlet (1H)

7.30 singlet (3H) CH_3-CBr_2-$CHBr_2$.

The ratio of 1,1,2,2-tetrabromopropane and 1,2-dibromopropene: 1,2,2,3-tetrabromopropane was equal to 6:1 and thus gave a ratio of allene:methylacetylene of 1:6. The yield of allene then equalled 13.5% and the percentage yield for methylacetylene equalled 42%. Methylacetylene and allene were brominated using the conditions above and the spectra of the products compared with those of the brominated pyrolysate.

(d)   Pyrazole (776mg) was pyrolysed at 850° and 0.3mm with no heat being applied for the sample introduction. The gas was distilled and brominated as above, and gave a mixture of 1,2-dibromopropene and 1,2,2-tetrabromopropane. The brominated products amounted to 2.772g and the n.m.r. spectrum indicated that the allene/methylacetylene ratio was 0.75:1. The yields of allene and methylacetylene were therefore calculated to be 38% and 52% respectively.

Allene gas was condensed into a gas bottle which was immersed in a dry ice/acetone bath. The gas collected was then chilled in liquid nitrogen and the flask evacuated. The gas sample was allowed to warm up to -80° and pyrolysed at 850° and 0.1mm. The product was distilled and brominated as before and the n.m.r. spectrum of the product showed no 1,2-dibromopropene or 1,1,2,2-tetrabromopropane, that is no isomerisation had taken place.
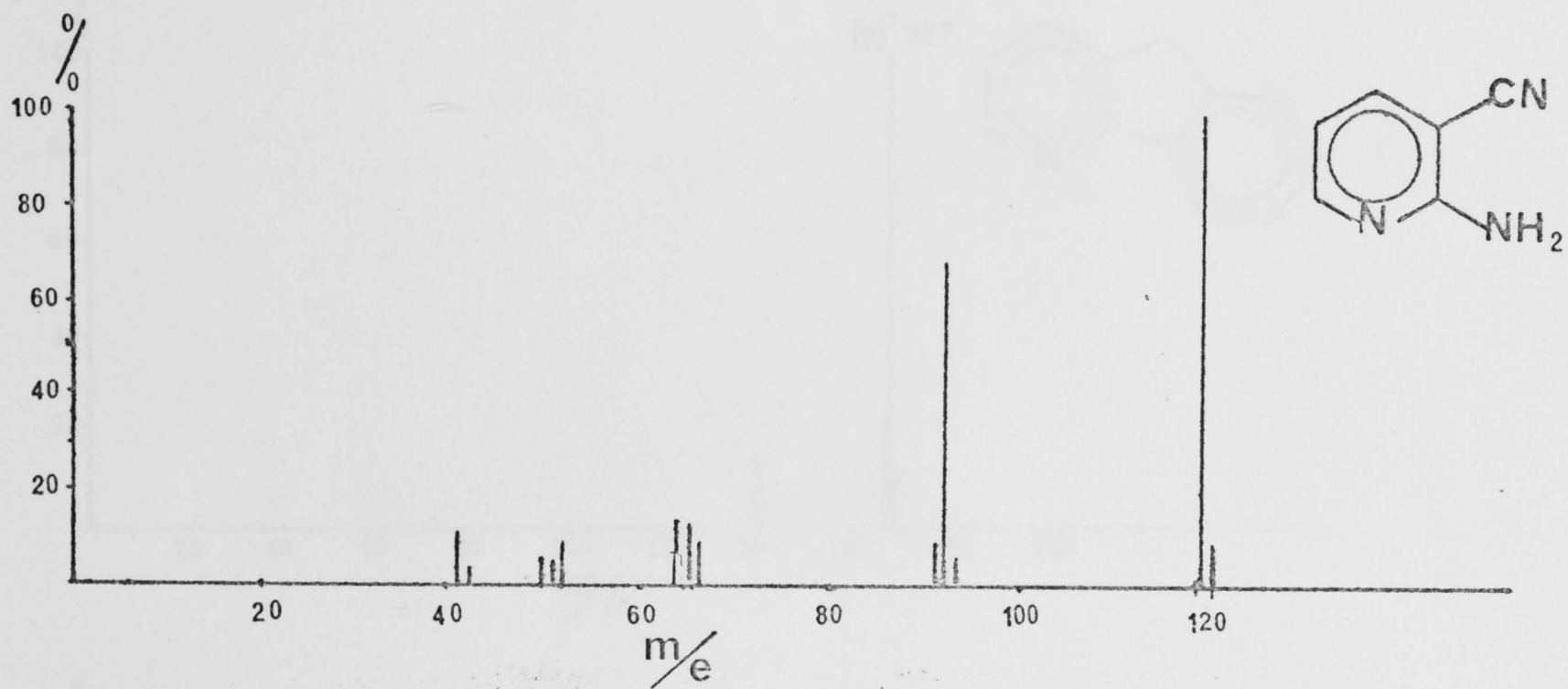
Methylacetylene gas was pyrolysed and brominated under the same conditions as for allene. The n.m.r. spectrum

showed the brominated pyrolysate to be a mixture of

1,2,2,3-tetrabromopropane and 1,2-dibromopropene.   From

the quantity of 1,2,2,3-tetrabromopropane formed the yield

of allene was calculated to be 19%.

(iv)

(v)

(vi)

98.
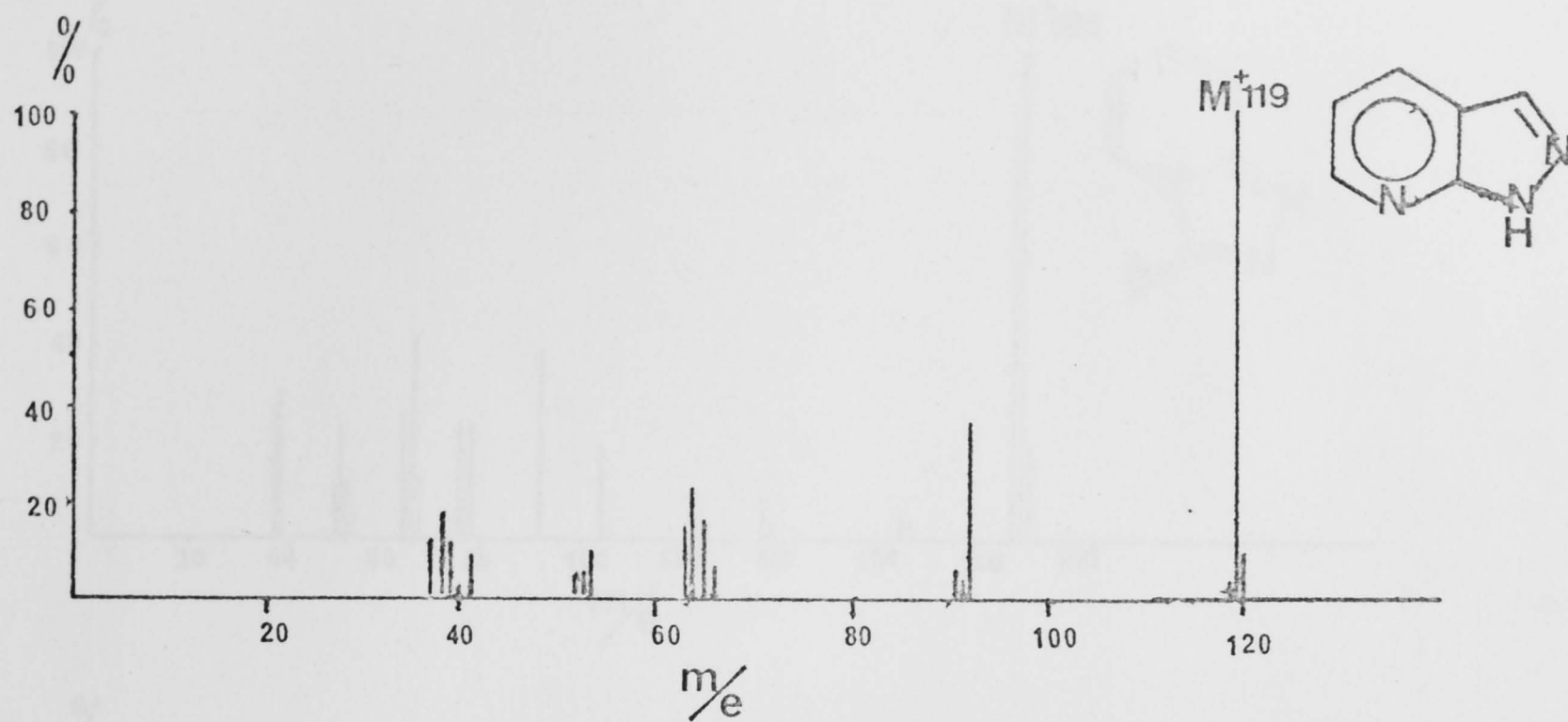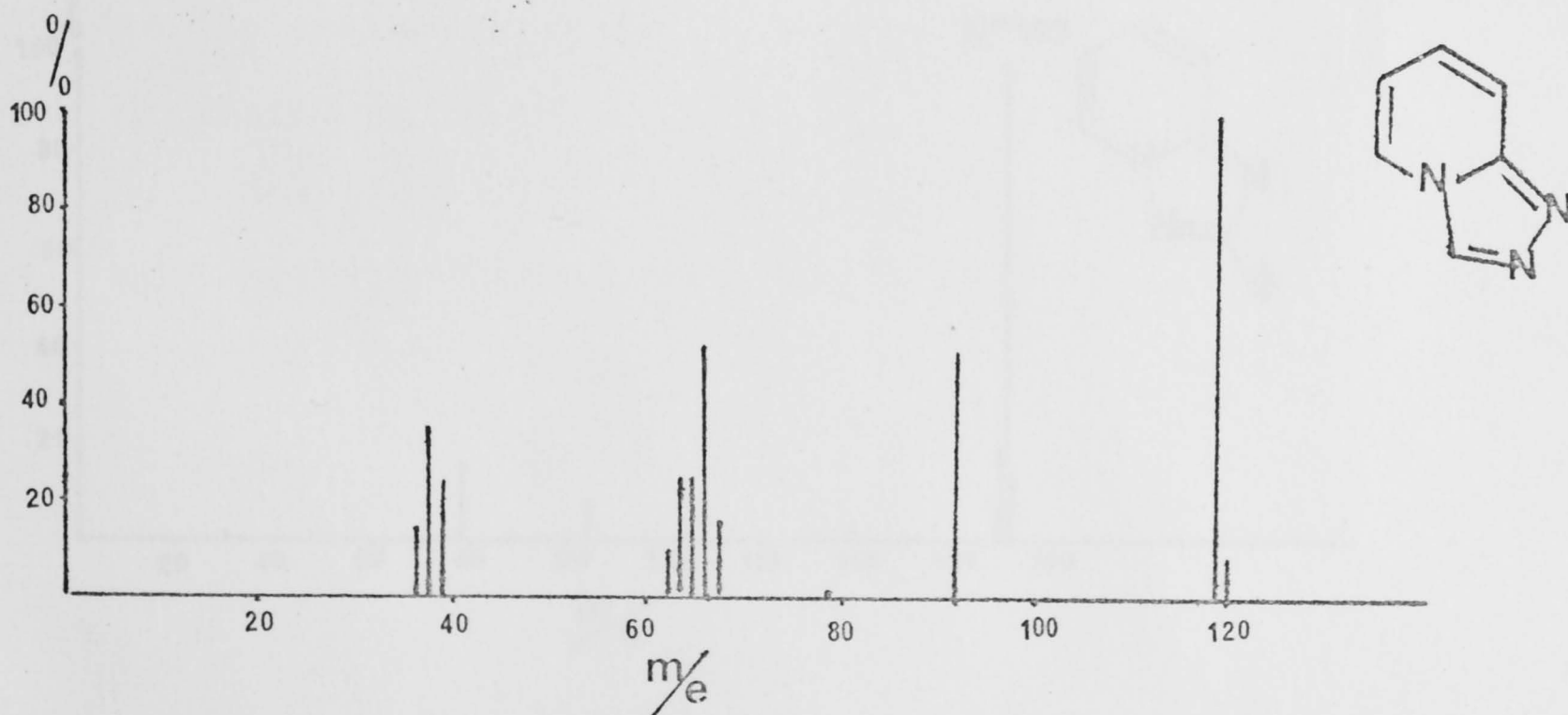
(vii)

(i) m.s. of IH - pyrazolo (3, 4b) pyridine.

(ii) m.s. of 2-aminonicotinonitrile.

(iii) m.s. of s-triazolo (4,3-a) pyridine.

(iv) m.s. of 3-phenyl-s-triazolo (4,3-a) pyridine.

(v) m.s. of 5H-indeno (1,2-b) pyridine.

(vi) m.s. of 2-phenyl-s-triazolo (1,5-a) pyridine.

(vii) m.s. of 3-methyl-s-triazolo (4,3-a) pyridine.

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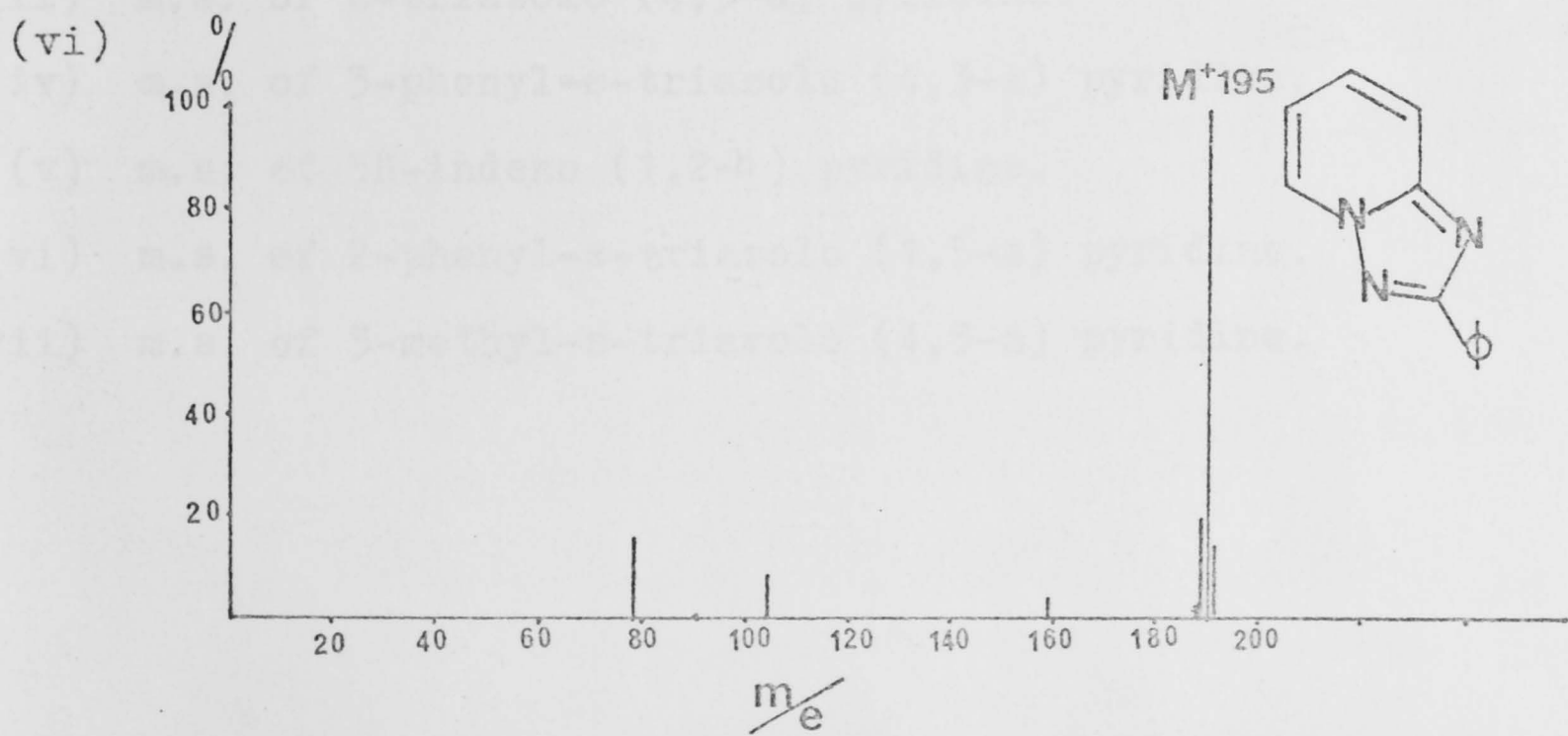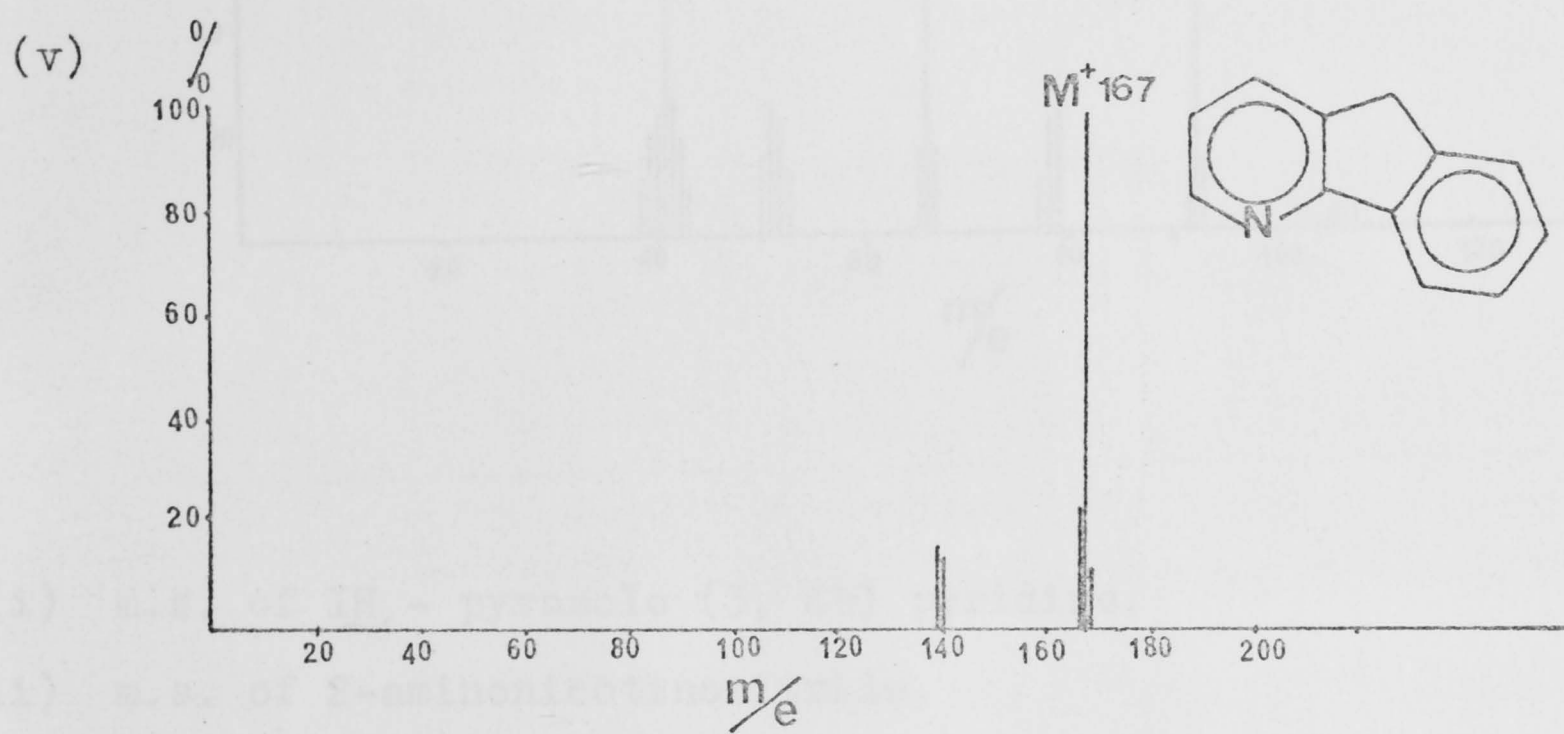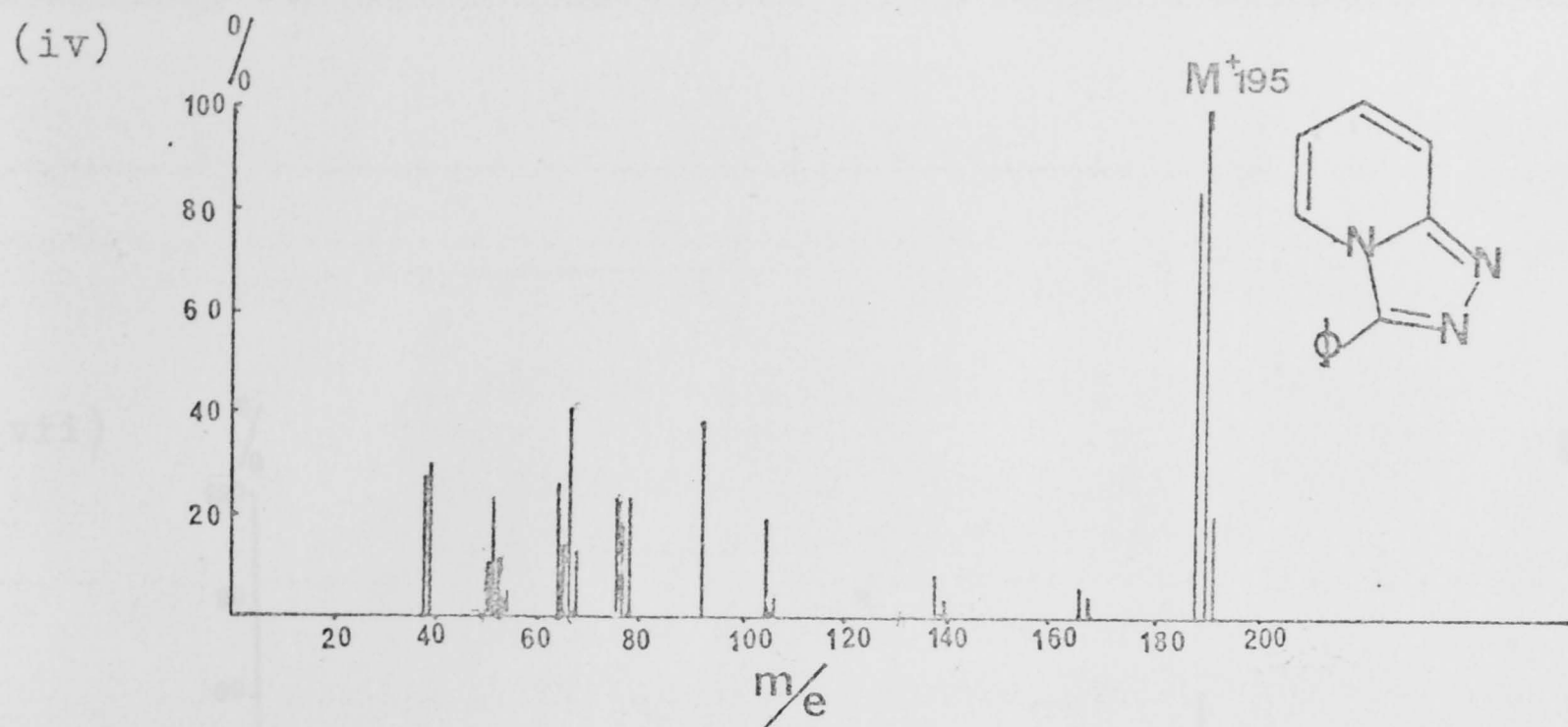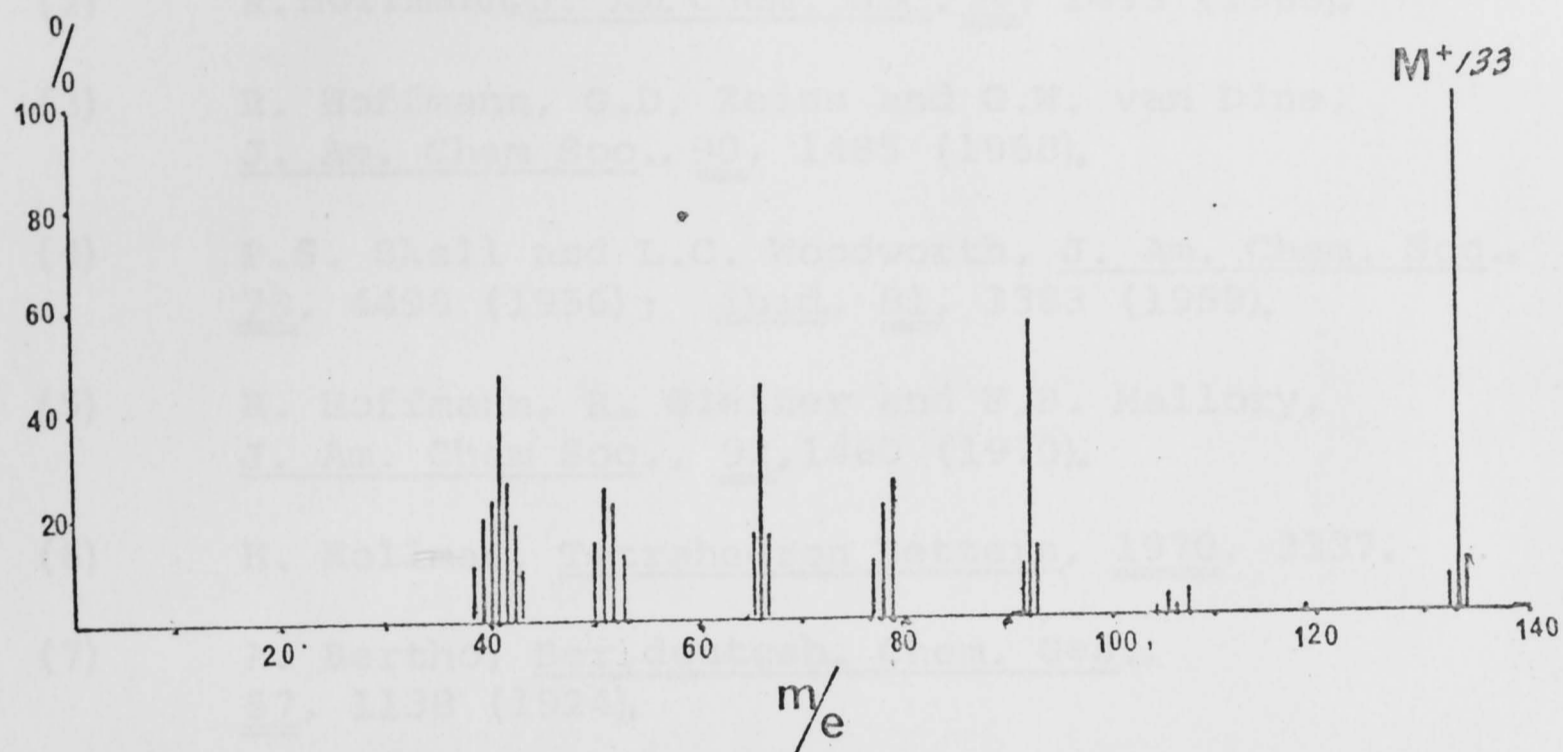(3)   R. Hoffmann, G.D. Zeiss and G.W. van Dine,
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