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SYNTHESIS AND CHEMISTRY OF 4-SUBSTITUTED-5-DIAZO-1,2,3-TRIAZOLES AND THEIR CORRESPONDING 1,2,3-TRIAZOL-4-YLIDENES

The Ohio State University

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THE SYNTHESIS AND CHEMISTRY OF 4-SUBSTITUTED- 
5-DIAZO-1,2,3-TRIAZOLES AND THEIR CORRESPONDING 1,2,3-TRIAZOL-4-YLIDENES

DISSERTATION
Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Graduate School of The Ohio State University

By
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The Ohio State University
1982

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Professor Jack Hine
Professor Leo Paquette
Professor Harold Shechter

Approved By
Advisor
Department of Chemistry
This work is dedicated to my parents
for their patience and love.
ACKNOWLEDGMENT

I wish to express my gratitude to Professor Harold Shechter for his advice during the course of this research and his expert guidance in the preparation of this dissertation. I would also like to thank my colleagues in Dr. Shechter's group for their valuable suggestions and inspiring ideas.
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Statement of Problem

This dissertation involves synthesis and study of the chemistry of various 4-substituted-5-diazo-1,2,3-triazoles (1) and their corresponding 1,2,3-triazol-4-ylidenes (2) (Eq. 1).

\[
\begin{align*}
\text{1} & \quad \text{2} \\
\text{Z} & \quad \text{Z} \\
\end{align*}
\]

(Eq. 1)

The objectives of the research are to: (i) prepare 5-substituted-1,2,3-triazole-4-diazonium salts (3) and their subsequent diazo compounds (Eq. 2) and study the physical and chemical properties of these carbene precursors; (ii) determine the effects of substituents (Z) on the behavior of diazo compounds (3) and their corresponding carbenes (1); (iii) obtain information as to the mechanisms of reaction of 1,2,3-triazol-4-ylidenes (2) with various substrates; (iv) investigate possible
cycloaddition reactions of diazotriazoles \( \text{I} \) with varied unsaturated substrates (Eq. 3); and (v) study the various deep-seated decomposition reactions of 1,2,3-triazol-4-ylidenes (2) possibly as in Eq. 4.
Chapter I  Historical

Five-membered ring diazoazoles (4) are of interest in synthesis\(^1\) and because of their possible thermal and photolytic conversions to their corresponding carbenes (5)(Eq. 5). Carbenes 5 are nitrogen analogs of cyclo-

\[ \begin{array}{c}
\text{A} & \text{D} \\
\text{B} & \text{C} \\
\end{array} \text{ or } \begin{array}{c}
\text{h} & \Delta \\
\text{5} + \text{N}_2 \\
\end{array} \quad (5) \]

where A, B, C, D = N or C pentadienylidene, a carbene which has been extensively studied for theoretical as well as synthetic purposes.\(^2-4\)

The present study of 4-diazo-1,2,3-triazoles (1) was initiated as part of a continuous program of investigation of aza-substituted cyclopentadienylidenes in this laboratory. The properties of 1 are expected to lie within those of diazocyclopentadiene (6) and diazotetrazole

\[ \begin{array}{c}
\text{N} \\
\text{N} \\
\text{Z} \\
\end{array} \quad (7) \]. The chemistry of 6 and Z however is vastly different
and will be systematically reviewed later.

1,2,3-Triazol-4-ylidenes (2), generated by decomposition of 1 with loss of nitrogen, are of theoretical interest. The triazolyldienes (2) might behave like a conventional singlet carbene 8a, with a pair of electrons occupying the sp$^2$ orbital, or a singlet carbene with a pair of electrons in the empty p-orbital as in 8b, or a diradical either in the singlet 8c or triplet states 8d.

![Diagram of structures 8a, 8b, 8c, 8d]

Of the four structures shown, 8b has the advantage of completion of an aromatic sextet. The pair of electrons in the carbenic p-orbital can be delocalized into the ring and thus be stabilized as a 6 π-electron system. Carbene 8b can be represented by 6 canonical forms as shown.

![Diagram of structures 9a, 9b, 9c, 9d, 9e, 9f]
Of some interest is that the empty sp² orbital on the carbene center might be stabilized by back donation of electrons from its alpha nitrogen atom and alpha carbon as in 9f. Because of the factors above, carbene 9b is presumably a resonance hybrid of 9a-f and thus 2 is anticipated to be electrophilic.

Doering and Depuy reported synthesis of diazocyclopentadiene (10a) in 1953. The arrangement of the π-orbitals in 10a is such that donation of electrons from the diazo group into carbon leads to an aromatic resonance system of six electrons: 10c and 10d. The exceptional stability of diazocyclopentadiene suggests that the canonical forms represented by 10c and 10d do contribute to the overall structure of the molecule.

Diazocyclopentadiene (10a) is a red liquid at room temperature which solidifies to dense yellow needles when cooled to below -23°C. The IR absorption band for the diazo group in 10a lies at 2082 cm⁻¹. Decomposition of
1\textsuperscript{10}a, either thermally or photolytically, generates cyclopentadienylidene (1\textsuperscript{11}). Carbene 1\textsuperscript{11} inserts into carbon-hydrogen bonds selectively\textsuperscript{6} and adds to olefins with near complete stereospecificity.\textsuperscript{7} The reacting state is proposed to be a singlet, although the ground state of 1\textsuperscript{11} is known to be a triplet.\textsuperscript{3} Reactions of 1\textsuperscript{11} with various benzenes are interesting. Thus benzene\textsuperscript{8} yields spironorcaradiene 1\textsuperscript{12} (Eq. 6), whereas hexafluorobenzene

\[
\begin{align*}
\text{C-H} + \text{C-H} & \rightarrow \text{C-C} \\
\text{11} & \quad \text{12}
\end{align*}
\]  

Eq. 6

gives adduct 1\textsuperscript{13} (Eq. 7), a cycloheptatriene. 2,5-Diphenyl-

\[
\begin{align*}
\text{C-H} + \text{C-F} & \rightarrow \text{C-C} \\
\text{11} & \quad \text{13}
\end{align*}
\]  

Eq. 7
cyclopentadienylidene (1\textsuperscript{14}a) and tetraphenylcyclopentadienylidene (1\textsuperscript{14}b) attack benzene to yield 1\textsuperscript{16} and 1\textsuperscript{17} (Eq. 8). Products 1\textsuperscript{16} arises presumably from aromatization of spironorcaradienes 1\textsuperscript{15}a (Eq. 8). Because the two \textit{alpha} positions of the cyclopentadiene ring in 1\textsuperscript{15}b are occupied by phenyl
groups, ring expansion of the five-membered ring occurs

to give 17 (Eq. 8). This rearrangement is somewhat unusual, since ring expansion of the seven-membered ring usually occurs. For example, 1-diazo-2,3,4-triphenyl-cyclopentadiene (18) photolyzes in benzene to yield 19 (Eq. 9).
There are nine diazoazacyclopentadienes, namely 2-diazopyrrole (20), 3-diazopyrrole (21), 3-diazopyrazole (22), 4-diazopyrazole (23), 2-diazoimidazole (24), 4-diazoimidazole (25), 4-diazo-1,2,3-triazole (26), 3-diazo-1,2,4-triazole (27) and diazotetrazole (28).

Of the nine diazoheterocycles, only five have been generated which are unsubstituted. They are diazopyrazole (23), 2-diazoimidazole (24), 4-diazoimidazole (25), diazotetrazole (28) and 4-diazo-1,2,3-triazole (26). Of the five however, all except 26 were generated in situ and attempts to isolate them often resulted in decomposition or serious explosion. 4-Diazo-1,2,3-triazole (26) is the only parent diazoazacyclopentadiene that has been isolated and found to be stable as a solid at room temperature. The white crystalline solid can be kept at room temperature.
for days without noticeable decomposition. Its unusual stability as compared to other diazoazacyclopentadienes is intriguing.

In studying the diazotriazole system and its corresponding carbenes, knowledge of the general behavior of diazoheterocycles is important. A survey of the chemistry of diazoazacyclopentadiene\textsuperscript{12,13} and their corresponding carbenes is now presented. Emphasis is placed on reactions with various aromatic substrates as well as those which are unique to each individual system.

**Pyrroles**

There are marked differences in the stabilities of 3-diazopyrroles and 2-diazopyrroles. The former require no special precautions in handling, but the latter decompose slowly in solution. 2-Aminopyrroles are very difficult to prepare and show none of the characteristics of primary aromatic amines.\textsuperscript{14} Diazotization of the unstable 2-aminopyrroles with nitrous acid results in decomposition.\textsuperscript{15} Pyrroles in which the 2-positions are vacant undergo nitrosation and are converted by addition of nitrous acid into 2-diazopyrroles.\textsuperscript{16} Little is known about the chemistry of these diazo compounds. 3-Diazopyrroles are much better behaved and are generally prepared by diazotization of the
corresponding amines. 3-Diazopyrroles are yellow and exhibit a characteristic diazo absorption at 2080-2180 cm⁻¹.

Diazotization of ethyl 4-amino-3,5-dimethylpyrrole-

\[
\begin{align*}
\text{Et}_2\text{C}&-\text{CH}_3
\end{align*}
\]

2-carboxylate yields diazonium salt 29 which couples with alkaline 2-naphthol to give 30 (Eq. 10). 3-Diazo-2,4,5-triphenylpyrrole (31) on prolonged heating in dilute sulphuric acid undergoes internal coupling. That coupling occurs with the the phenyl group at C-4 rather than C-2 is shown by formation of diketone 33 on oxidation of 32 with nitric acid (Eq. 11).
3-Diazo-2,5-diphenylpyrrole (34) has been extensively studied in this laboratory.\textsuperscript{19} Thermolysis or photolysis of 34 in benzene results in efficient ring-expansion to give 1,3-diphenyl-2H-cycloocta[c]pyrrole (35, Eq. 12), whereas photosensitization leads to aromatic substitution, yielding 2,3,5-triphenylpyrrole (36, Eq. 13). These results thus indicate that there may be important differences in the reactions of singlet and triplet carbenes with aromatic systems. The mechanism for formation of 35 may involve decomposition of 34 with loss of nitrogen to singlet 2,5-diphenyl-3H-pyrrolylidene (37), addition of 37 to benzene to form spironorcaradiene 38, electrocyclic isomerization to spirocycloheptatriene 39, 1,5-sigmatropic rearrangement to 40, and then hydrogen migration to give
Photosensitization of 34 with thioxanthene-9-one in benzene yields 36. Formation of 36 may be rationalized as involving triplet 2,5-diphenyl-3H-pyrrolylidene (41) and/or its triplet diazo precursor. Triplet 41 thus reacts with benzene to give triplet diradical 42 and then intersystem crossing to singlet diradical 43, hydrogen migration to 44, and then further hydrogen migration (1,5-sigmatropic) will give 36 (Scheme 2).

Reactions of 34 with substituted benzenes reveal some remarkable substituent effects. Electron-deficient benzenes such as benzonitrile, trifluoromethylbenzene
and nitrobenzene yield substituted 1,3-diphenyl-2H-cycloocta[c]pyrroles (35), presumably via 1,5-sigmatropic rearrangement of spirocycloheptatriene intermediate 39 as described in Scheme 1. Reactions of 35 with electron-rich benzenes result in o and/or p-substituted products 47, presumably via singlet 37 by collapse of spironorcaradienes 45 through substituent controlled dipolar processes as in Scheme 3.
Pyrazoles

Diazotization of 3-aminopyrazole (48) in concentrated acids (HX) yields pyrazole-3-diazonium salts (49). Such diazonium salts (49) undergo displacement reactions with nitrogen elimination and cycloaddition reactions (Eq. 14)\textsuperscript{20,21} Thus, Sandmeyer reactions yield 3-halopyrazoles (50, X=Cl,Br) and heating pyrazole-3-diazonium fluoroborate (49, X=BF\textsubscript{4}\textsuperscript{-})
with alkali fluorides yields 3-fluoropyrazole (51). When treated with diazomethane, pyrazole-3-diazonium chloride (49, X=Cl) forms 3-(1-tetrazolyl)pyrazole (52) along with pyrazolo[5,1-c]triazole (53, Eq. 14).

Heating 4-diazo-3,5-dimethylpyrazole (54) in benzene yields 3,5-dimethyl-4-phenylpyrazole (55), along with

\[ \text{54} \xrightarrow{\Delta} \text{55} + \text{56} + \text{57} \]
3,5-dimethylpyrazole (56) and biphenyl (57), apparently via hydrogen abstraction and coupling reactions (Eq. 15).\(^2\)

4-Diazopyrazole (58) has been synthesized and is being studied in this laboratory.\(^2\) The diazoazole decomposes thermally or photolytically in benzene to give 4-phenylpyrazole (59, Eq. 16). No products of ring expansion of benzene are obtained. Photolysis of 58 in substituted benzenes (toluene, anisole, chlorobenzene, benzonitrile, nitrobenzene) gives predominantly \(\sigma\)- and \(\pi\)-substituted products. Little selectivity is observed with respect to the ability of a substituent to direct the positions of insertion, since both electron-donating and electron-withdrawing groups on benzene lead to \(\sigma\)- and \(\pi\)-substitution.\(^2\) These experimental results seem to suggest triplet carbene processes and further work is under way to elucidate the mechanisms of these reactions.

3-Benzyl-4-diazo-5-phenylpyrazole (60) in hot acetic acid undergoes intramolecular coupling between its diazo and methylene groups to give 61 (Eq. 17).\(^2\)
Photolysis of 3-benzoyl-4-diazo-5-phenylpyrazole (62) and 5-benzoyl-3-diazo-4-phenylpyrazole (63) in benzene results in decomposition of the diazo compounds and formation of 3-benzoyl-4,5-diphenylpyrazole (64, Eq. 18) in both cases. Irradiation of 62 in aqueous acetone gives 4-hydroxypyrazole (65) and photolysis in acetic acid yields the corresponding acetate 66 (Eq. 19). However, photolysis of 5-benzoyl-3-diazo-4-phenylpyrazole (63) in aqueous acetone results in loss of nitrogen and hydrogen abstraction to yield 3-benzoyl-4-phenylpyrazole (67, Eq. 20).
3-\(\epsilon\)-Butyl-5-diazopyrazole (68a) and 5-diazo-3-phenylpyrazole (68b) react with pyrrolidine to form stable pyrrolidinylazopyrazoles 69a and 69b, respectively (Eq. 21).
Vacuum pyrolysis of $68a$ and $68b$ at 250°C and 60 mm Hg provides 3-t-butyl-2-cyano-2H-azirine ($70a$) and 2-cyano-3-phenyl-2H-azirine ($70b$), respectively (Eq. 22). A possible mechanism involves ring opening of carbenes $71$ to vinyl nitrenes $72$ which subsequently close to azirines $73$ (Eq. 23). Thermolysis of 3-t-butyl-5-diazopyrazole

\[
\begin{align*}
68a, \ R = t-C_4H_9 \\
b, \ R = Ph
\end{align*}
\]

(68a) in refluxing benzene gives 3-t-butyl-5-phenylpyrazole

(74) and a small yield of 2-t-butylpyrazolo(3,2-a)azocine (75, Eq. 24).
Substitution and ring-expansion products are also obtained when 68a is decomposed in substituted benzenes. Electron-withdrawing groups on benzene enhance azocine formation. There is high selectivity with respect to the ability of a benzene substituent to direct the positions of insertion. When the substituents are electron-donating by resonance (CH₃, CH₃O, Cl), only o- and p-substitution products are formed. When the substituents are electron-withdrawing (CN, NO₂), there is less selectivity with regard to the positions of substitution and m-substituted products along with smaller amounts of o- and p-isomers are obtained.

Imidazoles

2-Aminoimidazoles and 4-aminoimidazoles are readily diazotized to diazonium salts which undergo displacement reactions with nitrogen elimination. Some of these reactions provide synthetic routes to important pharma-
ceuticals. For example, 2-nitroimidazole (azomycin) and its mono, di and trimethyl derivatives \(^{77}\) have been prepared by treating their precursor amines \(^{76}\) with sodium nitrite, fluoroboric acid and powdered copper, the so-called Nitro-Sandmeyer reactions (Eq. 25).\(^{27}\)

\[
\begin{array}{c}
\text{NH}_2 \quad \text{NO}_2 \\
\text{R} \quad \text{R} \\
\text{R} \quad \text{R} \\
\end{array}
\xrightarrow{1) \text{HBF}_4}
\begin{array}{c}
\text{NO}_2 \\
\text{R} \quad \text{R} \\
\text{R} \quad \text{R} \\
\end{array}
\xrightarrow{2) \text{NANO}_2/\text{Cu}}
\]

(25)

\(2\)-Diazoimidazole (78) is prepared by diazotization of 2-aminoimidazole and neutralization of the intermediate diazonium salt.\(^{28}\) 2H-Imidazolylidene (79), generated by decomposition of 78 with loss of nitrogen, is a highly electrophilic carbene. Carbene 79 inserts into a C-H bond of cyclohexane to give 2-cyclohexylimidazole and substitutes exclusively in the o- and p-positions of cumene, N,N-dimethylaniline, anisole and fluorobenzene. The orientation in substitution of the above aromatics is interpreted in terms of dipolar opening of intermediate spironorcaradienes 80 (Scheme 4).\(^{28}\) Slightly different results have been reported by Vilarrosa.\(^{29}\) 2H-Imidazolylidene (81), generated also by photolysis or thermolysis of 2-diazoimidazole (78), reacts with substituted benzenes
(toluene, chlorobenzene, anisole and nitrobenzene) to give mixtures of 2-(o-, m- and p-substituted phenyl)imidazoles (82) (Scheme 5). Anisole, toluene and chlorobenzene

(Scheme 4)

(Scheme 5)

yield o- and p-substitution products containing small amounts of m-isomers, whereas nitrobenzene gives mostly the m-isomer, along with minor o- and p-substituted derivatives. It is suggested that 81 is a highly reactive carbene with strong singlet diradical character.29
4-Diazoimidazole (83) decomposes thermally or photo-
lytically in benzene to give 4-phenylimidazole (84,
Eq. 26). Photolysis of 83 in electron-rich benzenes
such as cumene, t-butylbenzene, chlorobenzene and bromo-
benzene yield predominantly o- and p-substituted products,
whereas electron-deficient benzenes such as trifluoromethyl-
benzene, benzonitrile and nitrobenzene give substantial
amounts of m-substituted derivatives along with minor
o-isomers.

Webster and Sheppard have prepared 2-diazo-4,5-dicyano-
imidazole (85) by diazotization of the corresponding amine.
Pyrolysis of 85 in halobenzenes (Cl, Br, I) is of interest in that dicyanoimidazole halonium ylides (88) are formed along with 4,5-dicyano-2-halophenylimidazoles (86) and
4,5-dicyano-2-halo-1-phenylimidazole (87, Eq. 27). Ylides rearrange to 87 upon heating. A unique reaction is observed in thermolysis of 85 in benzonitrile. The fused heterocycles 89 is formed which presumably arises from reactions of ylide 90 with a second molecule of benzonitrile (Eq. 28).  

\[
85 \xrightarrow{\Delta} 89
\]

Triazoles

1,2,4-Triazole-3-diazonium salts (91) with R = alkyl, aryl and carbomethoxy have been reported. The parent diazonium salt (91, R = H) has also been prepared and couples in high yields (78-82%) with N,N-dialkylanilines.
Treatment of $\mathbf{91}$ ($R = H$) with nitroalkane anions in sodium hydroxide solution yields hydrazones $\mathbf{93}$ (Eq. 29).  

5-Diazo-3-phenyl-1,2,4-triazole ($\mathbf{94}$) and its subsequent carbene have been investigated. Thermolysis or photolysis of $\mathbf{94}$ in benzene gives 3,5-diphenyl-1,2,4-triazole. Reactions of $\mathbf{94}$ with benzene substrates with electron-donating groups ($\text{CH}_3$, ($\text{CH}_3$)$_2$CH, $\text{CH}_3$O, Cl, Br) result in o- and p-substitution. On the other hand, decomposition of $\mathbf{94}$ in electron-deficient benzenes such as trifluoromethylbenzene, benzonitrile and nitrobenzene give m-substitution along with products derived from reactions of the carbene with the substituents. Decomposition of $\mathbf{94}$ in hexafluorobenzene results in 5-fluoro-1-pentafluorophenyl-3-phenyl-1,2,4-triazole ($\mathbf{96}$, Eq. 30). The intermediacy of fluoronium ylide $\mathbf{95}$ which undergoes
migration of its pentafluorophenyl group was proposed.  

\[
\begin{align*}
\text{(30)} \\
\end{align*}
\]

There is little information about 4-diazo-1,2,3-triazoles. The only such compound reported is 4-carboxamido-5-diazo-1,2,3-triazole (97). Diazoazole 97 is formed when 4-amino-5-carboxamido-1,2,3-triazole is treated with amyl(pentyl)nitrite in aqueous acetic acid. When the reaction is carried out using sodium nitrite in aqueous acetic acid followed by adjustment of the solution to pH 9 with dil sodium hydroxide, the product is 2,8-diazahypoxanthine (98), resulting from cyclization of 97 (Eq. 31).

\[
\begin{align*}
\text{(31)} \\
\end{align*}
\]
Tetrazole

Shevlin has isolated tetrazole-5-diazonium chloride (99) as a crystalline solid by treating 5-aminotetrazole with isoamyl nitrite in THF containing hydrochloric acid. The IR spectrum of the extremely explosive salt shows $\lambda_{\text{max}}$ 2275 cm$^{-1}$. Diazotetrazole (100) has not been extensively characterized because of its explosive nature. It is anticipated that (100) would decompose to three molecules of nitrogen and atomic carbon (Eq. 32). Pyrolysis of (99)

\[
\begin{align*}
N_2^+ \text{Cl}^- & \rightarrow \begin{array}{c}
\text{N} \\
\text{N}
\end{array} & \rightarrow & \cdot \text{C} + 3 \text{N}_2
\end{align*}
\]

(32)

in gaseous substrates such as carbon monoxide, propane, cyclopropane, cyclobutanone, and furan gives products that arise from reaction of atomic carbon with diluents. Products with the tetrazole ring retained are not observed.
Chapter II  Results and Discussion

The 1,2,3-triazole ring system has been well characterized. Books^4^ and reviews^46,47^ pertaining to the preparation and chemistry of 1,2,3-triazoles have been published recently. However, there are few reports of 4-diazo-1,2,3-triazoles. A study of the synthesis and chemistry of 4-substituted-5-diazo-1,2,3-triazoles and their corresponding carbenes has now been initiated.

In the present research, four 4-substituted-5-diazo-1,2,3-triazoles have been prepared and isolated as crystalline solids. They are 4-diazo-1,2,3-triazole (101), 4-diazo-5-phenyl-1,2,3-triazole (102), 4-carbethoxy-5-diazo-1,2,3-triazole (103) and 4-cyano-5-diazo-1,2,3-triazole (104).

Diazo compounds \( 101-104 \) are prepared by diazotization of their corresponding amines, \( 105-108 \), in dilute hydrochloric acid with sodium nitrite at 0°C (Eq. 33). After neutralization to pH 7 with sodium carbonate, the aqueous solutions are extracted repeatedly with dichloromethane. The amount
of dichloromethane needed depends on the substituent (Z) in the triazole. When Z = Ph, 300-400 ml of dichloromethane are sufficient for each 10 mmol of the diazo compounds, whereas when Z = H, CO$_2$C$_2$H$_5$, CN, usually 800-1000 ml of dichloromethane are needed to ensure complete transferral. After drying the dichloromethane extracts over anhydrous magnesium sulphate, the solvent can be removed to dryness to yield the diazo compounds as solids. For safety reasons, however, it is advisable to transfer concentrated solutions of a diazotriazole to a reaction vessel, add the reaction substrate and then effect total removal of dichloromethane under reduced pressure.

The main task for synthesis of these diazo compounds is therefore to prepare the precursor amines. Unlike 3-amino-1,2,4-triazoles, preparation of 4-amino-1,2,3-triazoles is quite tedious.
In the present work, 4-amino-1,2,3-triazole (105) was prepared by (i) debenzylation of 4-amino-1-benzyl-1,2,3-triazole (111) and (ii) hydrogenation of 4-nitro-1,2,3-triazole (113). The two routes to 105 involve integration of many literature contributions and are summarized in Methods I and II as follows:

**Method I** (Scheme 6) 4-Amino-1-benzyl-5-carbethoxy-1,2,3-triazole (109) is prepared from benzyl azide, ethyl cyanoacetate and sodium in ethanol. Hydrolysis of 109 with potassium hydroxide in ethanol and acidification yields 5-amino-1-benzyl-1,2,3-triazole-4-carboxylic acid (110), decarboxylation of which with hot dimethylaniline

![Scheme 6](image_url)
followed by debenzylation of the resulting amide, 111, with sodium in liquid ammonia affords 105 in low yields (Scheme 6).

**Method II (Scheme 7)** Reaction of nitromethane with ethyl ethoxymethylenemalonate in the presence of morpholine yields 1-morpholino-2-nitroethene (112). 1,3-Dipolar addition of tosyl azide to 112 furnishes 4-nitro-1,2,3-triazole (113) and tosyl morpholide (114). Selective hydrogenation of 113 over 5% palladium-on-charcoal yields 105 as the free amine (Scheme 7).

Method II is far superior to Method I in terms of yields as well as the purities of all intermediates and
the final product. Method I is acceptable overall except for the last step in which the benzyl group is removed reductively by sodium in liquid ammonia. The yield of this reduction step is poor and usually 105 is not isolated in pure form.

4-Amino-5-phenyl-1,2,3-triazole (106) is prepared by the method of Sutherland and Tenant and the synthetic scheme is summarized as follows: 5-amino-1-benzyl-4-phenyl-1,2,3-triazole (115) is prepared by condensation of benzyl azide, phenylacetonitrile and sodium in ethanol. Reduction with sodium in liquid ammonia leads to removal of the benzyl group on 115 (Scheme 8).

4-Amino-5-carbethoxy-1,2,3-triazole (107) is prepared by new methodology as follows: 1,3-dipolar addition of tosyl azide to ethyl cyanoacetate in sodium hydroxide/ethyl ether gives 4-carbethoxy-5-tosylamino-1,2,3-triazole (117),
presumably by Dimroth rearrangement\(^5^5\) of intermediate 116. Hydrolysis of 117 in concentrated sulphuric acid results in 107 as a white crystalline solid in 81% yield (Scheme 9).

\[
\text{PhCH}_2\text{N}_3 + \text{NCCH}_2\text{CN} \xrightarrow{\text{NaOEt, EtOH}} \begin{array}{c}
\text{PhCH}_2\text{N}^\text{CN} \\
\text{NH}_2 \\
\text{CN}
\end{array} + \begin{array}{c}
\text{PhCH}_2 \\
\text{N}^\text{Et}
\end{array}
\]

(Scheme 9)

4-Amino-5-cyano-1,2,3-triazole (108) is prepared by the method of Hoover and Day.\(^5^4\) Thus, condensation of benzylazide with malononitrile in the presence of sodium in ethanol gives a mixture of 118 and 119 which on reductive debenzylation with sodium in liquid ammonia affords 108 (Scheme 10).

\[
\begin{array}{c}
\text{CH}_3\text{SO}_3\text{N}_3 + \text{NCCH}_2\text{CO}_2\text{C}_2\text{H}_5 \\
\xrightarrow{\text{NaOH, ether}} \begin{array}{c}
\text{NH}_2 \text{CO}_2\text{Et} \\
\text{tos} \\
\text{N}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{Dimroth rearrangement} \\
\text{CH}_3\text{SO}_3\text{N}_3 + \text{NCCH}_2\text{CO}_2\text{C}_2\text{H}_5 \\
\xrightarrow{\text{H}_2\text{SO}_4, -15^\circ\text{C}} \begin{array}{c}
\text{NH}_2 \text{CO}_2\text{Et} \\
\text{tos} \\
\text{N}
\end{array}
\end{array}
\]

(Scheme 10)
Surprisingly, diazotriazole 101 is white, 102 is yellow and both 103 and 104 are tan solids. Solutions of 101, 102, 103 and 104 in dichloromethane are yellow. The diazotriazoles can be stored for prolonged periods without noticeable decomposition if light is excluded. 4-Diazo-1,2,3-triazole (101) and 4-cyano-5-diazo-1,2,3-triazole (104) are shock-sensitive and are brisantly explosive if tapped or scratched. All four diazo compounds explode violently at their melting points but are remarkably stable in refluxing benzene. For example, 80% of 4-diazo-5-phenyl-1,2,3-triazole (102) is recovered after refluxing in benzene for 48 hours.

Some physical and spectral properties of 101-104 are summarized in Table 1.

Table 1  Physical and Spectral Properties of 4-Diazo-1,2,3-triazoles (101-104)

<table>
<thead>
<tr>
<th></th>
<th>101</th>
<th>102</th>
<th>103</th>
<th>104</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP(Dec)</td>
<td>125-6°C</td>
<td>134-5°C</td>
<td>142-4°C</td>
<td>131-2°C</td>
</tr>
<tr>
<td>Color</td>
<td>white</td>
<td>yellow</td>
<td>tan</td>
<td>tan</td>
</tr>
<tr>
<td>IR(C=N)</td>
<td>2160 cm⁻¹</td>
<td>2155 cm⁻¹</td>
<td>2195 cm⁻¹</td>
<td>2200 cm⁻¹</td>
</tr>
<tr>
<td>UV(CH₃OH)</td>
<td>275 nm</td>
<td>285 nm</td>
<td>279 nm</td>
<td>279 nm</td>
</tr>
</tbody>
</table>
The diazo functional groups of diazotriazoles 101-104 absorb at uncharacteristically high IR frequencies (2155-2200 cm\(^{-1}\)) which suggest that they have significant triple bond character. The diazo group of diazocyclopentadiene (\(\text{6}\)) absorbs at 2082 cm\(^{-1}\) as compared\(^5\) to 2200 cm\(^{-1}\) for 4-cyano-5-diazo-1,2,3-triazole (104) (Scheme 11). The difference in absorption frequency can be explained by the electron-attraction effects of three nitrogens and the nitrile substituent in 104. Diazotriazole 104 is expected to have significant charge polarization as represented by canonical form 104b.

\[
\begin{align*}
\text{IR}(\text{N=N}) & : 2200 \text{ cm}^{-1} \\
\text{IR}(\text{N=N}) & : 2082 \text{ cm}^{-1}
\end{align*}
\]

(Scheme 11)

I Coupling Reactions

C-Coupling

Diazotriazoles 101, 102 and 104 couple readily with 2-naphthol in aqueous solution at 0 °C. 4-(2-Hydroxy-1-naphthylazo)-1,2,3-triazoles 120, 121, 123 are brightly colored and are obtained in 100, 92 and 89% yields,
respectively (Eq. 34). The reactions obviously involve

electrophilic attack of the diazo groups at the 1-position in 2-naphthol followed by tautomerization as shown in Scheme 12. The IR spectra of 120-122 in potassium bromide show no associated OH bands but bands at 1620-1630 cm\(^{-1}\)
are present which can be ascribed to carbonyl groups with intramolecular hydrogen bonds, thus suggesting the presence of hydrazone tautomers \(^{123}\).

Similarly, diazotriazole \(^{101}\) couples with \(N,N\)-dimethylaniline in aqueous solution to yield 4-(4-(dimethylphenylazo)-1,2,3-triazole \(^{124}\), an orange solid, in quantitative yield (Eq. 35). The reaction apparently occurs by electrophilic attack of the diazo group at the \(p\)-position of the aniline followed by proton shifts to give \(^{124}\).

\[
\begin{array}{c}
\text{N-Coupling} \\
\text{Diazoazoles have been reported to couple with amines to give triazenoazoles.}^{56} \text{ Of particular present interest are reactions of 5-diazo-1,2,3-triazole-4-carboxamide (97) with primary and secondary amines to give 5-}(\text{substituted-triazeno}-)1,2,3-triazole-4-carboxamides (125, Eq. 36).^{57}
\end{array}
\]
5-(3,3-Dimethyl-1-triazeno)-1,2,3-triazole-4-carboxamide (125, \( R_1=R_2=\text{CH}_3 \)) has been shown to have antineoplastic activity.

\[
\begin{align*}
\text{CONH}_2 & \quad + \quad \text{R}_1\text{R}_2\text{NH} \\
\text{125} & \quad \rightarrow \\
\text{N} & \quad \text{N} \\
\rightarrow \quad & \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{97} & \quad \text{CONH}_2 \\
\end{align*}
\]

A limited study has now been made to reactions of secondary amines with 4-diazo-1,2,3-triazoles of the present dissertation.

Morpholine reacts rapidly with 101 in water at 0 °C to give 4-(1-morpholinylazo)-1,2,3-triazole (126, Eq. 37, 85%). Triazentriazole 126 is white, stable and was identified by spectral methods and by elemental analysis.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\rightarrow \quad & \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{97} & \quad \text{CONH}_2 \\
\end{align*}
\]

A special feature of 126 is that all eight H's in the morpholine ring exhibit a singlet in its NMR spectrum, an example of accidental equivalence. The mechanism of
the reaction may involve nucleophilic attack of the amine at the terminal nitrogen of 101 to yield 127; subsequent migration of the proton gives 126 (Eq. 37). Similarly, phenyldiazotriazole 102 couples with pyrrolidine in water at 0°C to form 4-phenyl-5-(1-pyrrolidinylazo)-1,2,3-triazole (128), a stable tan product in 38% yield (Eq. 38).

\[ \begin{align*}
\text{102} & \quad + \quad \text{p} \quad \rightarrow \quad \text{128} \\
\end{align*} \]

**P-Coupling**

Triphenylphosphine is known to couple with many diazo compounds to form stable ylides. When a solution of triphenylphosphine in ethyl ether is added to 101 in ethyl ether, 4-(triphenylphosphoniumazo)-1,2,3-triazole ylide (129), an orange solid, deposits on the bottom of the reaction flask. However, ylide 129 is unstable and is hydrolyzed rapidly by atmospheric moisture during filtration.
to triphenylphosphine oxide and 1,2,3-triazole in 82 and 69% yields, respectively (Eq. 39).

\[
\begin{align*}
\text{Ph}_3\text{P} & + \text{PPh}_3 \\
\rightarrow & \\
\text{Ph}_3\text{PO} & + \text{N}_2
\end{align*}
\]

(39)

II Sandmeyer Reactions

Sandmeyer displacements are important reactions of benzenediazonium salts. There are also a few reports of reactions of the Sandmeyer type of azolediazonium salts. For example, pyrazole-3-diazonium salts yield 3-halo-pyrazoles and 4,5-dicyano-2-diazoimidazole and cuprous halides. Two limited studies have also been made in the 1,2,3-triazole system. Thus, 4-amino-1-methyl-1,2,3-triazole (130) gives 4-bromo-1-methyl-1,2,3-triazole (131) when treated with sodium nitrite, copper-bronze and hydrobromic acid (Eq. 40) and 5- diazo-1,2,3-triazole-4-carboxamide (97) affords 5-iodo-1,2,3-triazole-4-carbox-
amide (132) with potassium iodide in hydriodic acid

\[
\begin{align*}
\text{H}_2\text{N} & \text{N} \text{H} + \text{HBr} \xrightarrow{\text{NaNO}_2} \text{Br} \text{H} \\
\text{Cu-Bronze} & \quad \rightarrow \quad \text{Br} \text{N} \text{N} \text{CH}_3 \\
\end{align*}
\]  

solution (Eq. 41). 63

It was thus interesting to see if reactions of this type can be applied more generally to the 4-diazo-1,2,3-triazoles presently studied. Few halogeno-1,2,3-triazoles are known.

When 101, 102 and 104 in aqueous solution are each treated with freshly prepared copper(I) chloride or copper(I) bromide, evolution of gas occurs. The emulsions that result are broken by stirring and warming the reaction mixtures. Extractions with ether or chloroform afford the six halogenated triazoles 133-135a,b in 38-88% yields (Eq. 42).

No attempts were made to maximize the yields of 133-135a,b in these experiments. Replacement of the diazo group by
iodine occurs readily in reaction of 101 with potassium

\[
\text{\includegraphics{image.png}}
\]

\[\text{Cu}_2\text{X}_2/\text{HX}\]

\[X = \text{Cl}, \text{Br}\]

101 Z = H
102 Z = Ph
103 Z = CN

133a, Z = H, X = Cl
b, Z = H, X = Br

134a, Z = Ph, X = Cl
b, Z = Ph, X = Br

135a, Z = CN, X = Cl
b, Z = CN, X = Br

iodide in hydriodic acid solution to produce 4-iodo-1,2,3-triazole (136, Eq. 43, 68%). Displacements of the

\[
\text{\includegraphics{image.png}}
\]

Sandmeyer type are thus effective reactions of 4-diazo-1,2,3-triazole systems. Presumably these reactions involve 1,2,3-triazole-4-diazonium ion reactants. It would be valuable to extend such displacements to other nucleophiles.
III Cycloaddition Reactions

Due to possible charge polarization in diazoazoles 137, there is potential bifunctional reactivity of the derived betaine 137a. Reactions of 137a with unsaturated substrates such as acetylenes and ethylenes might provide a general route to fused azolo-1,2,4-triazines 138 (Eq. 44).

\[
\begin{align*}
\ce{N2} & \leftrightarrow \ce{N\equivN} \\
137 & \quad 137a & \quad 138 & \quad (44)
\end{align*}
\]

Cycloadditions of this type have been reported for other diazoazole systems. For example, 5-\(t\)-butyl-3-diazopyrazole (68a) adds readily to ethyl vinyl ether with elimination of ethanol to give 7-\(t\)-butylpyrazolo[3,2-\(c\)]1,2,4-triazine (139, Eq. 45). Pyrazolo[3,2-\(c\)]1,2,4-triazines (142) are

\[
\begin{align*}
\ce{N\@N} & \quad \ce{H\@H} \quad \ce{H\@H} \\
68a + \ce{HOC2H5} & \xrightarrow{\text{EtOH}} \ce{C4H9} & \quad 139 & \quad (45)
\end{align*}
\]
preparable from 3-diazopyrazole (140) and substituted

\[ \text{Reaction 46} \]

ynamines (141, Eq. 46). Further, 3-diazo-5-phenyl-1,2,3-triazole (94) undergoes cycloaddition with 1- (N-morpholinyl)-cyclohexene and elimination of morpholine to form 7-phenyl-1,2,4-triazolo-[5,1-c]cylohexa[e]1,2,4-triazine (143, Eq. 47). Recently, cycloadditions of

\[ \text{Reaction 47} \]

diazoazole have been extended to cumulenes. Thus, pyrazolo[5,1-d]1,2,3,5-tetrazin-4-ones (144) are obtained from 3-diazopyrazoles (140) and substituted isocyanates

\[ \text{Reaction 48} \]
Similarly, 3-diazo-5-phenyl-1,2,4-triazole (94) adds to phenyl isocyanate to afford 3,7-diphenyl-1,2,4-triazolo[5,1-d]1,2,3,5-tetrazin-4-one (145, Eq. 49). \[ \text{Ph} \quad \text{NCO} \quad \overset{\text{Ph-NCO}}{\longrightarrow} \quad \text{Ph} \quad \begin{array}{c} \text{N} \\ \text{N} \\ \text{N} \\ \text{N} \end{array} \quad (49) \]

Mackie and Tenant \(^{66}\) have reported coupling and cyclization reactions of 4-diazo-5-phenyl-1,2,3-triazole (102) with \(\alpha\)-keto esters, \(\alpha\)-cyano esters or \(\beta\)-diketones to give triazolo[5,1-\(c\)]1,2,4-triazines (146) and hydrazones 147 (Eq. 50). Hydrazones 147, on prolonged heating in aqueous ethanolic sodium acetate, yield 146. \(^{66}\)

It was of interest to explore the above reactions further and investigate their applicability to the present
4-diazo-1,2,3-triazoles. Diazotriazoles 101, 102 and 104 were then subjected to reactions with electron-rich ethylenes, acetylenes and various cyano-activated methylene compounds.

4-Diazo-5-phenyl-1,2,3-triazole (102) reacts with 1-morpholino-2-nitroethene (148) in dichloromethane to afford 6-nitro-3-phenyl-1,2,3-triazolo[5,1-c]1,2,4-triazine (149, Eq. 51, 48%). Triazine 149, a yellow high melting solid, was identified by spectral methods and by elemental analysis. Because of the polarity of ethene 148, the regiospecificity of addition is predictable.

\[
\begin{align*}
\begin{array}{c}
\text{Ph} \\
\text{N=}=N \\
\text{H} \\
\text{N=}=N \\
\text{Ph}
\end{array}
+ \begin{array}{c}
\text{O}_2\text{N} \\
\text{H} \\
\text{N=}=N \\
\text{H} \\
\text{N=}=N
\end{array}
\rightarrow \begin{array}{c}
\text{Ph} \\
\text{N=}=N \\
\text{H} \\
\text{N=}=N \\
\text{Ph}
\end{array}
\end{align*}
\tag{51}
\]

Thus enamine 148 couples with 102 to form zwitterion 150 followed by attack of ring nitrogen on imine carbon; sub-
sequent elimination of morpholine affords 149. (Scheme 13)

Diazotriazole 102 adds to phenyl isocyanate in dichloromethane to form 3,8-diphenyl-1,2,3-triazolo[5,1-d]-1,2,3,5-tetrazin-4-one (151, Eq. 52, 38%). Tetrazin-4-one

\[ \text{PhNSNPh} \rightarrow \text{Ph-NCO} \rightarrow \text{Ph} \]

151, a light brown crystalline solid, was identified by spectral methods and by its exact mass. Shortly after this reaction was studied in this laboratory, Ege and Gilbert\textsuperscript{65} reported the same reaction in 41% yield in a short communication.

Refluxing phenylacetylene and 4-cyano-5-diazo-1,2,3-triazole (104) in dichloromethane for 16 hours

\[ \text{NC} \rightarrow \text{Ph} \]

gives 8-cyano-3(4)-phenyl-1,2,3-triazolo[5,1-ç]1,2,4-triazine (152, Eq. 53, 38%). Triazine 152, an orange solid, is assigned by spectral means and exact mass measurement. The regiospecificity of the addition is uncertain and the
Mechanism of the reaction may involve a concerted [7+2] cycloaddition or a [3+2] addition followed by a [1,5] vinyl shift.

Attempted addition of dimethyl acetylenedicarboxylate (DMAC) to 104 failed. Thus refluxing equimolar amounts of DMAC and 104 in dichloromethane for 24 hours results in starting materials and intractables (Eq. 54). It appears that diazotriazole 104 prefers electron-rich or polarized dipolarophiles.

\[
\begin{align*}
\text{NC}_2\text{N=N} \quad & \quad \text{CO}_2\text{CH}_3 \\
\text{104} & \quad \longrightarrow \\
\text{CO}_2\text{CH}_3 \\
\text{153}
\end{align*}
\]

When 4-diazo-1,2,3-triazole (101) is treated with malononitrile (154a), ethyl cyanoacetate (154b) and cyanoacetamide (154c) in aqueous ethanol in the presence of sodium acetate, 7-amino-1,2,3-triazolo[5,1-c]1,2,4-triazines 155a, 155b, 155c are obtained in 100, 82 and 100% yields, respectively (Eq. 55). These reactions can be visualized as involving base-catalyzed coupling of the activated nitrile with 101 to form azo compounds 156 followed by intramolecular addition of ring nitrogen to the nitrile moiety and aromatization (Scheme 14).
When $R = \text{CO}_2\text{C}_2\text{H}_5$, competition between CN and $\text{CO}_2\text{C}_2\text{H}_5$ in ring closure does not materialize. Cyclization involving the nitrile moiety occurs preferentially and $158$, a product derived from attack on the ester group, was not observed (Scheme 15). The cyclization reactions of Equation 55 are rapid in that they are completed within
minutes. In contrast to the findings of Mackie and Tenant, intermediates such as 157a,b are not observed in the present system (compare Eq. 55 to Eq. 50).

On the other hand, acetylacetone couples with 101 in aqueous ethanol at room temperature in the presence of sodium acetate to yield 4-[3-(2,4-pentanedionyl)azo]-1,2,3-triazole (159, Eq. 56, 68%). Azo compound 159, a stable orange solid, show strong IR absorptions at 1650, 1635 and 1550 cm\(^{-1}\) consistent with the enol of diketone 159c. The molecular formula of \(C_7H_9N_5O_2\) assigned to 159 is confirmed by its mass spectrum and elemental analysis. The failure to obtain cyclization product 160 is surprising since 4-diazo-5-phenyl-1,2,3-triazole (102) is reported to react with acetylacetone to give 6-acetyl-7-methyl-3-phenyl-1,2,3-triazolo[5,1-c]-1,2,4-triazine (161, Eq. 57)
The absence of 160 can be explained on the basis that 1,3-diketone intermediate 159a converts to stabilized 159c which renders the ketone unavailable to further nucleophilic attack. Refluxing azo-adduct 159

$$\text{Ph} + \text{OCH}_2\text{CH}_3 \xrightarrow{\text{NaOEt}} \text{Ph}$$

(57)
in aqueous ethanol with excess sodium acetate still fails to give cyclization product 160 (Eq. 58).

\[
\begin{align*}
\text{159} & \xrightarrow{\Delta} \text{NaOEt} \\
\text{159} & \rightarrow \text{160}
\end{align*}
\]
IV Reactions with Ethers and Alcohols

Electrophilic carbenes have high affinities for electron-rich heteroatoms such as oxygen, sulphur and nitrogen. Thus stable ylides are formed from carbenes and alkyl sulphides (Eq. 59)\textsuperscript{67} and from carbethoxycarbene and isoquinoline (Eq. 60).\textsuperscript{68}

\[
\begin{align*}
R_2C=NN_2 & \xrightarrow{\text{h}_\nu} \text{CH}_3\text{SCH}_3 \xrightarrow{R} H_3C\text{S}^\ominus \text{C}_R^\ominus \\
R = & \text{CO}_2\text{CH}_3, \text{CO}_2\text{C}_2\text{H}_5, \text{COCH}_3
\end{align*}
\]  

(59)

There are numerous examples of reactions of carbenes with carbon-oxygen bonds.\textsuperscript{69} Although few stable oxygen ylides have been prepared from carbenes, many authors have postulated such species as intermediates which subsequently decompose to products. For example, decomposition of ethyl diazoacetate by either thermal or photolytic methods in styrene oxide yields products rationalized by ring expansion and fragmentation reactions.
of ylide $162$ (Eq. 61). $70$ 2-Phenylxetane gives ring expansion but no deoxygenation (Eq. 62). $71$

\[
\begin{align*}
\text{Ph} & \quad \text{N}_2 \quad \text{Ph} \\
\text{CO}_2\text{R} & \quad \text{Ph} \\
\text{O} & \quad \text{Ph} \\
\text{O} & \quad \text{Ph} \\
\text{C}_2\text{R} & \quad \text{Ph} \\
\text{C}_2\text{R} & \quad \text{Ph} \\
\text{H} & \quad \text{C}_2\text{R} \\
\text{N}_2 & \quad \text{Ph} \\
\text{CO}_2\text{R} & \quad \text{Ph} \\
\text{O} & \quad \text{Ph} \\
\text{O} & \quad \text{Ph} \\
\text{C}_2\text{R} & \quad \text{Ph} \\
\text{C}_2\text{R} & \quad \text{Ph} \\
\text{H} & \quad \text{C}_2\text{R} \\
\end{align*}
\]

(61)

As one might expect, ylides are not formed from carbenes in their triplet states. When diazomalonic ester $163$ is irradiated in dimethyl ether, $165$ is isolated as a decomposition product of oxygen ylide $164$. Sensitized photolysis however produces no $165$ (Eq. 63). $72$ Apparently
triplet complexes such as 166 are not formed or do not rearrange to 165 (Eq. 63).

4H-1,2,3-Triazolylidenes are certainly electrophilic. Study of decomposition of 4-diazo-1,2,3-triazoles in ethers and in alcohols was thus initiated in view of possible interesting chemistry of oxygen ylide intermediates. Products derived from ylide intermediates would also indicate involvement of singlet triazolylidenes.

When ethyl ether is added to 4-cyano-5-diazo-1,2,3-triazole (104) at room temperature, spontaneous evolution of gas occurs. The reaction is completed by reflux at 40°C for three hours. 4-Cyano-5-ethoxy-1,2,3-triazole (167) and 4-cyano-5-ethoxy-N-ethyl-1,2,3-triazole (168) are isolated as clear oils in 57 and 18% yields, respectively (Eq. 64).
The actual position of the triazole ethyl group in 168 has not been determined and is assigned arbitrarily on N-1 for reasons discussed later. Formation of 167 and 168 is presumed to involve the mechanisms of Scheme 16. Thus, ethyl ether facilitates reaction by attack on 104 to give zwitterion 169 which loses nitrogen to form oxygen ylide 170. Ylide 170 can undergo elimination of ethylene to give 167 or displacement on carbon alpha to oxygen to yield 168. It is not clear whether 168 results from intramolecular or intermolecular displacement processes. If intramolecular, 168 would be formed via a four-membered ring transition state. Similar behavior has been observed in photolysis of 3-diazo-5-phenylpyrazole (68b) in ethyl ether, and 171 and 172 are speculated to be formed by ionization-recombination or by bimolecular processes (Eq. 65).26

\[
\begin{array}{c}
\text{N}^+ \quad \text{N}^+ \\
\text{Ph} & \text{Ph}
\end{array}
\xrightarrow{\text{h} \nu \text{ (C}_2\text{H}_5\text{)}_2\text{O}}

\begin{array}{c}
\text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\
\text{Ph} & \text{Ph}
\end{array}
\xrightarrow{\text{C} = \text{N}}

\begin{array}{c}
\text{OC}_2\text{H}_5 \\
\text{Ph}
\end{array}
+ \begin{array}{c}
\text{OC}_2\text{H}_5 \\
\text{Ph}
\end{array}

\text{Et} \quad \text{Et}
\]

(65)

To investigate reactions with ethers further, 4-cyano-5-diazo-1,2,3-triazole (104) was added to dimethoxyethane (DME) at room temperature. Gas evolution occurs, although not as profusely as with ethyl ether. The reaction
is complete upon stirring the solution at room temperature for three hours. 4-Cyano-5-((2-methoxyethoxy)methyl)-1,2,3-triazole (173), 4-cyano-5-((1,2-dimethoxy)ethyl)-1,2,3-triazole (174) and 4-cyano-5-methoxy-1,2,3-triazole (176) are isolated in 19, 22 and 19% yields, respectively (Eq. 66) by column chromatography. A fourth product, 175, which has not been identified structurally, is obtained in 23% yield. The NMR and mass spectra of 175 are remarkably similar to that of 174. It is speculated that 175 may be an isomer of 174. Formation of 173 and 174 can be rationalized as insertion of 4-cyano-5H-1,2,3-triazolylidene (178) into the primary and secondary C-H bonds of DME.
(Scheme 17). Although methyl vinyl ether (177) was not detected, methoxytriazole 176 is presumably formed by

\[
\begin{align*}
103 & \rightarrow 173 + 174 \\
& \text{(Scheme 17)}
\end{align*}
\]

attack of DME on 4-cyano-5-diazo-1,2,3-triazole (104) with loss of nitrogen to form oxygen ylide 179 followed by elimination of methyl vinyl ether 177 to yield 176 (Scheme 18).

\[
\begin{align*}
103 & \rightarrow 176 + 177 \\
& \text{(Scheme 18)}
\end{align*}
\]

When 4-diazo-5-phenyl-1,2,3-triazole (102) is heated in isopropyl alcohol (82 °C) for six hours, acetone (180) and 4-phenyl-1,2,3-triazole (181) are obtained in 48% yields, respectively (Eq. 67). Acetone was identified by
preparing its 2,4-dinitrophenylhydrazone identical with an authentic sample. Triazole 181 is identified by its spectral properties and by comparison with an authentic sample.

The mechanism of reaction (Eq. 67) may involve attack of isopropyl alcohol on 102 to form triazolylazo ether 182 which collapses homolytically to free radicals 183 and 184. Abstraction of hydrogen by 183 leads to acetone and 187 which loses nitrogen to give reduction product 181 (Scheme 19, path 1). One of the many alternate mechanisms involves heterolytic cleavage of 182 (path 2) to alkoxide anion 186 and diazonium cation 185. Hydride abstraction from 186 gives acetone and 187, which loses nitrogen to yield 181 (Scheme 19).
V Thermal Decompositions in Saturated Hydrocarbons

Because of their polarities, 4-diazo-1,2,3-triazoles (101-104) are hardly soluble in saturated hydrocarbons. When 101 was thermolyzed as a suspension in cyclooctane at 100°C, a series of small explosions occurred inside the reaction vessel with evolution of smoke. Upon heating the suspension at 95-100°C for five hours, removal of solvent led to intractables and recovery of 72% of the starting material. Due to the hazards, the system was not pursued further.

The solubility of phenyldiazotriazole 102 in cyclooctane is much improved. When 102 is thermolyzed in cyclooctane at 150°C for two hours, a brown oil was obtained after removing the solvent. Chromatography on silica gel using benzene as elutant gave an involatile light yellow oil assigned as 4-cyclooctyl-5-phenyl-1,2,3-triazole (188, Eq. 68, 47%). Identification of 188 was made from

\[
\begin{align*}
\text{102} & \xrightarrow{\Delta, -N_2} \text{189} \\
\text{189} & \xrightarrow{1,5 \text{ H-Shift}} \text{188}
\end{align*}
\]
its spectra and its elemental analysis. The NMR spectrum of 188 shows a nice multiplet at $\delta 5.15$ corresponding to one proton assigned as the hydrogen attached to tertiary carbon. The chemical shift is unusually low for a saturated C-H signal and confirms the high combined deshielding effects of the benzene and triazole rings. Isolation of 188 is indicative of generation of 4-phenyl-5H-1,2,3-triazolylidene (189). Singlet carbene 189 inserts into a C-H bond of cyclooctane in a 1,1 manner followed by a 1,5 H-shift to give 188 (Eq. 68).

Refluxing 102 in cyclohexane affords insertion product 190 as the only isolable product in 42% yield (Eq. 69). 4-Cyclohexyl-5-phenyl-1,2,3-triazole (190),

![Diagram](Image)

a white crystalline solid, was assigned from its spectra and elemental analysis. Because of the thermal stability of 102, more than 60 hours of reaction time is needed for its complete decomposition.

It has been reported that when ethyl diazoacetate (191) is photolyzed in cyclohexane, intermolecular 192 as well as intramolecular insertion products 193 and 194...
are obtained (Eq. 70). Thermolysis of 4-carbethoxy-5-
\[
\begin{align*}
&\text{H}_2\text{N} & \text{O} \\
&\text{H} & \text{O} \\
&\text{N}_2 \\
&\text{hv} \\
&\text{hv}
\end{align*}
\]

\[191\]

\[
\begin{align*}
&\text{hv} \\
&\text{hv}
\end{align*}
\]

\[192\]

\[193\]

\[194\]

\[195\]

diazo-1,2,3-triazole (104) in cyclooctane however gives
only 4-carbethoxy-5-cyclooctyl-1,2,3-triazole (195,
Eq. 71, 68%). Insertion product 195, a white solid, is
identified from its spectra and exact mass. Products 196

\[196\]

and 197 as derived from intramolecular insertions were not
found (Eq. 71).
VI Reactions with Arenes

The reactions of varied carbenes and arenes have been recently reviewed. Of relevance to this dissertation is that the behavior of azolylidenes and aromatics have been of interest to this and other laboratories. The chemistry of different diazoazoles is highly varied and there are as yet no general patterns or mechanisms for their reactions with aromatics. For example, 3-diazo-2,5-diphenylpyrrole (34) and 3-diazo-5-phenylpyrazole (68a) decompose thermally or photolytically in appropriately substituted benzenes to form [8,5] bicyclic compounds resulting from ring expansion of the benzenes via spiro-norcaradiene intermediates (Refer to Eq. 12 and Eq. 24). On the other hand, 2-diazoimidazole (24), 4-diazoimidazole (25), 4-diazopyrazole (23) and 3-diazo-5-phenyl-1,2,4-triazole (94) effect substitution of varied benzenes (Refer to Historical).

A study of decomposition of 4-diazo-1,2,3-triazoles in various aromatic substrates was deemed desirable. This investigation would serve two purposes. Firstly, reactions with substituted benzenes may provide insight as to the intermediates involved by examination of the size and direction of the substituent effects on aromatic substitution.
Secondly, the reaction products might give information as to whether singlet or triplet processes are involved.

Due to the poor solubilities of 100-104 in hydrocarbons and the explosion hazards in these experiments, only limited studies of thermolysis of the diazotriazoles in aromatics have been made. When 4-diazo-1,2,3-triazole (101) was refluxed in benzene for three days, 4-phenyl-1,2,3-triazole (198, 48%) and isomeric cyanocycloheptatrienes (201, 18%) were isolated as the only tractable products along with a small amount of starting material (10%).

\[
\begin{align*}
\text{H} & \quad \text{N} \quad \text{N} \\
\text{H} & \quad \text{N} \quad \text{N} \\
\text{H} & \quad \text{N} \quad \text{N} \\
\text{H} & \quad \text{N} \quad \text{N} \\
\end{align*}
\]

(72)

Phenyltriazole 198 was identified by spectral methods and by comparison with an authentic sample. The formation of 201 is significant. The identification of 201 and the mechanism of its formation will be discussed in detail later. Refluxing 4-diazo-5-phenyl-1,2,3-triazole (102) in benzene for 60 hours resulted in complete decomposition of 102 and at least six products were obtained as evident by TLC. However, two products were isolable and identified as
4,5-diphenyl-1,2,3-triazole (199) and 4-phenyl-1,2,3-triazole (198) in 28 and 11% yields, respectively (Eq. 73). The other products are extremely difficult to separate because of serious streaking on silica gel chromatographic columns.

![Reaction Scheme](image)

The mixture exhibits strong IR absorption at 2200-2250 cm\(^{-1}\) suggesting the presence of a cyano group. The mixture however has not been structurally identified further.

Substitution products 198 in Equation 72 and 199 in Equation 73 may arise from addition of the corresponding 4H-1,2,3-triazolylidenes to benzene to give spironorcaradiene intermediates 200, aromatization of which leads to triazoles 198 and 199 (Scheme 20). The presence of 198, a reduction

![Reduction Scheme](image)
product (Eq, 73), seems to suggest some triplet (or singlet) 
carbenic processes involving hydrogen abstraction from 
compounds in the system.

The chemistry of 4H-1,2,3-triazolylidenes generated 
by photolysis and thermolysis is quite different. Thus, 
irradiation of 101 in benzene for three hours produced 
isomeric cyanocycloheptatrienes (201) and 4-phenyl-1,2,3-
triazole (198) in 54% and 26% yields, respectively (Eq. 74).

Because of the vast differences in their polarities, 201 
was readily separated from 198 by column chromatography. 
Formation of 201 is significant and the products are 
assigned on the basis of the following evidence. The 
IR spectrum of 201 shows absorptions at 2250 and 2200 cm⁻¹ 
indicative of cyano groups. The exact mass of the product 
is 117.057846, corresponding to an empirical formula of 
C₈H₇N. The elemental analysis of 201 also agrees with this 
assignment. The empirical formula of 201 thus has two less 
nitrogen atoms than expected for substitution product 198. 
The NMR spectrum of 201 is complicated but informative 
(refer to Appendix) in that a triplet at 8 2.35 corres-
ponding to two saturated protons ($H_7$, allylic), a multiplet at $\delta\ 5.2-5.8$ ($H_{1,6}$), a multiplet at 6.1-6.4 ($H_{2,5}$) and a multiplet at 7.0-7.25 ($H_{3,4}$) corresponding to a total of five vinylic protons are exhibited. Gas chromatography revealed that 201 is a mixture of many components which can only be assigned in general as positional isomers. Due to the large number of isomers possible by sigmatropic rearrangement processes, no efforts were made to separate or identify the products individually. The isomers will be discussed further later.

Formation of 198 can be rationalized by excitation of 101, loss of nitrogen, conversion to triazolylidene 202 and then substitution as in Scheme 20. There are at least three plausible mechanisms that explain the formation of 201 (Schemes 21, 22, 23). With the observations and evidence that will be presented, mechanism I (Scheme 21) seems to be in operation.

**Mechanism I**

Photolysis of 101 results in loss of one molecule of nitrogen to form $4H$-1,2,3-triazolylidene (202), presumably in an excited state. The resulting energy-rich singlet
carbene 202b undergoes ring scission to form α-diazo-acetonitrile (203) instead of reacting with benzene to yield 198. Subsequent photolytic loss of nitrogen from 203 generates cyanocarbene 204 which is trapped by benzene. Cyanonorcaradiene 205 undergoes ring expansion to yield cyanocycloheptatrienes 201a (Scheme 21).
Mechanism II

Triazolylidene 202 generated by loss of nitrogen from \( \text{101} \) is trapped by benzene to give tricyclic spironorcaradiene 206. Unstable spironorcaradiene 206 then undergoes a six electron transformation involving migration of hydrogen and loss of a second molecule of nitrogen to form cyanonorcaradiene 205 as shown in Scheme 22. Whether the transformation to 205 would be concerted or stepwise or photolytically induced is open for speculation. Norcaradiene 205 then ring-expands to 201 (Scheme 22).
Mechanism III

A third possible mechanism involves spironorcaradiene 206 as in Scheme 22. Instead of ring scission as in Mechanism II, spironorcaradiene 206 aromatizes to phenyltriazole 198, which then dehydrogenates photolytically to α-phenyldiazoacetonitrile (207). The intermediacy of 207 has indeed been reported in photolysis of 198 in methanol and in dichloromethane. Thus, diazo compound 207 would lose nitrogen photolytically to give phenylcyano carbene (209) which inserts intramolecularly to form 210, opening of which gives cyanocycloheptatrienylidene (211) and reduction would yield 201 (Scheme 23).
(Scheme 23)
To investigate the possibility of Mechanism III, 4-phenyl-1,2,3-triazole (198) was prepared independently and photolyzed in benzene under conditions identical for irradiation of 101 in the solvent. After three hours of photolysis, 198 was recovered quantitatively. Further irradiation of 198 for 16 hours resulted in traces of intractables and 92% recovery of initial 198. Triazole 198 is thus photolytically stable and mechanism III (Scheme 23) can therefore be excluded from further consideration (Eq. 75).

![Chemical structure](attachment:image.png)

Mechanism I, decomposition of 4H-1,2,3-triazolylidene (202) to diazoacetonitrile (203), seemed attractive and has certain precedent. Thus, 3H-pyrazolylidenes (71), generated by vacuum pyrolysis of 3-diazopyrazoles, isomerize via ring-opening and reorganization to 2H-azirines (73) (Scheme 24). Further, irradiation of

(Scheme 24)
1,4,5-triphenyl-1,2,3-triazole (212) in benzene produces triphenylketenimine (215) and 2,3-diphenylindole (216, Eq. 76) in equal ratio. Formation of 215 and 216 by 1,2-phenyl and hydrogen migrations suggests the intermediacy of carbenes 214a and 214b (Eq. 76). Other well known examples of triazole ring cleavage are the thermal, acid- or base-catalyzed interconversions of 5-amino-1-phenyl-triazole and 5-anilinotriazole (217→218) observed by Dimroth. The rearrangements were proposed to involve diazo-imine intermediates 219a and 219b (Scheme 25).
More directly, Dewar and Petit\textsuperscript{80} reported in 1956 synthesis of cyanonorcaradiene (205), later identified as cyanocycloheptatriene (201), by photolysis of $\alpha$-diazocetonitrile (203) in benzene for six hours (Eq. 77). Thus, irradiation of 203 apparently involves

\[
\begin{align*}
&\text{N}^+\text{N}^- \\
&\begin{array}{c}
\text{H} \\
\text{CN}
\end{array}
\end{align*}
\xrightarrow{h\nu}
\begin{align*}
&\begin{array}{c}
\text{H} \\
\text{CN}
\end{array}
\xrightarrow{\text{ring-expansion}}
&\begin{array}{c}
\text{H} \\
\text{CN}
\end{array}
\end{align*}
\]

loss of nitrogen to give cyanocarbene (204) which adds to benzene forming norcaradiene 205 and then 201 by ring-expansion (Eq. 77).

Attempts were then made to convert 4-diazo-1,2,3-triazole (101) photolytically to diazoacetonitrile (203). Thus 101 was photolyzed in benzene and aliquots of the reaction mixture were collected every five minutes. Weak bands at 2240 and 2100 cm$^{-1}$ assignable to $\equiv\text{C}=\text{N}$ and $\equiv\text{N}$ IR absorptions in diazoacetonitrile (203) were observed along with that (2160 cm$^{-1}$) for the diazo band in 101. The above evidence for conversion of 101 to 203 however were ruled inconclusive. Attempts to trap 203 in the photolysis aliquots by addition to $\beta$-naphthol to give
coupling product 220 were without success (Scheme 26). These experiments do not exclude the possibility however that diazoacetonitrile (203) is rapidly destroyed photolytically or that 203 collapses concertedly with loss of nitrogen to give cyanocarbene (204).

There is also the mechanistic possibility that diazoacetonitrile (203) isomerizes to 4H-1,2,3-triazolylidene (202) which then attacks benzene to give 4-phenyl-1,2,3-triazole (198, Eq. 78). To investigate this possibility, α-diazoacetonitrile (203), prepared by diazotization of α-aminoacetonitrile sulphate, was
photolyzed in benzene. Triazole 198 was not detected. Cyanocycloheptatriene (201) is the lone product obtained as described previously by Dewar and Petit (Eq. 77). These experiments thus minimize any significance to an equilibrative relationship between 203 and 202 that leads to aromatic substitution to yield 198 (Eq. 78).

Study was then directed to the photolytic reactions of 101 with electropositively- and electronegatively-substituted benzenes. On the basis of reactions of 4H-1,2,3-triazolylidene (202) as an electrophilic singlet, it was expected that increasing the electron density of the benzenes would increase the formation of 4-(substituted-phenyl)-1,2,3-triazoles (221) and reduce conversion to substituted cyanonorcaradienes (222) and/or substituted cyanocycloheptatrienes (223).

![Chemical structures](image-url)

When 4-diazo-1,2,3-triazole (101) is photolyzed in toluene, p-xylene, trifluoromethylbenzene, fluorobenzene and bromobenzene, mixtures of the corresponding X-substituted cyanonorcaradienes 222 and/or cyanocycloheptatrienes 223a-e are isolated in 33-67% yields (Eq. 79).
Products derived from substitution of the benzene by 4H-1,2,3-triazolylidene (202) are not observed in any case.

\[ \text{N} \overset{\text{hv}}{\text{N} - \text{N}} \]

\[ \text{a-g} \]

\[ \text{X} = \text{CH}_3 \]
\[ \text{b, X} = 1,4\text{-diCH}_3 \]
\[ \text{c, X} = \text{CF}_3 \]
\[ \text{d, X} = \text{F} \]
\[ \text{e, X} = \text{Br} \]

The progress of the reactions was monitored by measuring the volumes of gas evolved. In general, the photolyses were allowed to proceed for three hours and approximately two equivalents of nitrogen were collected which fits the proposed mechanisms.

Cyanonorcaradienes 222a-e and cyanocycloheptatrienes 223a-e were readily isolated from the product mixtures by elution through silica gel columns using benzene/hexane. These distillable, colorless liquid products were identified from the following evidence: the IR spectra of 222-223a-e exhibit intense absorptions for
cyano groups at 2200-2250 cm\(^{-1}\). Usually doublets of varying intensities are exhibited for conjugated and unconjugated cyano groups in the product. The NMR spectra of 222-223a-e are extremely complicated due to the large number of isomers present and are of little analytical value. Although the different isomers cannot be assigned individually, integration of certain NMR signals can be used to estimate the relative amounts of norcaradienes and cycloheptatrienes in the products. The \(^1\)H NMR spectra of 222-223a-e in CDCl\(_3\) show absorptions at \(\delta\) 3.0-4.0, characteristic of the cyclopropyl hydrogens, \(H_1\) and \(H_6\), in the norcaradienes (222). The integrated signals were used to determine the amounts of norcaradienes 222 present. The \(H_1\) and \(H_6\) signals in the cycloheptatrienes (223), on the other hand, occur at lower fields (\(\delta\) 5.0-6.0) since the protons are vinylic. Integration of such signals allows determination of the relative amounts of cycloheptatrienes. The mass spectra and elemental analyses of
222-223a-e indicate empirical formulae with two nitrogen atoms less than that expected of substitution product 221. The physical and spectral properties of the X-substituted cycloheptatrienes and norcaradienes (222-223) prepared are tabulated in Tables 2 and 3.
Table 2. *Infrared (C≡N) and Mass Spectra of Cyanocycloheptatrienes and Cyanonorcaradienes (222-223).*

<table>
<thead>
<tr>
<th>X</th>
<th>IR (cm⁻¹)</th>
<th>Mass Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C≡N</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2250</td>
<td>117 (m/e)</td>
</tr>
<tr>
<td></td>
<td>2220</td>
<td>90 (M - HCN)</td>
</tr>
<tr>
<td>CH₃</td>
<td>2240</td>
<td>131 (m/e)</td>
</tr>
<tr>
<td></td>
<td>2218</td>
<td>116 (M - CH₃)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>104 (M - HCN)</td>
</tr>
<tr>
<td>1,4-diCH₃</td>
<td>2250</td>
<td>145 (m/e)</td>
</tr>
<tr>
<td></td>
<td>2205</td>
<td>130 (M - CH₃)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>118 (M - HCN)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>103 (M - HCN - CH₃)</td>
</tr>
<tr>
<td>CF₃</td>
<td>2222</td>
<td>185 (m/e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>166 (M - F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>165 (M - HF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>116 (M - CF₃)</td>
</tr>
<tr>
<td>Br</td>
<td>2240</td>
<td>197 isotopes</td>
</tr>
<tr>
<td></td>
<td>2220</td>
<td>195</td>
</tr>
<tr>
<td></td>
<td></td>
<td>171 (M - HCN)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>169 (M - HCN - Br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>116 (M - Br)</td>
</tr>
<tr>
<td>F</td>
<td>2250</td>
<td>135 (m/e)</td>
</tr>
<tr>
<td></td>
<td>2220</td>
<td>115 (M - HF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>108 (M - HCN)</td>
</tr>
</tbody>
</table>
Table 3. Physical and Spectral Properties of Cyanocyloheptatrienes and Cyanonorcaradienes (222-223).

<table>
<thead>
<tr>
<th>X</th>
<th>222 %</th>
<th>223 %</th>
<th>Yield %</th>
<th>M/e calc.</th>
<th>M/e obs.</th>
<th>Elemental Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>100</td>
<td>0</td>
<td>53</td>
<td>117.05846</td>
<td>117.05822</td>
<td>C 82.02 H 6.02 N 11.95</td>
</tr>
<tr>
<td>CH₃</td>
<td>85</td>
<td>15</td>
<td>67</td>
<td>131.07349</td>
<td>131.073094</td>
<td>C 82.48 H 6.92 N 10.68</td>
</tr>
<tr>
<td>1,4-diCH₃</td>
<td>50</td>
<td>50</td>
<td>34</td>
<td>145.089144</td>
<td>145.089632</td>
<td>C 82.72 H 6.84 N 10.28</td>
</tr>
<tr>
<td>CF₃</td>
<td>30</td>
<td>70</td>
<td>65</td>
<td>185.045228</td>
<td>185.045800</td>
<td>C 58.38 H 3.27 N 7.57</td>
</tr>
<tr>
<td>Br</td>
<td>20</td>
<td>80</td>
<td>54</td>
<td>194.968411</td>
<td>194.968992</td>
<td>C 49.01 H 3.09 N 7.14</td>
</tr>
<tr>
<td>F</td>
<td>50</td>
<td>50</td>
<td>35</td>
<td>135.048424</td>
<td>135.048833</td>
<td>C 49.43 H 3.23 N 6.88</td>
</tr>
</tbody>
</table>
A number of puzzling questions remain, one of which is based on the assumption that 4H-1,2,3-triazolylidene (202) is an electrophilic singlet carbene. If benzene substitution (Scheme 27, path a) and isomerization to α-diazoacetonitrile (203) (Scheme 27, path b) are competing kinetic processes, increasing the electron density of a benzene ring should favor substitution (path a). In contrast to expectations based on this concept, no substitution products are obtained in photolysis of 101 in toluene, p-xylene and bromobenzene, whereas 4-phenyl-1,2,3-triazole (128) is found in 26% yield from benzene (compare Eq. 79 and Eq. 74). The reasons for these results are as yet unclear.

(Scheme 27)

The product distributions in photolysis and thermolysis of 101 in benzene are different (compare Eq. 72 and Eq. 74). In photolysis, cyanocycloheptatriene (201, 54%) is the major product, whereas phenyltriazole 198 is the main product obtained in thermolysis (48%). The difference in product distribution can be rationalized by (1) the more excited
carbene generated by photolysis which facilitates the conversion of 4H-1,2,3-triazolylidene (202) to α-diazo-acetonitrile and/or (2) the increased solubility of 101 in benzene at elevated temperature (thermolysis) which accounts for the better capture of 202 by benzene and therefore more substitution product.

The cyanonorcaradienes (222a−e) and the cyanocycloheptatrienes (223a−e) obtained from a specific benzene (Eq. 79) are mixtures of many isomers as evident by gas chromatography and their complicated NMR spectra. Attempts to separate or identify each component individually were futile.

There are three basic types of isomers involved in these cycloheptatriene-norcaradiene systems: 1) position isomers, 2) valence tautomers (cycloheptatriene≠norcaradiene) and 3) geometric isomers and conformers when the C-7 positions of the norcaradienes and the cycloheptatrienes are substituted by different groups. To illustrate the problems in photo-induced position-scrambling in cycloheptatrienes and norcaradienes, an example is presented. In photolysis of 4-diazo-1,2,3-triazole (101) in toluene, cyanocarbene 204, generated as proposed in Mechanism I (Scheme 21), has three possible positions of addition to toluene as shown. Norcaradienes 224a, 224b and 224c tautomerize to cycloheptatrienes 225a, 225b and 225c, respectively. Each cycloheptatriene positional isomer can in turn have six other isomers resulting from a series
of photolytically allowed 1,7 H-shifts. A total of 21 positional isomers are possible as illustrated in Scheme 28.
(Scheme 28)
The position isomers illustrated above do not include the valence tautomerism of norcaradiene$\Leftrightarrow$cycloheptatriene systems. Such equilibria have been studied since the discovery of Buchner's ester$^{81}$ and definitive proof that many of these products, including Buchner's ester, have cycloheptatriene structures only become available with the advent of nuclear magnetic resonance spectroscopy.$^{82}$

In the products presently obtained from decomposition of 4-diazo-1,2,3-triazole (101) in aromatic substrates, there are examples where norcaradienes predominate, where cycloheptatrienes predominate and where there are mixtures which equilibrate rapidly. Substituents on C-7 of cycloheptatrienes-norcaradienes have major effects on the relative stabilities of valence tautomers.$^{83}$ Generally, electron-withdrawing substituents on C-7 favor the cycloheptatrienes, yet there are other factors to be considered.$^{84}$ Thus, the parent compound is a cycloheptatriene (227a), the 7-cyano derivative is a cycloheptatriene (227b), the 7,7-dicyano derivative is a norcaradiene (226c), the 7,7-bis(trifluoromethyl) derivative is a cycloheptatriene (227d), whereas the 7,7-dicarbomethoxy and the 7-cyano-7-trifluoromethyl derivatives are rapidly equilibrating mixtures of the
two \((\ref{eq:226} \equiv \ref{eq:227})\). 7-Cyano-7-phenyl \((\ref{eq:226f})\) and 7-carbeth-

\[
\begin{align*}
\text{a, } R_1 &= H; R_2 = H \\
\text{b, } R_1 &= H; R_2 = \text{CN} \\
\text{c, } R_1 &= \text{CN}; R_2 = \text{CN} \\
\text{d, } R_1 &= \text{CF}_3; R_2 = \text{CF}_3 \\
\text{e, } R_1 &= \text{CF}_3; R_2 = \text{CN} \\
\text{f, } R_1 &= \text{Ph}; R_2 = \text{CN} \\
\text{g, } R_1 &= \text{CO}_2\text{C}_2\text{H}_5; R_2 = \text{CN}
\end{align*}
\]

oxy-7-cyano \((\ref{eq:226g})\) derivatives are norcaradienes which
do not tautomerize to cycloheptatrienes even at elevated
temperatures.

In addition to the positional isomers and valence
tautomers described above, there are still other isomers
to be considered. For norcaradienes and cycloheptatrienes
carrying different substituents on C-7, norcaradiene
\ref{eq:228a} and cycloheptatriene \ref{eq:229a} each can exist in isomeric
forms as shown. Such phenomena are recognizable from the
NMR spectrum of \ref{eq:228} and will be discussed with specific
examples later.
To understand better the decomposition reactions of 4-diazo-1,2,3-triazole (101) with aromatics, study was extended to nitrobenzene. Photolysis of 101 in nitrobenzene for five hours was found to give nitrosobenzene (231), 4-(3-nitrophenyl)-1,2,3-triazole (232) and nitro-substituted cyanocycloheptatrienes and cyanonorcaradienes 233-234 in 18, 42 and 8% yields, respectively (Eq. 80).

\[
\begin{align*}
\text{N—N} & \quad \rightarrow \\
\text{NO}_2 & \quad \rightarrow \\
\text{CN} & \\
\text{H} & \\
\end{align*}
\]

Nitrosobenzene (231) was isolated by fractional distillation and identified and quantified by gas chromatography using authentic samples of 231 and toluene as...
internal standards. Nitrophenyltriazole 232 and cyano-
nitrocycloheptatrienes/norcaradienes 233-234 were isolated
by column chromatography. Nitrophenyltriazole 232, a
tan solid (mp. 197-198°C), was assigned from its mass,
IR and NMR spectra. The NMR spectrum of 232 exhibits an
unsymmetrical multiplet at $8.05$ and a singlet at
$7.92$ corresponding to 3 and 1 hydrogens, respectively.
This evidence alone is inconclusive. It is possible,
however, to rule out the $p$-isomer since 4-(4-nitrophenyl)-
1,2,3-triazole, prepared by nitration of 4-phenyl-1,2,3-
triazole$, exhibits significant differences in its NMR
splitting pattern. Cyanonorcaradienes-cyanocyloheptatrienes
233-234 were identified from their IR and mass spectra.

Formation of nitrosobenzene (231, Eq. 80) is
significant and may involve Scheme 29. Thus, 4H-1,2,3-
triazolylidene (202), generated by photolytic loss of
nitrogen from 4-diazo-1,2,3-triazole (101), is trapped
by nitrobenzene to give zwitterion 235, which cleaves to
nitrosobenzene (231) and possibly 1,2,3-triazol-4-one
(236) (Scheme 29). Triazolone 236 is not expected to

![Diagram](Scheme 29)
be stable and presumably decomposes to hydrogen cyanide, nitrogen and carbon monoxide (Eq. 81).

\[
\text{V S} \quad \begin{array}{c}
\text{N} - N \\
\text{236}
\end{array}
\rightarrow \text{N}_2 + \text{HCN} + \text{CO} \quad (81)
\]

The ability of certain electrophilic carbenes to abstract oxygen from reaction substrates is not uncommon. Recently oxygen abstraction from nitrobenzene by azolylidenes to yield nitrosobenzene has been observed in this laboratory.\textsuperscript{28,38} Thus, 5-phenyl-3H-1,2,4-triazolylidene (237) reacts with nitrobenzene to give 3-(3-nitrophenyl)-5-phenyl-1,2,4-triazole (238), nitrosobenzene (231) and benzonitrile (239) in 17, 45 and 48\% yields, respectively (Eq. 82).\textsuperscript{38} Similarly, nitrosobenzene (231) and 2-(3-nitrophenyl)-imidazole (240) along with minor amounts of 2-(2-nitrophenyl)-imidazole and
2-(4-nitrophenyl)-imidazole are produced in decomposition of 2-diazoimidazole (24) in nitrobenzene\textsuperscript{28} (Eq. 83).

\[
\begin{align*}
\text{N}_2 \quad \text{+} \quad \text{O}^\ominus \text{N}^\oplus \quad \xrightarrow{\text{h}_\nu \quad \text{or} \quad \Delta} \quad \text{N}_2 \text{H} \text{H} \text{N} \equiv \text{N} \equiv \text{N} \equiv \text{H} \text{N} \equiv \text{N} \equiv \text{N} \equiv \text{H} \text{N} \equiv \text{N} \equiv \text{N} \equiv \text{H} \\
\text{24} \quad \text{240} \quad \text{231}
\end{align*}
\]

Formation of 4-(3-nitrophenyl)-1,2,3-triazole (232) in Equation 80 suggests dipolar opening of the intermediate spironorcaradienes 241a-c. The collapse of 241a-c may be controlled by the nitro substituent. Ring-openings will occur preferentially such that the positive charges are not conjugated directly with the electron-withdrawing substituents. Such dipolar intermediates, 242a and 242e, thus give the meta-substituted phenyltriazole 232 (Scheme 30).
(Scheme 30)
Cycloheptatrienes and norcaradienes $233-234$ may be formed by Mechanism I (Scheme 31). Thus, isomerization of high energy $4H$-$1,2,3$-triazolylidene $(202)$ gives $\alpha$-diazooacetonitrile $(203)$ which loses nitrogen to yield cyanocarbene $(204)$. Carbene $(204)$ adds to nitrobenzene to form $233$ which ring-opens to $234$ (Scheme 31).

![Scheme 31](image)

From the results of reactions of $101$ with various benzenes, Mechanism I, decomposition of $101$ to $\alpha$-diazooacetonitrile $(203)$, is believed to lead to formation of cyanonorcaradienes $222$ and cyanocycloheptatrienes $223$ (Eq. 79). Mechanism II however cannot be excluded in which spiro-$1,2,3$-triazolonorcaradienes $243$ undergo decomposition with nitrogen evolution and hydrogen migration to give $244$ and $245$. It was then decided to study the reactions of benzenes with $4$-diazoo-$1,2,3$-triazoles ($102-104$) containing varied substituents in the 5-position. The migratory abilities of the 5-substituents would certainly be different than for hydrogen and it was of interest to determine what types of reactions
prevail (Scheme 32).

(Scheme 32)

The behavior of 4-diazo-5-phenyl-1,2,3-triazole (102) with benzene was then investigated. When 102 was photolyzed in benzene three hours, the initial light yellow solution changed to a bright orange-colored suspension. TLC revealed at least eight products, many of which are brightly colored under visible light. Careful separation by column chromatography led to six characterizable products: 4,5-diphenyl-1,2,3-triazole (246), 7-cyano-7-phenylnorcaradiene (247), benzoyl cyanide azines (278), trans-9,10-dicyano-9,10-dihydrophenanthrene (249), 9,10-dicyano-phenanthrene (250) and a sixth product 251, which has not been identified, in 13, 38, 5, 8, 11 and 6% yields, respectively (Eq. 86).

Substitution of benzene by 5-phenyl-4H-1,2,3-triazolylidene (252), identified by spectral methods and by
comparison with an authentic sample, is minor (6%) as was the case with 4H-1,2,3-triazolylidene (202, Eq. 74). The remaining products appear to be derived from phenyl-diazoacetonitrile (207) arising from isomerization of 252 in keeping with Mechanism I (Eq. 87).

The major reaction product is a colorless crystalline mixture of exo and endo-7-cyano-7-phenylnorcaradienes (253a and 253b). The 300 MHz NMR of 253a and 253b leaves no doubt that they are norcaradienes (compare Appendix 1 and 2) and that the phenyl and cyano groups occupy exo
and endo positions. No valence tautomerizations of 253 to cycloheptatrienes or hydrogen or phenyl migrations were observed.

Norcaradienes 253a and 253b have planes of symmetry and thus in each H₄ = H₆, H₂ = H₅ and H₃ = H₄. The H₁ and H₆ signals in 253a and 253b occur at δ 3.49 as two doublets, one for each isomer. Each doublet is the resultant of splitting by one adjacent proton (H₂ = H₅, J₁₂ = 4.5 Hz). These signals are at lower fields than anticipated for cyclopropanes because the protons are both allylic and adjacent to two geminal substituents, leading to downfield shifts of about 1.00-1.58 units. The H₂ = H₅ signals centered at δ 6.18 (2H) consist of eight lines corresponding to two sets of doublets of doublets. For each isomer, H₂ is split by H₁ and H₃ and H₅ by H₄ and H₆. The H₃ and H₄ signals centered at δ 6.45 are split into a doublet because of the adjacent protons. The four lines arise because there are two isomers. The signals for the aromatic protons occur at δ 7.25 as a multiplet. It is reasonable to assume that 253a and 253b result from phenylcyanocarbene (254) as in Equation 88. Indeed
authentic phenyldiazocetonitrile (207) has been reported to thermolyze in benzene to 7-cyano-7-phenynorcaradiene (253, 32%, stereochemistry unspecified) along with unidentified products that are probably "dimers of phenylcyanocarbene" (254). Much of the present behavior of 102 corresponds to that of 207 in that four products have been found which are derivable from two equivalents of 207.

The most convincing evidence for the intermediacy of phenyldiazocetonitrile (207) in the present experiments is isolation of benzoyl cyanide azines (248). The azines were identified from their analyses and spectra and by comparison of melting point with the literature value. The stereochemistry of azine 248 has not been determined. Mechanisms which account for 248 are illustrated.
9,10-Dicyano-9,10-dihydrophenanthrene (249) and 9,10-dicyanophenanthrene (250) were assigned from their IR and NMR spectra and by comparison of their melting points with literature values. Phenanthrenes 249 and 250 are possibly formed from 254 and 207 by sequences as follows:

\[
\begin{align*}
\text{Ph} & \quad \text{NC} \\
\text{Ph} & \quad \text{Ph} \\
\text{K} & \quad \text{NC} \\
\text{CN} & \quad \text{Ph} \\
\text{N}_2 & \quad \text{Ph} \\
\text{NC} & \quad \text{Ph} \\
\text{CN} & \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{CN} \\
\text{NC} & \quad \text{Ph} \\
\text{NC} & \quad \text{Ph}
\end{align*}
\]

\[\alpha, \alpha'-\text{Dicyanostilbene (256)}\] has been shown previously to photolyze readily to 9,10-dicyano-9,10-dihydrophenanthrene (249) which converts in the presence of oxygen to 9,10-dicyanophenanthrene (250). 89

The molecular structure of 251, an orange solid with a melting point of 278-280 °C, is unknown. The product has (1) a simple IR spectrum implying a high degree of symmetry, (2) absorption at 2215 cm\(^{-1}\) assignable to a conjugated C≡N group, (3) a molecular weight of 308 and (4) a molecular formula of C\(_{22}\)H\(_{16}\)N\(_2\) corresponding to an adduct of two phenylcyanocarbene (254) units and one benzene unit. The
NMR spectrum of 251 shows all absorptions above δ 6.8. An interesting possibility may involve addition of two phenylcyanocarbenes (254) to benzene followed by aromatization of 257 to give 258, 259 and 260 (Eq. 89).

\[ \begin{align*}
2 \quad & C_6H_5^+ \quad + \quad \text{CNC} \\
& \text{254} \quad \rightarrow \quad C_6H_5 \quad \text{CN} \\
& \text{257} \quad \rightarrow \quad C_6H_5 \quad \text{CN} + \quad C_6H_5 \quad \text{CN} + \quad \text{CN} \\
& \text{258} \quad \text{259} \quad \text{260}
\end{align*} \]

(89)

To further understand the photo-decomposition reactions of 4-diazo-5-phenyl-1,2,3-triazole (102) in aromatics, study was extended to toluene. When 102 was photolyzed in toluene, three isolable products were obtained from column chromatography as follows: 4-(4-methylphenyl)-5-phenyl-1,2,3-triazole (261), methyl-substituted-7-cyano-7-phenylnorcaradienes (262a-c) and an unidentified compound 263 in 8, 17 and 33% yields, respectively (Eq. 90).

Substitution product 257 was assigned from the following evidence: its mass spectrum exhibits strong signals at 235, 220 and 145 corresponding to ions M/e,
M/e-CH$_3$ and M/e-C$_6$H$_5$CH$_3$, respectively. The NMR spectrum of 261 shows a CH$_3$ signal at $\delta$ 2.48 (3H) and a multiplet at 7.32 and 7.88 corresponding to the unsubstituted phenyl group (5H). The four ring hydrogens in the tolyl group resonate as two doublets at $\delta$ 7.18 and 7.65 leaning towards each other with a coupling constant of $J = 9.2$ Hz. Although the above evidence is not absolute, the fact that the aromatic protons of the tolyl group occur as two symmetric doublets is good indication that the product is $p$-tolyl derivative 257. Norcaradienes 262a-c, a distillable (140-145°C/0.35 mmHg) yellow viscous oil, were isolated as a mixture of many isomers (Eq. 91). The mass spectrum and elemental analysis of the mixture are satisfactory and no valence tautomerization to
cycloheptatrienes was observed as evident by NMR, nor was there isomerization due to hydrogen or phenyl shifts. Norcaradienes 262a–c can be present in exo and endo forms and aromatics 264a–c arise presumably from 262a–c during distillation and/or column chromatography. The composition

\[
\text{EXO} + \text{ENDO}
\]

of the distillate (based on NMR) is about 15% 262a, 40% 262b, 30% 262c and 12% of aromatics 264a–c. The NMR methyl absorptions of 262a, 262b and 262c occur at δ 1.60, 2.07 and 1.97, respectively and allow quantitative analysis of the components. The assignments of the –CH₃ signals are based on a study by Berson in which remarkably similar results were observed in thermolysis of dicyano-diazomethane (265) in toluene (Eq. 92). In reactions of 265 and toluene under conditions which minimize aromatization and isomer interconversion, the product consists of 5–10%
of 266a, 5-10% of total aromatics 267a-c and 40-45% each of 266b and 266c. A prior study also suggests that 266a-c equilibrate at elevated temperatures and that 266b is the most stable isomer thermodynamically.

When 102 is heated in toluene at 95°C for 60 hours, slightly different products were found as compared to photolysis (compare Eq. 90). A mixture of methyl-substituted-7-cyano-7-phenylnorcaradienes (262a-c) was obtained as the major product in 54% yield, along with 4-(4-methylphenyl)-5-phenyl-1,2,3-triazole (261, 24%) and the reduction product, 4-phenyl-1,2,3-triazole (198, 6%). Bis adducts such as 263 in Eq. 90 were not found in the thermolysis reaction.

Substitution product 261, derived presumably from
4-phenyl-5H-1,2,3-triazolylidene (252) and toluene, was obtained in a higher yield than from photolysis (24% vs. 8%). This suggests that carbene 252, generated photolytically, is excited and may have a shorter lifetime for trapping by solvent. Higher energy carbene intermediate 252 might isomerize to α-phenyldiazocetonitrile (207) rather than attack toluene.

The ratios of the three norcaradienes, 262:262b:262c (50:50:0.5), are similar to that from photolysis. However, in thermolysis, less 262c and more aromatics 264a-c (refer to Eq. 90) were observed as evident by less -CH₃ absorption at δ 1.60 and more at δ 2.30 corresponding to methyls in 262a and 264a-c, respectively. The differences may be due to the long heating period (60 h) which causes equilibration of isomers 262a-c and aromatizations.

Substitution at the p-position to give 261 suggests electronically-controlled dipolar opening of intermediate spironorcaradiene 268 (Scheme 33). The absence of the o-tolyl product can be rationalized on the basis of steric effects that prohibit formation of the other possible spironorcaradiene intermediates.

A small amount of reduction product 198 was obtained (6%) in the thermolysis experiment. Phenyltriazole 198 is also formed in thermal decomposition of 102 in benzene
(refer to Eq. 73). These observations suggest that singlet carbene \( 252 \), upon generation by thermolysis, has long enough life-time to undergo intersystem crossing (ISC) to triplet carbene \( 268 \), reduction of which by hydrogen abstraction from the reaction environment results in \( 198 \) (Scheme 34).
Formation of norcaradienes 262a-c is explained by Mechanism I (Scheme 35). Thus, decomposition of 102 by photolysis or thermolysis generates 4-phenyl-5H-1,2,3-triazolylidene (252) which isomerizes to α-phenyldiazoacetonitrile (207). Photolytic loss of nitrogen from 207 forms phenylcyanocarbene (254) which adds to toluene to give norcaradienes 262a-c (Scheme 35).

Investigation was then extended to photolysis of 4-carbethoxy-5-diazo-1,2,3-triazole (103) in benzene. The product obtained after irradiation was clean and TLC showed only one component to be present. Purification of the product by elution through a silica gel column with hexane/benzene led to 7-carbethoxy-7-cyanonorcaradiene (269) and ethyl α-phenylcyanoacetate (270) in 23 and 58% yields, respectively (Scheme 36).

Norcaradiene 269a-b, a colorless crystalline solid
(Scheme 36)

(mp. 175-176°C), was identified by NMR, IR, UV and elemental analyses. The 300 MHz ¹H NMR spectrum of 269a-b shows unequivocally that it is a mixture of exo (269a) and endo (269b) norcaradienes as illustrated. The NMR signals for H₁ and H₆ occur at 3.24 as two doublets, one for each isomer. The isomer is due to splitting by an adjacent proton (H₂ = H₅). The value is somewhat low for protons on a cyclopropane ring but is explained by the combined deshield-
ing effects of two electron-withdrawing groups and two double bonds. The signals for \( H_2 = H_5 \) center at \( \delta 6.22 \) (2H) and are represented by eight lines corresponding to two sets of doublets of doublets, one for each conformer. The \( H_3 \) and \( H_4 \) signals at \( \delta 6.43 \) are split into a doublet by the adjacent protons at \( H_2 = H_5 \). The four lines are due to the two isomers, \( 269a \) and \( 269b \). The UV spectrum of \( 269a-b \) (\( \lambda_{\text{max}}^{\text{cyclohexane}} 271 \text{ nm} \)) is that expected for a norcaradiene chromaphore and is different from that of 7-cyanocycloheptatriene \( 205 \) (\( \lambda_{\text{max}}^{\text{cyclohexane}} 255 \text{ nm} \)).

Cyanoacetate \( 270 \) was identified by NMR and by comparison with the physical and spectral properties of an authentic sample.

Formation of \( 269 \) is explained by Scheme 36. Thus, photolysis of \( 103 \) results in loss of nitrogen and formation of singlet 5-carbethoxy-4H-1,2,3-triazolylidene \( (271) \), an energy-rich carbene which isomerizes by ring scission to ethyl diazocynoacetate \( (272) \). Subsequent loss of nitrogen from \( 272 \) results in cyanocarbene \( 273 \) which adds to benzene to give norcaradienes \( 269a \) and \( 269b \), aromatization of which yields \( 270 \) (Scheme 36). Transformations of \( 269a \) and \( 269b \) to \( 270 \) are readily effected by exposure of \( 269a-b \) to a variety of mild chromatographic adsorption materials and by heating. Since the crude initial reaction
product revealed only one component to be present, it is presumed that 270 was formed from 269a-b on handling. The intermediacy of ethyl diazocyanacetate (272) in photolysis of 103 in benzene (Scheme 36) is supported by the report that methyl diazocyanacetate (274) photolyzes in benzene to 7-carbomethoxy-7-cyanonorcaradiene (275, 39%, Eq. 94).

\[
\text{NC-C-CO}_2\text{CH}_3 \xrightarrow{\text{h} \mu \text{N}_2} \text{NC-C-O}_2\text{CH}_3
\]  

(94)

In a further extension, 4-cyano-5-diazo-1,2,3-triazole (104) was photolyzed in benzene for three hours. With no surprise, 7,7-dicyanonorcaradiene (276) and phenylmalononitrile (277) were obtained in 28 and 43% yields, respectively (Scheme 37). Norcaradiene 276 and malononitrile
277 were identified by spectral methods and by comparison with authentic samples. The NMR spectrum of 7,7-dicyano-norcaradiene (276) is not as complicated as that of other norcaradienes of this study because of the symmetry of 276. At room temperature, H₁ and H₆ in 276 give NMR signals at δ 3.41, characteristic of cyclopropyl hydrogens in norcaradienes carrying electronegative groups on C₇. The signal moves to δ 3.68 at 40 °C indicating increased amounts of 7,7-dicyanocycloheptatriene in equilibrium at the increased temperature. It is clear however that at even higher temperatures, norcaradiene 276 predominates since H₁ and H₆ in cycloheptatrienes occur at much lower fields. Also H₂,3,4,5 in 276 exhibit multiplets at δ 6.28 and 6.62.

Formation of norcaradiene 276 by photolysis of 10₄ in benzene presumably occurs as in Scheme 37. Thus, decomposition of diazotriazole 10₄ results in 4-cyano-5H-1,2,3-triazolylidene (278). This high energy carbene (278) isomerizes to relatively stable diazomalononitrile (279), which loses nitrogen photolytically to give dicyanocarbene (280). Then carbene 280 adds to benzene to yield dicyanonorcaradiene 277 which aromatizes to 276 (Scheme 37). In support of Mechanism I, it has been reported that photolysis or thermolysis of diazomalononitrile (279) in benzene gives 7,7-dicyanonorcaradiene.
The physical and spectral properties of Z-substituted cyanocycloheptatrienes and/or cyanonorcaradienes obtained from photolysis of 4-substituted-5-diazo-1,2,3-triazoles (101-104) are summarized in Tables 4 and 5.
Table 4  Physical Properties and Elemental Analyses of Cyanocycloheptatriene (201) and Cyanonorcaradienes (253, 269, 276).

<table>
<thead>
<tr>
<th>Z</th>
<th>B.P./M.P.</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>40-43 °C</td>
<td>C 82.02 H 6.02 N 11.95</td>
</tr>
<tr>
<td></td>
<td>0.28 mm Hg</td>
<td>C 81.91 H 6.11 N 11.82</td>
</tr>
<tr>
<td>Ph</td>
<td>137 °C</td>
<td>C 87.01 H 5.74 N 7.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 86.75 H 6.01 N 7.28</td>
</tr>
<tr>
<td>C≡N</td>
<td>97-98 °C</td>
<td>C 76.04 H 4.25 N 19.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 76.15 H 4.37 N 19.56</td>
</tr>
<tr>
<td>CO₂C₂H₅</td>
<td>175-176 °C</td>
<td>C 69.83 H 5.86 N 7.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C 69.67 H 6.22 N 7.08</td>
</tr>
</tbody>
</table>
Table 5 Spectral (IR, UV, NMR) Properties of Cyanocycloheptatriene (201) and Cyanonorcaradienes (253, 269, 276).

<table>
<thead>
<tr>
<th>Z</th>
<th>IR (cm⁻¹)</th>
<th>UV (nm)</th>
<th>NMR (CDCl₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2250 (neat)</td>
<td>255</td>
<td>2.35 (t, 2H, H₇,₇)</td>
</tr>
<tr>
<td></td>
<td>2200</td>
<td></td>
<td>5.2-5.8 (m, 2H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.1-6.4 (m, 2H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.0-7.2 (m, 2H)</td>
</tr>
<tr>
<td>Ph</td>
<td>2230 (KBr)</td>
<td>276</td>
<td>3.49 (m, 2H, H₁,₆)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.28 (m, 2H, H₂,₅)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.44 (m, 2H, H₃,₄)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.37 (m, 5H, Ph)</td>
</tr>
<tr>
<td>C≡N</td>
<td>2245 (KBr)</td>
<td>271</td>
<td>3.47 (d, 2H, H₁,₆)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.2-6.8 (m, 4H, H₂,₃,₄,₅)</td>
</tr>
<tr>
<td>CO₂C₂H₅</td>
<td>2240 (KBr)</td>
<td>268</td>
<td>1.36 (t, 3H, ester)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.24 (m, 2H, H₁,₆)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.31 (q, 2H, ester)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.22 (m, 2H, H₂,₅)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6.43 (m, 2H, H₃,₄)</td>
</tr>
</tbody>
</table>
4-Cyano-5H-1,2,3-triazolylidene (278), generated by photolysis of 104 in benzene, isomerizes exclusively to diazomalononitrile (279, Scheme 37). It was of interest to see if carbene 278 can be intercepted by more electron-rich aromatics. Thus, investigation was extended to anisole. Heating 104 in anisole at 60-65°C for five hours resulted in 4-cyano-5-(2-methoxyphenyl)-1,2,3-triazole (278), 4-cyano-5-(4-methoxyphenyl)-1,2,3-triazole (279) and 4-cyano-5-phenoxy-1,2,3-triazole (280) in 28, 21 and 12% yields, respectively (Eq. 96). Products derived from diazomalononitrile were not observed.

\[ \begin{align*} 
\text{104} & \rightarrow \begin{array}{c} \text{N} \\ \text{N} \end{array} \quad \begin{array}{c} \text{N} \\ \text{N} \end{array} \\
& \begin{array}{c} \text{OCH}_{3} \\ \text{OCH}_{3} \\ \text{CN} \\ \text{CN} \\ \text{CN} \\ \text{N} \end{array} + \begin{array}{c} \text{H} \\ \text{H} \\ \text{N} \\ \text{N} \\ \text{N} \\ \text{N} \end{array} \\
& \begin{array}{c} \text{278} \\ \text{279} \\ \text{280} \end{array} 
\end{align*} \]

The assignment of o-anisyl isomer 278 is based on its spectra and elemental analysis. The NMR spectrum of 278 exhibits a doublet at \( \delta 7.09 \) and a multiplet at \( \delta 7.55 \) corresponding to one and three ring hydrogens, respectively. p-Anisyl derivative 279 was identified by comparing its melting point with the literature value and by its NMR spectrum. The NMR spectrum of 279 shows two symmetric doublets at \( \delta 7.09 \) and 7.83 indicative of
p-substitution. Aromatic ether 280 was assigned from its exact mass (186) and its NMR spectrum which shows five aromatic hydrogens and no methyl signal.

The absence of products derived from dicyanocarbene is surprising. The result suggests that carbene 278, generated by thermolysis, is trapped by anisole more effectively than when 104 is photolyzed and isomerization to diazomalononitrile does not occur.

Formation of o- and p-substitution products 278 and 279 presumably involves dipolar openings of intermediate spironorcaradienes 281a-c. The directions of ring-openings are controlled by the o-methoxy substituent and lead to intermediates 282b-d (Scheme 38) in which the positive charge can be directly stabilized by the electron-donating substituent.
(Scheme 38)
Phenoxytriazole 280 may arise from cleavage of oxygen ylide 283. The fate of the CH₃ group is unclear and may be displaced by the reaction environment. Efforts to detect N-methyltriazole and/or methyl anisoles are as yet unsuccessful (Scheme 39).

Scheme 39

In summation, the following points can be concluded regarding the behavior of 4H-1,2,3-triazolylidenes (202, 252, 275, 278) in arenes in general.

(1) Triazolylidenes 202, 252, 275, 278, generated by the decomposition of the corresponding diazo compounds, tautomerize to the α-diazoacetonitriles which subsequently lose nitrogen and undergo addition reaction with benzenes to form norcaradienes and cycloheptatrienes.

(2) Some of the triazolylidenes are trapped by benzene to form tricyclic spironorcaradienes which is supported by the attainment of substitution products.
Correlation between the electronic effect of the aromatic solvents and the selectivity and reactivity of the carbenes was not observed.

Product distributions are not uniform for the thermolysis and photolysis reactions. For thermolysis, usually more aromatic substitution is observed, whereas, more product derivable from the cyanocarbenes is obtained in photolysis. This may be explained by the higher energy of the carbenes generated by photolysis which facilitates the isomerization process. Increasing solubility of the diazo compounds at elevated temperature in thermolysis increases the chance of capture of the carbene by the solvent molecule and therefore more substitution product.

Tautomerization of triazolylidene to \( \alpha \)-diazooacetonitrile \((202\neq203)\) is not a reversible process.

Mechanism I appears to be the major pathway base on the following evidence:

(i) the formation of benzyol cyanide azine \((248)\) described in equation 86 can only be explained by the presence of phenylidazoacetonitrile \((207)\).

(ii) independent studies of decomposition of \( \alpha \)-diazooacetonitrile \((203)\), phenylidazoacetonitrile \((207)\), methyl diazocyanoacetate \((274)\) and diazomalono-nitrile \((279)\) in benzene gave products similar to
our findings suggests the intermediacy of 203, 207, 274 and 279 in the decomposition of 101, 102, 103 and 104, respectively in benzene.

(iii) Replacing hydrogen on carbon at position 4 with Z groups such as Ph, CN, CO₂C₂H₅ do not change significantly the course of reaction. The products obtained are that expected of the corresponding cyanocarbenes. This finding also serves to disprove Mechanism II because of the poor migratory aptitude of CN and CO₂C₂H₅ and the fact that Mechanism II involves migration of such a group in a key step.

(7) If mechanism I is indeed the major process in the decomposition of 4-diazo-1,2,3-triazoles (101-104), it provides a precedent to a transformation involving a heterocyclic diazo compound decomposes to a carbene, which tautomerizes with ring scission to form an acyclic diazo compound which decomposes to form another carbene.

\[ \text{diazo} \rightarrow \text{carbene} \rightarrow \text{diazo} \rightarrow \text{carbene} \]

(8) This transformation may provide a general synthetic method for various substituted cyanocarbenes.
Chapter III Experimental

Melting Points. Melting points were determined using a Thomas Hoover capillary point apparatus and are uncorrected.

Elemental Analyses. Elemental analyses were performed by Microanalysis, Inc., Wilmington, Delaware.

Ultraviolet Spectra. Ultraviolet spectra were obtained using a Cary Model 1605 recording spectrophotometer.

Infrared Spectra. Infrared spectra were determined on a Perkin-Elmer Model 457 Grating Infrared Spectrophotometer. All spectra were calibrated to a polystyrene absorption peak at 1601 cm⁻¹. Solid samples were prepared as KBr wafers or in dichloromethane solution and liquid samples as liquid films unless otherwise stated.

¹H Nuclear Magnetic Resonance Spectra. Proton magnetic resonance spectra were determined on Varian Model A-90 or Bruker WP-300 instruments by Dr. C. Cortrell and are reported in parts per million from internal tetramethylsilane on the 8 scale.

Mass Spectra. Mass spectra were determined by Mr. C. Weisenberger on an AEI-MS 9 instrument at an ionization energy of 70 eV. Samples on which exact mass were measured exhibited no significant peaks at m/e greater than those of the parent.
**Gas Chromatography.** Gas chromatography was performed using a Wilkins Aerograph, Model 920, with a thermal conductivity detector. Column material was composed of 25% SE-30 on chromosorb W-AW-DCMS (0.25" x 12').

**Column Chromatography.** Column chromatography was effected on MN Laboratories' Silica Gel for Column Chromatography (70-270 mesh) or MC & B's Silica Gel (100-200 mesh).

**Solvents.** All solvents were dried, distilled and deoxygenated prior to use in decomposition experiments.

**Decompositions.** The decompositions (both thermal and photochemical) of 4-diazo-1,2,3-triazoles were carried out under nitrogen. All photolyses were performed with a Hanovia 450 watt medium pressure mercury lamp placed in a Pyrex immersion well (150 ml capacity). The well was fitted with a photochemical reactor containing the solution to be irradiated.
1-Morpholino-2-nitroethene was prepared by modification of the method of Hurd and Sherwood as follows:

To a stirred solution of ethyl ethoxymethylene-malonate (162 g, 0.75 mol) and nitromethane (91.5 g, 1.5 mol) was added morpholine (130.3 g, 1.5 mol) in one portion. (The morpholine was dried over sodium hydroxide pellets and distilled at 128–129°C). The reaction is exothermic and the yellow solution turned orange red. The product, after crystallization (2h), was filtered and washed with cold ether. Ether (100 mL) was added to the filtrated and the solution was cooled to obtain an additional crop. The two portions, on combination and recrystallization from ethanol, yielded 1-morpholino-2-nitroethene, yellow crystals (54.5 g, 48%): mp 141–141°C (lit. mp 141–141°C); IR (KBr) 1630 (C=C), 1540, 1380 (-NO₂) cm⁻¹; NMR(CDC₁₃) δ 3.33 (t, 4 H, H₁), 3.75 (t, 4 H, H₂), 6.65 (d, H₃, J = 11.7 Hz), 8.05 (d, H₄, J = 11.7 Hz); mass spectrum, m/e calcd for C₆H₁₀N₂O₃, 158.069136, obsd 158.069499.

4-Nitro-1,2,3-triazole. A solution of 1-morpholino-2-nitroethene (152 g, 0.33 mol), tosyl azide (65 g, 0.33 mol) and absolute ethanol (800 mL) was refluxed 50 h. When the solution was cooled, tosyl morpholide (40–45 g) crystallized and was collected by filtration. Evaporation
of the solvent under vacuum left a brown oil residue. Chloroform (300 mL) was added and the resulting suspension was swirled until the product crystallized. Filtration and washing the white crystals with chloroform afforded 4-nitro-1,2,3-triazole (21.2 g, 56%): mp 159°C (lit. mp 158-159°C); IR(KBr) 3250, 3170 (N-H), 1550, 1345 cm⁻¹(NO₂); NMR(CDC1₃) δ 9.0 (s, C CH), 13.2 (br, N-H); mass spectrum m/e calcd for C₂H₂N₄O₂, 114.017773, obsd 114.017514.

4-Amino-1,2,3-triazole. A mixture of 4-nitro-1,2,3-triazole (10.0 g, 0.88 mol), 5% palladium-on-charcoal (3 g) and absolute ethanol (350 mL) was shaken in a Paar hydrogenator under a constant pressure of 60 psi of hydrogen for 6 h at room temperature. The catalyst was carefully removed by filtration over celite. Removal of the solvent under reduced pressure left a green oily residue which crystallized on standing overnight. This product was dissolved in absolute ether and filtered. The filtrate was concentrated and chilled to give white crystals of 4-amino-1,2,3-triazole (4.2 g, 57%): mp 73-74°C (lit. mp 74-75°C); IR(KBr) 3380, 3320, 3160, 3102, 2920, 1612, 1560, 1530, 1335, 1260, 780, 685 cm⁻¹; NMR(DMSO/D₆, CDC1₃) δ 4.65 (br s, -NH₂), 7.0 (s, triazole), 13.50 (br s, N-H); mass spectrum calcd for C₂H₂N₄, 84.043594, obsd 84.043824.
4-Diazo-1,2,3-triazole. To a stirred solution of 4-amino-1,2,3-triazole (0.84 g, 0.01 mol) in 2N hydrochloric acid (10 mL) at 0°C was added (10 min) a solution of sodium nitrite (0.76 g, 0.011 mol) in water (1 mL). The yellow diazonium salt which initially precipitated went back into solution after the addition was completed. Dichloromethane (100 mL) was added to the aqueous solution which was neutralized to pH 7 by addition of solid sodium carbonate. The aqueous layer was extracted repeatedly with dichloromethane (800 mL). The organic layers were combined and desiccated over anhydrous magnesium sulfate (4-5 g). The solvent was removed under reduced pressure to yield white crystalline 4-diazo-1,2,3-triazole (0.61 g, 65%): mp 125-126°C (explosion). The product is extremely shock sensitive and will explode if scratched or tapped. For safety reasons, the product was best transferred as a concentrated solution in dichloromethane to the reaction vessel. Further physical properties of diazotriazole 101 are: IR(CH₂Cl₂) 2160 (≡N=≡N), 1600 (aromatic), 1100 (C-N); NMR(CDCl₃) δ 8.6 (s, triazole); mass spectrum calcd for C₂H₅N₁, 95.032890, obsd 95.033188; m/e 95, 67 (M-N₂)+, 39 (M-2N₂)+; UV(methanol) max 275 nm.

5-Amino-1-benzyl-4-phenyl-1,2,3-triazole. A mixture of benzyl azide (39.9 g, 0.3 mol) and phenylacetonitrile (36.0 g, 0.30 mol) was refluxed with sodium (6.9 g, 0.30 mol)
in methanol (200 mL). The solid which separated from the hot solution was collected upon cooling and combined with material obtained by evaporation of the methanolic filtrated followed by trituration with water. Recrystallization of the crude product from ethanol/benzene afforded pure 5-amino-1-benzyl-4-phenyl-1,2,3-triazole (72 g, 93%): mp 157-158°C (lit. 158°C); IR(KBr) 3310, 3200, 3060, 3030, 1640, 770, 700 cm⁻¹; NMR(CDC₁₃) δ 5.30 (s, 2 H, benzyl CH₂), 6.30 (br s, –NH₂), 7.22 (m, 5 H, benzyl phenyl), 7.5 (m, 5 H, phenyl).

5-Amino-4-phenyl-1,2,3-triazole. A suspension of 5-amino-1-benzyl-4-phenyl-1,2,3-triazole (23.8 g, 0.095 mol) in liquid ammonia (600 mL) was stirred with small pieces of sodium (5.6 g, 0.24 mol) until the transient blue-green color produced initially became permanent. Ammonium chloride was added to discharge the blue-green color and the mixture was evaporated at room temperature overnight. The crude solid obtained was stirred with water (200 mL) and the resulting suspension was filtered to remove initial 5-amino-1-benzyl-4-phenyl-1,2,3-triazole (1.2 g). The aqueous filtrate was acidified with concentrated hydrochloric acid and then adjusted to pH 8 by dropwise addition of concentrated ammonium hydroxide. The solid which separated from the aqueous solution was recrystallized.
from water to yield 4-amino-5-phenyl-1,2,3-triazole
(9.25 g, 61%): mp 124 °C (lit.53 mp 125 °C); IR(KBr)
3410, 3330, 3260 (N-H), 1630 (NH₂), 1605 (C=C), 760, 690
(mono-substituted benzene).

4-Diazo-5-phenyl-1,2,3-triazole (102). A stirred solution
of 5-amino-4-phenyl-1,2,3-triazole (1.6 g, 0.01 mol) in
2N hydrochloric acid (10 mL) was cooled to 0 °C. Sodium
nitrite (0.76 g, 0.011 mol) in water (1 mL) was added.
The reaction mixture was allowed to stir 10 min. Dichloro-
methane (100 mL) was added and the aqueous solution was
neutralized to pH 7 with sodium carbonate. When carbon
dioxide evolution ceased, the dichloromethane and the
aqueous layers were separated. The aqueous solution was
then extracted repeatedly with dichloromethane (300 mL).
The organic layers were combined and dried over anhydrous
magnesium sulfate. The solvent was removed to yield
yellow crystalline 4-diazo-5-phenyl-1,2,3-triazole (102,
1.16 g, 68%): mp 134-135 °C (explosion); IR(CH₂Cl₂)
2150 (=N=N), 1170 (C-N); NMR(CDCl₃) δ 7.45 (m, 3 H,
phenyl), 7.70 (m, 2 H, phenyl); UV(methanol) λ max 285 nm.

4-Carbethoxy-5-tosylamino-1,2,3-triazole. To a vigorously
stirred solution of tosyl azide (98 g, 0.5 mol) in
anhydrous ether (400 mL) was added ethyl cyanoacetate
(56.5 g, 0.5 mol) in 10% aqueous sodium hydroxide solution (1.0 mol) at 5°C. The reaction was exothermic and the temperature rose to 15-20°C. The mixture was then stirred for 1 h. The aqueous layer was separated from the ether and then washed several times with ether. Upon neutralization of the aqueous solution with 2N sulphuric acid, the product precipitated. Recrystallization from water yielded white 4-carbethoxy-5-tosylamino-1,2,3-triazole (100.5 g, 65%): mp 138°C (lit. mp 138°C); IR(KBr) 3260 (N-H), 1740 (C=O), 1600 (aromatic), 1550 (triazole), 1100 (-SO₂-); NMR(DMSO/D₆) 1.35 (t, J = 7.0 Hz, OCH₂CH₃), 2.40 (s, CH₃, tosyl), 4.30 (q, J = 7.0 Hz, OCH₂CH₃), 7.30 (d, 2 H, J = 7.5 Hz, phenyl), 7.85 (d, 2 H, J = 7.5 Hz, phenyl), 9.45 (br s, N-H); mass spectrum, m/e (310)- too small for exact mass measurement.

4-Amino-5-carbethoxy-1,2,3-triazole. A solution of 4-carbethoxy-5-tosylamino-1,2,3-triazole (10.0 g, 0.032 mol) in 100% sulphuric acid (300 mL) was stirred at -15°C for 1 h. Ice (1 kg) was added slowly so that the temperature did not go over 0°C. The solution was diluted with water (2 L) and extracted with ether (2 L). The organic layer was dried over magnesium sulphate and the solvent was removed under reduced pressure to yield white crystalline 4-amino-5-carbethoxy-1,2,3-triazole (4.07 g, 81%): mp 159-160°C(Sublm); IR(KBr) 3460, 3310, 3260 (N-H), 1705 (C=O),
1640 (NH₂), 1150 (C-N); NMR(DMSO/D₆) δ 1.35 (t, 3 H, CO₂CH₂CH₃), 4.30 (q, 2 H, CO₂CH₂CH₃), 6.15 (br s, 2 H, NH₂); mass spectrum m/e calcd for C₅H₈N₄O₂, 156.064720, obsd 156.065060.

4-Carbethoxy-5-diazo-1,2,3-triazole (103). A solution of 4-amino-5-carbethoxy-1,2,3-triazole (0.42 g, 2.7 mmol) in 2N hydrochloric acid (10 mL) was cooled to 0°C and sodium nitrite (0.20 g, 3.0 mmol) in water (1 mL) was added. The slightly yellow solution was then neutralized with sodium carbonate and extracted with dichloromethane (800 mL). The organic fractions were combined, dried (MgSO₄) and rotary evaporated to yield tan 4-carbethoxy-5-diazo-1,2,3-triazole (103, 0.32 g, 72%): mp 142-144°C (explosion); IR(CH₂Cl₂) 2195 (=.N=N), 1760, 1730 (C=O), 1600 (aromatic), 1100 cm⁻¹; NMR(CDCl₃) δ 1.42 (t, 3 H, J = 7.0 Hz, CO₂CH₂CH₃), 4.50 (q, 2 H, J = 7.0 Hz, CO₂CH₂CH₃); UV(methanol) λₘₐₓ 279 nm.

5-Amino-1-benzyl-4-cyano-1,2,3-triazole and 5-amino-1-benzyl-4-carbiminoethoxy-1,2,3-triazole. A mixture prepared from malononitrile (19.83 g, 0.30 mol), benzyl azide (39.9 g, 0.30 mol), absolute ethanol (500 mL) and sodium (6.9 g, 0.30 mol) was stored at room temperature for 20 h. The solution was poured into ice water (2 L) and stirred for approximately 3 h until the oil which separated had solidified.
The solid was removed, washed with cold water, and dried in vacuo. The dried material was extracted with petroleum ether (250 mL) and again dried to give a white solid mixture of 5-amino-1-benzyl-4-cyano-1,2,3-triazole and 5-amino-1-benzyl-4-carbiminoethoxy-1,2,3-triazole (28.75 g). This mixture was used without further purification for the next reductive step.

4-Amino-5-cyano-1,2,3-triazole. The mixture of 5-amino-1-benzyl-4-cyano-1,2,3-triazole and 5-amino-1-benzyl-4-carbiminoethoxy-1,2,3-triazole (28.75 g) obtained above was suspended in liquid ammonia (500 mL) and small pieces of sodium were added with stirring until a permanent blue color was produced. The color was discharged with a small amount of ammonium chloride and the solvent was allowed to evaporate overnight. The residue was dissolved in 2N hydrochloric acid (50 mL) and the solution was extracted repeatedly with ether (300 mL). Evaporation of the ether gave tan crystals of 4-amino-5-cyano-1,2,3-triazole (8.26 g, 47%): mp 227-228°C (lit. mp 226-228°C); IR (KBr) 3360, 3210, 3130 (N-H), 2240 (C=O), 1660 (-NH₂), 1620 cm⁻¹ (C=N); NMR(DMSO/D₆) δ 6.4 (br s, NH₂); mass spectrum m/e calcd for C₅H₆N₅, 109.062735, obsd 109.062473.

4-Cyano-5-diazo-1,2,3-triazole (104). To 4-amino-5-cyano-1,2,3-triazole (1.09 g, 10 mmol) in 2N hydrochloric acid
(10 mL) at 0°C was added sodium nitrite (0.76 g, 11 mmol) in a minimal amount of water. Dichloromethane (100 mL) was added to the light yellow mixture and the aqueous solution was neutralized with sodium carbonate. After the organic layer had been separated, the aqueous solution was extracted with dichloromethane (800 mL). The fractions were combined and desiccated over anhydrous magnesium sulphate. Dichloromethane was totally removed to yield tan crystalline 4-cyano-5-diazo-1,2,3-triazole (\(\text{H}2\text{O}\)) 129, 0.74 g, 62%: mp 125-126°C (explodes); IR(CH\(_2\)Cl\(_2\)) 2200 (\(\pi\text{N}=\text{N}\)), 1490, 1350, 1333, 1160, 1100; UV(methanol) \(\lambda_{\text{max}}\) 279 nm.

4-(2-Hydroxy-1-naphthylazo)-1,2,3-triazole (120). 4-Amino-1,2,3-triazole (0.42 g, 5 mmol) was diazotized in dil hydrochloric acid as previously described. The acidic solution was neutralized with sodium carbonate and kept in the dark at 0°C.

In the meantime, a solution of 2-naphthol (1.08 g, 7.5 mmol) and ethanol (50%, 20 mL) was made alkaline (pH 8) with 0.1 N sodium hydroxide. The mixture was stirred and protected from light while the solution containing 4-diazo-1,2,3-triazole was added in small portions in 15 min. Instantaneous precipitation of product was observed. Filtration, washing with water and drying in vacuo yielded 120 (1.05 g, 100%): orange crystals, mp (DMF/H\(_2\)O) 175-176°C; IR(KBr) 3370 (N-H), 1629 cm\(^{-1}\) (enol);
NMR(DMSO/D$_6$) $\delta$ 8.58 (d,d, H$_2$), 8.05 (s, H$_8$), 7.90 (d,d, H$_3$),
7.25-7.80 (m, H$_{4,5,6}$), 6.9 (d, H$_7$); mass spectrum calcd
for C$_{12}$H$_9$N$_5$O, 239.117982, 
obsd 239.118450.

4-(2-Hydroxy-1-naphthylazo)-5-phenyl-1,2,3-triazole (121).
4-Diazo-5-phenyl-1,2,3-triazole and 2-naphthol gave 121
by the previously described method in 92% yield: red
solid; mp(aqueous ethanol) 193-194°C; IR(KBr) 3340 (N-H),
1625 (enol); NMR(DMSO/D$_6$) $\delta$ 8.50 (dd, H$_2$), 7.82 (dd, H$_3$),
7.3-7.8 (m, H$_{4,5,6}$), 7.0-7.2 (m, phenyl), 6.81 (d, H$_7$);
Anal. Calcd for
C$_{18}$H$_{13}$N$_5$O: C, 68.60; H 4.16.
Found: C, 68.58; H 4.13.

4-Cyano-5-(2-hydroxy-1-naphthylazo)-1,2,3-triazole (122).
4-Cyano-5-diazo-1,2,3-triazole and 2-naphthol gave 122
by the previously described method in 89% yield: orange
solid; mp(CHCl$_3$) 250-251°C; IR(KBr) 3320-3420 (broad, N-H),
2215 (C=N), 1630 (enol), 1590 (C=C); NMR(DMSO/D$_6$) $\delta$ 8.65
(dd, H$_2$), 7.95 (dd, H$_3$), 7.3-7.8 (m, H$_{4,5,6}$), 6.9 (d, H$_7$);
mass spectrum, m/e 264, 246
(M-H$_2$O)$^+$, 237 (M-HCN)$^+$, 236 (M-N$_2$)$^+$
144 (2-naphthol)$^+$; exact mass calcd for $C_{13}H_8N_6O$, 264.139245, obsd 264.139837;

Anal. Calcd for $C_{13}H_8N_6O$: C, 59.10; H, 3.05; N, 31.81.

Found: C, 59.12; H, 3.46; N, 31.50.

4-(4-(Dimethylamino)phenylazo)-1,2,3-triazole (124). A solution of 4-diazo-1,2,3-triazole (101, 0.14 g, 1.5 mmol) in water (10 mL) was added to N,N-dimethylaniline (0.36 g, 3 mmol). The red suspension was cooled, filtered and washed with cold water, dilute acetic acid and then water to furnish orange phenylazotriazole 124 (0.32 g, 100%):

mp (CHCl$_3$) 161-162 °C; IR(KBr) 3140, 3120 (N-H), 3020 (aromatic C-H), 1605 (C=C), 820 (p-substituted benzene);

NMR(CDC$_3$) $\lambda$ 3.05 (s, 6 H, N-CH$_3$), 6.80 (d, 2 H, J = 7.0 Hz, phenyl), 7.70 (d, 2 H, J = 7.0 Hz, phenyl), 8.05 (s 1 H, triazole H); mass spectrum, 216 (m/e), 120 (N,N-dimethylaniline)$^+$; exact mass calcd for $C_{10}H_{12}N_6$, 216.112338, obsd 216.112873;

Anal. Calcd for $C_{10}H_{12}N_6$: C, 55.54; H, 5.59; N, 38.86.

Found: C, 55.54; H, 5.64; N, 38.80.

4-(1-morpholinylazo)-1,2,3-triazole (126). A solution of 4-diazo-1,2,3-triazole (101, 0.84 g, 5 mmol) in water (10 mL) was added to excess morpholine (10 mL). The aqueous solution was stirred for 2 h at room temperature and then extracted repeatedly with dichloromethane (100 mL). The organic layer
was washed with water (10 mL) and dried over sodium sulphate. Removal of solvent under reduced pressure yielded a yellow oil which crystallized on standing. Trituration with ether and recrystallization from chloroform/ether gave 126 as white crystals (0.77 g, 85%): mp 126-127°C; IR(KBr) 3200-3300 (N-H), 3130 (N-H), 1105, 1015 (ring breathing); NMR(CDCl₃) δ 3.85 (s, 8 H, morpholine H's), 7.68 (s, 1 H, triazole H), 9.85 (br, N-H); exact mass calcd for C₆H₁₀N₆O, 182.091603, obsd 182.092213;
Anal. Calcd for C₆H₁₀N₆O: C, 39.58; H, 5.54; N, 46.15.
  Found : C, 39.63; H, 5.41; N, 46.12.

4-Phenyl-5(pyrrolidinyazo)-1,2,3-triazole (128). An aqueous solution of 4-diazo-5-phenyl-1,2,3-triazole (102, 0.86 g, 5 mmol) prepared as previously described was added in 10 min to pyrrolidine (10 mL). The mixture was stirred for 1 h at room temperature and extracted repeatedly with dichloromethane (200 mL). The organic fractions were combined and washed twice with water (10 mL), dried over sodium sulphate and evaporated to dryness to afford 128 as tan crystals (0.46 g, 38%): mp(chloroform/ether) 242°C; IR(KBr) 3100, 2970, 1095, 990; NMR(CDCl₃) δ 1.98 (m, 4 H, H₁), 3.65 (m, 4 H, H₂), 7.25 (m, 3 H, phenyl), 8.05 (m, 2 H, phenyl),
Attempted Synthesis of 4-(Triphenylphosphoniumazo)-1,2,3-triazole (129). To 4-diazo-1,2,3-triazole (101, 0.48 g, 5 mmol) in ether (50 mL) was added triphenylphosphine (1.45 g, 5.5 mmol) in ether (5 mL). The pale orange precipitate which formed immediately was filtered but decomposed to a red oil upon drying. Separation of the oily residue by elution through a silica gel column with benzene yielded triphenylphosphine oxide (1.14 g, 82%): mp 170°C (lit. mp 170°C); and 1,2,3-triazole (0.24 g, 69%); bp 93°C/11 mmHg (lit. bp 208-210°C); NMR(CDCl₃) δ 7.9 (s, 1 H, CH), 15.9 (br s, 1 H, NH).

4-Chloro-1,2,3-triazole (123a). To a warm solution of copper (II) sulphate pentahydrate (5 g, 20 mmol) and sodium chloride (2.7 g, 22 mmol) in water (20 mL) was added aqueous sodium metabisulphite (2.5 g, 25 mL). Cooling the solution resulted in precipitation of white copper (I) chloride. The suspension was washed twice with dil sulphurous
acid and the supernatant liquid was decanted. Addition of conc. hydrochloric acid (15 mL) to the suspension gave a dark green solution which was cooled to 0°C.

4-Diazo-1,2,3-triazole (101, 0.95 g, 10 mmol) in water (10 mL) was added to the above solution. Gas evolution occurred instantaneously. The brown suspension was warmed on a steam bath for 30 min during which time the emulsion cleared. The aqueous layers were saturated with sodium chloride and extracted repeatedly with dichloromethane (200 mL). The organic layers were combined and dried over magnesium sulphate. Removal of the solvent at reduced pressure yielded 4-chloro-1,2,3-triazole (133a) as tan crystals (0.65 g, 63%): mp 71°C (lit. 92°C mp 71°C); IR(KBr) 3150 (N-H), 3100 (aromatic), 1105, 1000 cm⁻¹; NMR(CDC₁₃) δ 7.65 (s, 1 H, triazole), 12.2 (br, N-H); mass spectrum m/e calcd for C₂H₂N₃Cl, 102.993724, obsd 102.993418.

4-Bromo-1,2,3-triazole (133b). To a stirred warm solution of copper(II) sulphate pentahydrate (5 g, 20 mmol) and sodium bromide (2.25 g, 22 mmol) in water (18 mL) was added aqueous sodium metabisulphite. The solution was cooled and the supernatant liquid decanted. The white precipitate was washed twice with dil sulphurous acid and cooled in an ice bath. Hydrobromic acid (48%, 20 mL) was added and the solution turned black.

To the above solution was added 4-diazo-1,2,3-triazole
(101, 0.95 g, 10 mmol) in water (10 mL). Gas was evolved immediately. The suspension was warmed on a steam bath for 15 min during which time the emulsion cleared. The aqueous solution was saturated with salt and extracted repeatedly with dichloromethane (200 mL). The organic layers were combined and dried over anhydrous magnesium sulphate. Removal of solvent at reduced pressure yielded tan crystalline 4-bromo-1,2,3-triazole (133b, 0.56 g, 38%): mp 105-106°C (lit. 92 mp 108°C); IR(KBr) 3150, 1112, 985; NMR(CDCl₃) δ 7.60 (s, 1 H, triazole), 12.1 (br s, N-H); mass spectrum m/e calcd for C₂H₂N₃Br, 148.994383, obsd 148.994738.

4-Chloro-5-phenyl-1,2,3-triazole (124a). 4-Diazo-5-phenyl-1,2,3-triazole (102) was converted by copper(I) chloride to 4-chloro-5-phenyl-1,2,3-triazole by the previously described method in 52% yield: yellow solid; mp (ethyl acetate/hexane) 111-112°C; IR(KBr) 3450 (N-H), 1600 (C=C), 1100, 1050 (triazole ring breathing); NMR(CDCl₃) δ 7.50 (m, 3 H, phenyl), 8.05 (m, 2 H, phenyl); mass spectrum m/e calcd for C₆H₅N₃Cl, 178.992789, obsd 178.993214;
Found : C, 53.42; H, 3.06.

4-Bromo-5-phenyl-1,2,3-triazole (134b). 4-diazo-5-phenyl-1,2,3-triazole (101) was converted by copper(I) bromide to 4-bromo-5-phenyl-1,2,3-triazole (134b) by the previously described method in 48% yield: yellow solid; mp 158°C
(lit.\textsuperscript{75} mp 158.5-159.5 °C); IR(KBr) 3440 (N-H), 1602 (C=C), 1105, 1000 cm\textsuperscript{-1} (ring breathing); NMR(DMSO/D\textsubscript{6}) & 7.50 (m, 3 H, phenyl), 7.98 (m, 2 H, phenyl).

4-Chloro-5-cyano-1,2,3-triazole (135a). 4-cyano-5-diazo-1,2,3-triazole (104) was converted by copper(I) chloride to 4-chloro-5-cyano-1,2,3-triazole (135a) by the previously described method in 88% yield: tan solid; mp 152-153 °C; IR(KBr) 3230 (N-H), 2260 (C=N), 1615 (C=C), 1100, 980 cm\textsuperscript{-1} (triazole ring breathing); mass spectrum, m/e 131, 130, 129, 128 (Cl isotopes), 101 (M-HCN)+, 94 (M-Cl)+; exact mass calcd for C\textsubscript{3}HN\textsubscript{4}\textsuperscript{35}Cl, 127.988973, obsd 127.989472; Anal. Calcd for C\textsubscript{3}HN\textsubscript{4}Cl: C, 28.04; H, 0.78. Found: C, 28.71; H, 0.82.

4-Bromo-5-cyano-1,2,3-triazole (135b). 4-cyano-5-diazo-1,2,3-triazole (104) was converted by copper(I) bromide to 4-bromo-5-cyano-1,2,3-triazole (135b) by the previously described method in 56% yield: tan solid; mp 134-135 °C; IR(KBr) 3210 (N-H), 2256 (C\textequiv N), 1600 (C=C), 1080 (ring-breathing); mass spectrum, m/e 175, 174, 173, 172 (Br isotopes), 145 (M-HCN)+, 93 (M-HBr)+; exact mass calcd for C\textsubscript{3}HN\textsubscript{4}\textsuperscript{79}Br, 171.938510, obsd 171.939027.
4-Iodo-1,2,3-triazole (136). To a solution of potassium iodide (3.3 g, 20 mmol), water (50 mL) and sufficient hydriodic acid to lower the pH to 1 was added 4-diazo-1,2,3-triazole (101) in 2N hydrochloric acid (10 mL) in 30 min. Nitrogen was evolved. The mixture was stirred at room temperature for 2 h. The brown color due to iodine was discharged with sodium metabisulfite. The clear solution was saturated with salt and extracted with ether (100 mL) to yield white crystalline 4-iodo-1,2,3-triazole (136, 1.33 g, 68%): mp(ethyl acetate/hexane) 106-108 °C (lit.93 mp 110-111°C); IR(KBr) 3120 cm⁻¹ (N-H); NMR(CDC1₃) δ 7.8 (s, triazole H); mass spectrum. m/e calcd for C₂H₂N₃I, 194.929531, obsd 194.929956.

Anal. Calcd for C₂H₂N₃I: C, 12.31; H, 1.03; I, 65.10.

Found: C, 12.06; H, 1.12; I, 64.78.

6-Nitro-3-phenyl-[1,2,3]triazolo[5,1-c][1,2,4]triazine (149)
To a stirred solution of 4-diazo-5-phenyl-1,2,3-triazole (102, 0.62 g, 6.5 mmol) in dichloromethane (30 mL) was added (15 min) 1-morpholino-2-nitroethene (1.13 g, 7.2 mmol) in dichloromethane (20 mL). The resulting mixture was refluxed for 1 h. Solvent removal under reduced pressure afforded a mass of yellow solids which were washed several times with cold water and dried in vacuo. Several Re-crystallization from aqueous methanol afforded 149
(0.76 g, 48%): yellow solid; mp 247-248°C; IR(KBr)
3075, 1595, 1580, 1545, 1315, 780, 695 cm⁻¹; NMR
(DMSO/D₆) δ 7.5 (m, 3 H, phenyl), 8.25 (m, 2 H, phenyl),
9.60 (s, triazine H); mass spectrum, m/e calcd for
C₁₀H₆N₆O₂, 242.108457, obsd 242.112978;
Found : C, 49.23; H, 2.74.

3,7-Diphenyl-[1,2,3]triazolo[5,1-d][1,2,3,5]triazine-4-one (151).
4-Diazo-5-phenyl-1,2,3-triazole (102, 1.71 g, 10 mmol) in
dichloromethane (50 mL) was added dropwise (10 min) to a
cold solution of phenyl isocyanate (1.19 g, 10 mmol) in
dichloromethane (20 mL). The reaction mixture was stirred
for 3 h. Concentration and addition of ether precipitated
151 (1.1 g, 38%); brown crystals; mp(chloroform/ether)
141-142°C (lit. 141-142°C); IR(KBr) 3040 (aromatic C-H),
1775 (C=O), 1600, 1130, 1010, 760, 695 cm⁻¹; NMR(DMSO/D₆)
δ 7.0-7.3 (m, 5 H, phenyl), 7.3-7.6 (m, 3 H, phenyl),
7.8-8.0 (m, 2 H, phenyl); mass spectrum, m/e calcd for
C₁₅H₁₀N₆O₂, 290.074853, obsd 290.075463.

8-Cyano-3(4)-phenyl-[1,2,3]triazolo[5,1-c][1,2,4]-triazine (152). To 4-cyano-5-diazo-1,2,3-triazole (104, 0.37 g,
3.1 mmol) in dichloromethane (50 mL) was added phenyl-
acetylene (0.35 g, 0.35 mmol) in dichloromethane (20 mL).
The resulting mixture was refluxed 16 h at which time its infrared spectrum contained no diazo band. The solvent was totally removed under reduced pressure and the yellow brown solid was recrystallized several times from aqueous ethanol to give 152 (0.26 g, 38%): mp(aq ethanol) 159-160°C; IR(KBr) 3100, 3075, 3000, 2900, 2840, 2240, 1605, 1270, 1220, 772, 683 cm⁻¹; NMR(DMSO/D₆) δ 7.3-7.6 (m, 3 H, phenyl), 7.8-8.02 (m, 2 H, phenyl), 8.18 (s, 1 H, triazine); mass spectrum, m/e calcd for C₁₁H₆N₆, 222.098376, obsd 222.098914.

Attempted Cycloaddition of 4-Cyano-5-diazo-1,2,3-triazole and Dimethyl Acetylenedicarboxylate. A solution of 4-cyano-5-diazo-1,2,3-triazole (104, 0.37 g, 3.1 mmol) and dimethyl acetylenedicarboxylate (0.48 g, 3.4 mmol) in dichloromethane (50 mL) was refluxed for 24 h. The light yellow solution was concentrated to yield an oily residue. The product was eluted through a column of silica gel with dichloromethane to remove the unreacted DMAC. Further elution with dichloromethane/methanol (9:1) yielded a brown intractable solid which tlc revealed to be intractable material as evidenced by streaking.

7-Amino-6-carbethoxy-[1,2,3]triazolo[5,1-c][1,2,3]-triazine (155b). 4-Amino-1,2,3-triazole (0.84 g, 10 mmol) in dil hydrochloric acid (2N, 10 mL) was treated with sodium nitrite (0.75 g, 11 mmol) to give 4-diazo-1,2,3-triazole
(101, 0.64 g, 6.7 mmol, 67%). The aqueous solution was made alkaline (pH 8) by adding sodium carbonate. To the above solution was added a mixture of ethyl cyanoacetate (0.76 g, 6.7 mmol) and sodium acetate (2.0 g) in aqueous ethanol (50%, 20 mL). The suspension was stirred at room temperature for 2 h. The orange solid was filtered and washed with cold water to yield 155b (1.14 g, 82%): mp (aq ethanol) 174-175°C; IR (KBr) 3180 (N-H), 1740 (C=O), 1620 (NH₂), 1580 cm⁻¹ (C=C); NMR (DMSO/D₂, CDCl₃): δ 1.38 (t, 3 H, CO₂CH₂CH₃), 4.30 (q, 2 H, CO₂CH₂), 8.55 (s, 1 H, triazole H), 14.50 (br, NH₂); mass spectrum, m/e 208, 180 (M-N₂)⁺, 162 (M-CH₃CH₂OH)⁺, 134 (M-CO₂C₂H₅)⁺; exact mass calcd for C₇H₆N₆O₂ 208.070868, obsd 208.071371.


7-Amino-6-carboxamido-[1,2,3]triazolo[5,1-c][1,2,4]-triazine (155c). 4-Diazo-1,2,3-triazole (101, 0.64 g, 6.7 mmol) and cyanoacetamide (0.56 g, 6.7 mmol) gave a quantitative yield of 155c by the previously described method: brown solid; mp (aq ethanol) 285°C; IR (KBr) 3350, 3250 3180 (N-H), 1700 (C=O), 1630 (NH₂), 1095 cm⁻¹ (C-N); mass spectrum, m/e 179, 151 (M-N₂)⁺, 44 (CONH₂)⁺; exact mass calcd for C₅H₅N₇O, 179.055554, obsd 179.055991;

7-Amino-6-cyano-[1,2,3]triazolo[5,1-c][1,2,4]-triazine (155a). 4-Diazo-1,2,3-triazole (101, 0.64 g, 6.7 mmol) and malononitrile (0.44 g, 6.7 mmol) gave a quantitative yield of 155a by the previously described method: orange solid; mp(aq ethanol) 290 °C; IR(KBr) 3310, 3200, 3160 (N-H), 2220 (C≡N), 1635 cm⁻¹ (NH₂); NMR(DMSO/D₆, CDCl₃) δ 7.9 (s, ring H), 8.4 (br s, 2 H, NH); mass spectrum, exact mass calcd for C₁₅H₁₁N₁₀, 161.065893, obsd 161.066219.

4-[3-(2,4-Pentanedionylazo)]-1,2,3-triazole (159). 4-Amino-1,2,3-triazole (0.84 g, 10 mmol) in dil hydrochloric acid (2N, 10 mL) was treated with sodium nitrite (0.75 g, 11 mmol) to give 4-diazo-1,2,3-triazole (101, 0.64 g, 6.7 mmol). The aqueous solution was made alkaline (pH 8) by adding sodium carbonate. To the above solution was added a mixture of acetylacetone (1.1 g, 11 mmol) and sodium acetate (2.0 g) in aqueous ethanol (50%, 20 mL). The orange suspension was stirred at room temperature for 20 min. The orange solid was filtered and washed with cold water to yield 159 (1.95 g, 68%): mp(ethanol/chloroform) 147-148 °C; IR(KBr) 3160 (N-H), 1650, 1635, 1555 cm⁻¹ (enol); NMR(CDCl₃) δ 2.22 (s, 3 H, CH₃), 2.40 (s, 3 H, CH₃), 3.30 (br s, OH), 7.2 (s, 1 H, ring H), 12.0 (br s, N-H); mass spectrum, m/e calcd for C₁₅H₁₁N₁₀O₂, 195.075619, obsd 195.076131; Anal. Calcd for C₁₅H₁₁N₁₀O₂: C, 43.10; H, 4.65; N, 35.90. Found: C, 43.29; H, 4.74; N, 36.03.
Attempted Cyclization of 159. A mixture of 159 (0.1 g, 0.51 mmol) and sodium acetate (1 g) in aqueous ethanol (90%, 20 mL) was stirred at room temperature for 10 h. TLC showed only the starting material. The mixture was refluxed for 2 h. Removal of solvent and trituration with water afforded a yellow solid (0.13 g). Recrystallization with ethanol/chloroform gave the orange starting material 159 (0.085 g, 85%): mp 147°C, mixed mp with authentic sample 147°C.

Reaction of 4-Cyano-5-diazo-1,2,3-triazole (104) with Ethyl ether. To 4-cyano-5-diazo-1,2,3-triazole (104, 0.37 g, 3.1 mmol) was added anhydrous ethyl ether (50 mL) in one portion. Gas evolution was observed immediately. The solution was refluxed for 3 h, at which time, the IR diazo band disappeared. The reaction mixture was concentrated and eluted through a silica gel column with benzene/ethyl acetate (7:3). The first elutant was a white semi-solid (colorless liquid at room temperature), identified as N-ethyl-4-ethoxy-1,2,3-triazole (168, 93 mg, 18%); IR(CH₂Cl₂) 3105, 2990, 2940, 1575, 1340, 1120, 1050 cm⁻¹; NMR(CDC₃) δ 1.36 (t, J = 7.4 Hz, OCH₂CH₃), 1.40 (t, J = 7.2 Hz, NCH₂CH₃), 3.89 (sextet, J = 7.4 Hz, 4 H, N-CH₂ and O-CH₂); mass spectrum, m/e calcd for C₇H₁₀N₄O, 166.074598, obsd 166.074943.
Further elution yielded a tan solid identified as 4-cyano-5-ethoxy-1,2,3-triazole (167, 0.24 g, 57%):
mp(ethyl acetate/hexane) 89-90ºC; IR(KBr) 3140, 3080, 2980, 2860, 1595, 1320, 1250, 1120, 950, 805 cm⁻¹;
NMR(DMSO/D₆, CDCl₃) δ 1.38 (t, J = 7.5 Hz, O-CH₂CH₃), 3.92 (q, J = 7.5 Hz, O-CH₂), 11.6 (br s, NH); mass spectrum, m/e calcd for C₅H₆N₄O, 138.065472, obsd 138.065793;
Found : C, 43.19; H, 4.63.

Reaction of 4-Cyano-5-diazo-1,2,3-triazole (104) with Dimethoxyethane. To 4-cyano-5-diazo-1,2,3-triazole (104, 0.37 g, 3.1 mmol) was added dimethoxyethane (50 mL). Gas evolution was observed. The reaction mixture was stirred for 3 h at which time the diazo absorption disappeared. Concentration of the reaction product and elution of the oil residue on a silica gel column with dichloromethane led to four products. The first elutant yielded a colorless oil identified as 4-cyano-5-(1,2-dimethoxy)ethyl-1,2,3-triazole, a 2 C-H insertion product (174, 0.12 g, 22%): IR(CH₂Cl₂) 3130, 2980, 2850, 2250, 1725, 1450, 1265, 1110, 1030, 805 cm⁻¹;
NMR(CDC₃) δ 3.30 (s, 6 H, O-CH₃), 3.95 (d, J₁₂ = 5.7 Hz, 2 H, H₁), 5.65 (t, J₂₁ = 5.7 Hz, H₂), 8.05 (s, N-H); mass spectrum, m/e calcd for C₇H₁₀N₄O₂, 182.094457, obsd 182.094965.
The second elutant was identified as 4-cyano-5-(2-methoxyethoxy)methyl-1,2,3-triazole, a 1°C-H insertion product (173, 0.11 g, 19%): colorless oil; IR(CH\(_2\)\(_2\)Cl\(_2\)) 3130, 2930, 2831, 2240, 1730, 1450, 1100, 1040 cm\(^{-1}\); NMR(CDC\(_3\)) \(\delta\) 3.30 (s, 3 H, OCH\(_3\)), 3.48 (m, 2 H, H\(_1\)), 3.72 (m, 2 H, H\(_2\)), 5.70 (s, 2 H, H\(_1\)), 7.98 (s, NH); mass spectrum, m/e calcd for C\(_7\)H\(_{10}\)N\(_4\)O\(_2\), 182.0944457, obsd 182.0949752.

The third product eluted from the column was unidentified (0.13g, 23%); IR(CH\(_2\)\(_2\)Cl\(_2\)) 3130, 2960, 2250, 1725, 1440, 1265, 1110, 1030, 805 cm\(^{-1}\); NMR(CDC\(_3\)) \(\delta\) 3.40 (d, J = 2.0 Hz, 6 H, O-CH\(_3\)), 3.80 (m, 2 H), 5.82 (q, J = 4.2 Hz, 1 H), 8.38 (s, N-H); mass spectrum, m/e calcd for C\(_7\)H\(_{10}\)N\(_4\)O\(_2\), 182.0944457, obsd 182.094925.

The fourth fraction afforded the fragmentation product 4-cyano-5-methoxy-1,2,3-triazole (176, 73 mg, 19%); white solid; mp 107-109°C; IR(KBr) 3145, 3060, 2970, 2950, 2255, 1585, 1105, 960, 800 cm\(^{-1}\); NMR(CDC\(_3\)) \(\delta\) 4.05 (s, 3 H, OCH\(_3\)), 9.7 (s, N-H); mass spectrum, m/e calcd for C\(_4\)H\(_4\)N\(_4\)O, 124.059437, obsd 124.059748.

**Thermolysis of 4-Diazo-5-phenyl-1,2,3-triazole (102) in Isopropyl alcohol.** A solution of 102 (0.62 g, 6.5 mmol)
in isopropyl alcohol (100 mL) was refluxed (82°C) for 6 h. The reaction mixture was fractionally distilled to give a colorless liquid which formed a hydrazone when treated with 2,4-dinitrophenylhydrazine solution. The precipitate was filtered and washed with cold water to give acetone 2,4-dinitrophenylhydrazone (0.74 g, 3.1 mmol, 48%): mp 128°C (mixed mp with authentic sample 128°C).

The isopropyl alcohol was totally removed under reduced pressure to afford a brown solid. Purification of the product by elution through a silica gel column with benzene/ethyl acetate (8:2) yielded 4-phenyl-1,2,3-triazole (181, 0.58 g, 62%); mp 147-148°C. The spectral data of 181 are identical with that of an authentic sample.

**Thermolysis of 4-Diazo-5-phenyl-1,2,3-triazole (102) in Cyclooctane.** 4-Diazo-5-phenyl-1,2,3-triazole (102, 0.62 g, 6.5 mmol) was heated in cyclooctane (100 mL) at 150°C for 2 h. Upon vacuum distillation of the solvent, a brown oily residue was obtained. Elution of the product mixture through a silica gel column with benzene/ethyl acetate (9:1) yielded 4-cyclooctyl-5-phenyl-1,2,3-triazole (188, 0.78 g, 47%) as a yellow oil. Insertion product 188 is not distillable and attempts to effect its crystallization failed. The properties of 188 are: IR(neat) 3320 (N-H), 3060 (aromatic), 2930 (CH₂), 1595 (C=C), 750, 690 cm⁻¹ (mono-substituted benzene); NMR(CDCl₃) δ 1.70 (m, 10 H, CH₂), 2.25 (m, 4 H,
CH₂CTCH₂, 5.15 (sextet, 1 H, t-CH), 7.53 (m, 3 H, phenyl), 8.42 (m, 2 H, phenyl); mass spectrum, m/e calcd for $C_{16}H_{21}N_3$, 255.135142, obsd 255.135605;
Anal. Calcd for $C_{16}H_{21}N_3$: C, 75.26; H, 8.29; N, 16.46.
    Found : C, 74.65; H, 8.36; N, 16.12.

Thermolysis of 4-Diazo-5-phenyl-1,2,3-triazole (102) in Cyclohexane. 4-Diazo-5-phenyl-1,2,3-triazole (102, 0.62 g, 6.5 mmol) was refluxed (80°C) in cyclohexane (100 mL) for 60 h. Removal of solvent under reduced pressure gave a brown semi-solid residue. The product was purified by elution through a silica gel column with benzene/hexane (1:1) to yield a yellow oil which crystallized on standing to afford 4-cyclohexyl-5-phenyl-1,2,3-triazole (190, 0.62 g, 42%) as a white solid: mp(pet ether) 126-127°C; IR(KBr) 3320 (N-H), 3060 (aromatic), 2930, 2860, 1660 cm⁻¹ (C=C); NMR(CDCl₃) $\delta$ 1.50-2.50 (m, 10 H, cyclohexane CH), 4.78 (heptate, 1 H, $J = 4$ Hz, t-CH), 7.48 (m, 3 H, phenyl), 8.30 (m, 2 H, phenyl); mass spectrum, m/e calcd for $C_{14}H_{17}N_3$, 227.098436, obsd 227.098917;
Anal. Calcd for $C_{14}H_{17}N_3$: C, 73.98; H, 7.54.
    Found : C, 74.51; H, 7.79.

Thermolysis of 4-Carbethoxy-5-diazo-1,2,3-triazole (103) in Cyclooctane. 4-Diazo-5-carbethoxy-1,2,3-triazole (103, 0.60 g, 3.6 mmol) was heated in cyclooctane (100 mL) at 150°C
for 5 h. Vacuum distillation of the solvent yielded a clear residual oil. Elution of the product through a silica gel column with benzene/ethyl acetate (9:1) yielded 4-carbethoxy-5-cyclooctyl-1,2,3-triazole (195, 0.61 g, 68%): white solid; mp 156-157°C; IR(KBr) 3315 (N-H), 3060, 2930, 1735 (C=O), 1110 cm⁻¹; NMR(DMSO/D₆,CHCl₃) δ 1.30 (m, 13-14 H's, cyclooctyl H's), 1.45 (t, 3 H, J = 7.1 Hz, CO₂CH₂CH₃), 4.10 (dp, 1 H, J = 7.9 Hz, t-CH), 4.40 (q, 2 H, J = 7.1 Hz, CO₂CH₂), 7.5 (br d, NH); mass spectrum, m/e calcd for C₁₃H₂₁N₃O₂, 251.109436, obsd 251.109943.

Thermolysis of 4-Diazo-1,2,3-triazole (101) in Benzene.

4-Diazo-1,2,3-triazole (101, 0.62 g, 6.5 mmol) was suspended in benzene (150 mL) which had been dried, freshly distilled and degassed with nitrogen. The suspension was refluxed at 80°C for 60 h. The light brown solid suspension in the reaction mixture was filtered and recrystallized from aqueous methanol to yield white 4-phenyl-1,2,3-triazole (198, 0.24 g). Concentration of the benzene solution and elution through a silica gel column with hexane/benzene (7:3) yielded isomeric cyanocycloheptatrienes 201 (0.083 g, 11%) as a yellow liquid. Vacuum distillation of the product (40-43°C/0.28 mm Hg), bulb to bulb) afforded 201 as a colorless sweet smelling liquid: IR(neat) 3030, 2960, 2920, 2850, 2250, 2220, 1600, 1530, 1440, 1390, 740, 710, 690 cm⁻¹;
NMR(CDC13) δ 2.25 (t, J7,6 = 6.0 Hz, H7), 5.2–5.8 (m, H1,6), 6.1–6.4 (m, H2,5), 7.0–7.1 (m, H3,4); mass spectrum, m/e 117, 90 (M-HCN)+; exact mass calcd for C8H7N, 117.057846, obsd 117.058220;

Anal. Calcd for C8H7N: C, 82.02; H, 6.02; N, 11.95. Found: C, 81.91; H, 6.11; N, 11.82.

Further elution with benzene/ethyl acetate (8:2) yielded a white solid identical to the filtered solid obtained earlier. The two portions were combined to give 4-phenyl-1,2,3-triazole (198, total yield 0.55 g, 58%): mp (aq methanol) 147–148°C (lit.71 mp 147–148°C); IR(KBr) 3160, 3120 (N-H), 3075, 3015, 2970, 1470, 1460, 1085, 1010, 975, 770, 700 cm⁻¹; NMR(DMSO/D6, CDC13) δ 7.32 (m, 3 H, phenyl), 7.80 (m, 2 H, phenyl), 7.90 (s, 1 H, triazole H), 14.7 (br s, N-H); mass spectrum m/e calcd for C8H7N3, 145.063994, obsd 145.064351.

Photolysis of 4-Diazo-1,2,3-triazole (101) in Benzene.
4-Diazo-1,2,3-triazole (101, 0.62 g, 6.5 mmol) was suspended in benzene (125 mL). The suspension was photolyzed with a 450 watt medium pressure mercury lamp for 3 h. Approximately two stoichiometric equivalents of nitrogen were collected in a gas trap (275 mL, 12.2 mmol, assuming ideal gas law). The light brown solid suspension was filtered and recrystallized
from aqueous methanol to yield white 4-phenyl-1,2,3-triazole (198, 0.19 g). Concentration of the benzene solution and elution through a silica gel column with benzene yielded isomeric cyanocycloheptatrienes (0.41 g, 54%) as a yellow liquid. Vacuum distillation of the product (40-43 °C/0.28 mm Hg, bulb to bulb) afforded a colorless sweet smelling liquid. The spectral properties and analyses are similar to that obtained in the thermolysis reaction.

Further elution with benzene/ethyl acetate (8:2) yielded a white solid identical to the filtered solid obtained earlier. The two portions were combined to give 4-phenyl-1,2,3-triazole (198, total yield 0.25 g, 26%). Spectral properties of 198 is similar to that obtained in the thermolysis reaction and agree satisfactorily with literature values.

**Trimethylsilyl Azide.** Trimethylsilyl chloride (27.2 g, 0.32 mol) was added in portion to a suspension of sodium azide (20.3 g, 0.32 mol) in diglyme (125 mL). The resulting suspension was stirred at 70 °C for 60 h under nitrogen. The volatile material was transferred in vacuum to a round-bottom flask. Distillation of the crude product at 95-99 °C yielded trimethyl azide (21.9 g, 76%).
4-Phenyl-1,2,3-triazole (198)\textsuperscript{77} A solution of phenylacetylene (7.65 g, 75 mmol) and trimethylsilyl azide (8.63 g, 75 mmol) in toluene (150 mL) was refluxed 72 h. A few drops of water were added to hydrolyze the aminotrimethylsilyl group of the adduct. The solution was then refluxed for 18 h. Cooling the mixture led to crystallization of 4-phenyl-1,2,3-triazole (198, 8.48 g, 78%): white platelets; mp(aq methanol) 147-148\textdegree C (lit.\textsuperscript{77} mp 147-148\textdegree C); IR(KBr) 3160, 3120, 3075, 3015, 2970, 2880, 1470, 1460, 1085, 1010, 975, 770, 700 cm\textsuperscript{-1}; NMR(CDC\textsubscript{13}) \delta 7.32 (m, 3 H, phenyl), 7.88 (m, 2 H, phenyl), 7.90 (s, 1 H, triazole H), 14.7 (br, N-H).

Photolysis of 4-Phenyl-1,2,3-triazole (198) in Benzene. A mixture of 198 (0.10 g, 0.69 mmol) suspended in re-distilled benzene (125 mL) was irradiated 3 h. Removal of solvent under reduced pressure resulted in recovery of 198 (0.10 g, 100%): mp 147-148\textdegree C. Photolysis was continued for 16 h. After removal of the benzene, a slight brown solid was obtained which on recrystallization from aqueous methanol yielded pure white platelets of 198 (0.92 g, 92%).

Photolysis of α-Diazoacetonitrile (203) in Benzene. To a solution of aminoacetonitrile bisulfate (0.77 g, 5 mmol) in 2N hydrochloric acid (10 mL) at 0\textdegree C was added sodium
nitrite (0.38 g, 5.5 mmol) in a minimum amount of water. The mixture was stirred vigorously for 15 min. Ethyl ether (100 mL) was added and the aqueous solution was neutralized with sodium carbonate. The α-diazoacetonitrile (203) was then extracted repeatedly with ether (200 mL). The organic solution was dried over anhydrous sodium sulphate and concentrated. (Caution! it is important that the diazo nitrile be prepared only in dilute solution; 203 is highly explosive when concentrated). Benzene (125 mL) was added and ether was totally removed. The resulting benzene solution was irradiated for 6 h. Concentration and elution of the yellow oil through a silica gel column afforded pure cyanocycloheptatrienes 201 (0.26 g, 45%, based on aminoacetonitrile). The spectral data for 201 are identical with that of an authentic sample.

Photolysis of 4-Diazo-1,2,3-triazole (101) in toluene. A suspension of 4-Diazo-1,2,3-triazole (101, 0.62 g, 6.5 mmol) in toluene (125 mL) was irradiated 3 h. The reaction mixture was concentrated and eluted through a silica gel column with hexane/benzene (1:1). Vacuum distillation of the light yellow oil (60–67°C/ 0.5 mm Hg, bulb to bulb) afforded isomeric methylcyanocycloheptatrienes – norcaradienes 222–223a as a colorless liquid (0.57 g, 67%); IR(neat) 3080, 3030, 2960, 2910, 2240(w), 2218(s), 1625, 1440,
1380, 1030, 760, 735, 720, 705, 670 cm$^{-1}$; the NMR spectrum of the mixture is very complicated due to reasons described in the Discussion of Results; NMR(CDC$_3$) δ 1.8-2.5 (m, CH$_3$ and H$_7$), 3.65 (m, H$_{1,6}$, norcaradiene), 5.30 (m, H$_{1,6}$, cycloheptatriene), 6.15 (m, H$_{2,5}$, cycloheptatriene), 6.55 (m, H$_{2,3,4,5}$, norcaradiene), 7.15 (m, H$_{3,4}$, cycloheptatriene); mass spectrum, m/e 131, 116 (M-CH$_3$)$^+$, 104 (M-HCN)$^+$, 89 (M-CH$_3$-HCN)$^+$; exact mass calcd for C$_9$H$_9$N, 131.073495, obsd 131.073094.

**Anal.** Calcd for C$_9$H$_9$N: C, 82.48; H, 6.92; N, 10.68.

Found : C, 82.72; H, 6.84; N, 10.28.

**Photolysis of 4-Diazo-1,2,3-triazole (101) in p-xylene.**

A suspension of 101 (0.62 g, 6.5 mmol) in p-xylene was irradiated for 3 h. The reaction mixture was concentrated and eluted through a silica gel column with hexane/benzene (1:1). The first eluant was identified as p-xylene. The second fraction was a yellow liquid which vacuum distilled (70-73 °C at 0.5 mm Hg, bulb to bulb) to afford dimethylcyano-cycloheptatrienes -norcaradienes 222-223b (0.32 g, 34%): colorless liquid, IR(neat) 3030, 2960, 2910, 2250, 2205, 1640, 1440, 1380, 1260, 910, 810, 730, 645 cm$^{-1}$; NMR(CDC$_3$) δ 1.40 (m, 3 H, CH$_3$), 1.72 (m, 3 H, CH$_3$), 2.15 (m, H$_7$).
cycloheptatriene), 3.40 (m, H$_{1,6}$, norcaradiene), 5.22
(m, H$_{1,6}$, cycloheptatriene),
5.5-6.2 (m, H$_{2,5}$, norcaradiene),
6.85-7.05 (m, H$_{3,4}$, cycloheptatriene);
mass spectrum, m/e 145, 130
(M-CH$_3$)$^+$, 118 (M-HCN)$^+$, 103
(M-CH$_3$-HCN)$^+$; exact mass calcd
for C$_{10}$H$_{11}$N, 145.089144, obsd 145.089632.

Further elution with ethyl acetate failed to afford
any tractable product.

Photolysis of 4-Diazo-1,2,3-triazole (101) in Trifluoro-
methylbenzene. A solution of 101 (0.62 g, 6.5 mmol) in
trifluoromethylbenzene (125 mL) was irradiated 3 h. The
reaction mixture was concentrated and chromatographed
on a silica gel column using benzene. The first product
eluted was a yellow oil. Distillation under vacuum
(90-97°C at 0.5 mm Hg) afforded trifluoromethylcyano-
cycloheptatrienes -norcaradienes 222-223c (0.78 g, 65%) :
colorless liquid; IR(neat) 3060, 3020, 2960, 2930, 2880,
2220, 1650, 1270-1360, 1140-1180, 760 cm$^{-1}$; NMR(CDC$_3$) $^*$$^*$ $^*$$^*$
(m, H$_7$), 2.55 (m, H$_7$), 3.85
(m, H$_{1,6}$, norcaradiene), 5.85
(m, H$_{1,6}$, cycloheptatriene),
6.30 (m, H$_{2,3,4,5}$, norcaradiene,
H$_{2,5}$, cycloheptatriene), 6.90
(m, H₃,4, cycloheptatriene); mass spectrum, m/e 185, 166 (M-F)+, 165 (M-HF)+, 116 (M-CF₃)+; exact mass calcd for C₉H₆NF₃, 185.045228, obsd 185.045800;

Anal. Calcd for C₉H₆NF₃: C, 58.38; H, 3.27; N, 7.57.
Found: C, 58.25; H, 3.48; N, 7.48.

Photolysis of 4-Diazo-1,2,3-triazole (101) in Bromobenzene.
A solution of 101 (0.62 g, 6.5 mmol) in bromobenzene (125 mL) was irradiated for 3 h. The reaction products were concentrated and eluted through a silica gel column with benzene. The initial elutant was identified as bromobenzene. The second product collected off the column was white crystalline and believed to be a bis-adduct of cyanocarbene and bromobenzene (7.8 mg, < 1%); mp 185-190°C; mass spectrum, m/e 234, 236, 238 (br isotopes), 155, 157 (M-Br)+; IR(KBr) 2235 cm⁻¹ (C≡N).

The third product, a yellow oil, was vacuum distilled (80-90°C at 0.3 mm Hg) to give bromocyanocycloheptatrienes norcaradienes 222-223e (0.68 g, 54%); IR(neat) 3060, 2930, 2240(w), 2220(vs), 1610, 1570, 1435, 1030, 895, 832, 760(vs), 730 cm⁻¹; NMR(CDCl₃)  2.4-3.3 (m, H₇), 3.80 (m, H₁,6, norcaradiene), 5.4-6.0 (m, H₂,3,4,5, norcaradiene, H₂,5, cycloheptatriene), 7.0-7.6 (m, H₃,4, cycloheptatriene); mass spectrum, m/e 197, 196,

Photolysis of 4-Diazo-1,2,3-triazole(101) in Fluorobenzene.

A solution of 101 (0.62 g, 6.5 mmol) in fluorobenzene (125 mL) was irradiated for 3 h. The reaction mixture was concentrated and eluted through a silica gel column with hexane/benzene (2:8) to yield a yellow oil. Vacuum distillation (90-95°C at 0.38 mm Hg, bulb to bulb) yielded fluorocyanocycloheptatrienes-norcaradienes 222-223d as a colorless, sweet-smelling liquid (0.3 g, 35%); 222-223d will turn black if kept in a glass container for a period of time; IR(neat) 3090, 3070, 3040, 2960, 2250, 2220, 1650, 1630, 1560, 1150, 1035, 850, 770, 630 cm⁻¹; NMR (CDCl₃) δ 2.45-3.20 (m, H₇); 3.82 (d, J = 6.2 Hz, H₁,6, norcaradiene), 4.65 (t, J = 6.2 Hz, H₁,6, cycloheptatriene). These two signals apparently indicate a rapidly equilibrating mixture of norcaradiene and cycloheptatriene at room temperature. 5.1-5.8 (m, H₁,6, cycloheptatriene), 6.0-6.7 (m, H₂,3,4,5, norcaradiene and H₂,5, cycloheptatriene),
7.0 (m, H₃,₄, cycloheptatriene); mass spectrum, m/e 135, 115 (M-F), 108 (M-HCN); exact mass calcd for C₈H₆NF, 135.048424, obsd 135.048833.

Photolysis of 4-Diazo-1,2,3-triazole (101) in Nitrobenzene

4-Amino-1,2,3-triazole (0.84 g, 10 mmol) was diazotized by the previously described method in 65% to yield 4-diazo-1,2,3-triazole 101 (0.62 g, 6.5 mmol).

A solution of 101 (0.62 g, 6.5 mmol) in nitrobenzene (125 mL) was irradiated for 3 h. the yellow reaction mixture was fractionally distilled to give a green liquid which on analysis by gas chromatography (10% OV-1 on Chromosorb W, 12' X 1/8", 120 °C, authentic nitrosobenzene and toluene as internal standard) was found to be nitrosobenzene (0.13 g, 18%). After complete removal of solvent, the residue was chromatographed on silica gel column using benzene/ethyl acetate (7:3). The first elutant was a yellow oil, identified as isomeric cyanonitrocycloheptatriene 233 (84 mg, 8%): IR(neat) 3070, 2930, 2870, 2222, 1600, 1530, 1450, 1350, 1340, 825 cm⁻¹; mass spectrum, m/e calcd for C₈H₆N₂O₂, 162.074562, obsd 162.074937.

Further elution with benzene/ethyl acetate (1:1) afforded 4-(3-nitrophenyl)-1,2,3-triazole as a tan solid
Photolysis of 4-Diazo-5-phenyl-1,2,3-triazole (102) in Benzene. 4-Amino-5-phenyl-1,2,3-triazole (106, 1.6 g, 10 mmol) was diazotized as previously described to give 4-diazo-5-phenyl-1,2,3-triazole (102, 1.2 g, 6.8 mmol, 68%). A suspension of 102 (1.2 g, 6.8 mmol) in benzene (125 mL) was irradiated for 3 h. A total of 260 mL of nitrogen was evolved from the bright orange solution. Benzene was removed under reduced pressure and the product mixture was eluted through a silica gel column with hexane/benzene (1:1). The first product obtained was benzoyl cyanide azine, a yellow solid (248, 0.08 g, 5%): mp(ethanol) 204-205°C (lit. mp 205-206°C); IR(KBr) 2220, 1590, 1555, 1445, 1280, 1020, 770, 680 cm⁻¹; NMR(CDC13) δ 8.1 (m, phenyl), 7.5 (m, phenyl); mass spectrum, m/e 258, 231 (M-HCN)⁺, 115 (C₆H₅CCN)⁺; exact mass calcd for C₁₆H₁₀N₄, 258.090541, obsd 258.091196.

The second fraction collected, a yellow solid, was recrystallized from ether/benzene to afford pure 7-cyano-7-phenylnorcaradiene (0.49 g, 38%): a colorless crystalline product; mp 137-138°C (lit. mp 137.5-138.5°C); IR(KBr)
3050, 3020, 2920, 2240, 1600, 1480, 1450, 1425, 1395, 740, 700, 690 cm⁻¹; NMR(CDCl₃) δ 3.49 (4 lines, H₁, J₁₂ = 4.5 Hz), 6.18 (8 lines, H₂, J₂₁ = 4.5 Hz, J₂₃ = 6.7 Hz), 6.45 (4 lines, H₃, J₃₂ = 6.7 Hz), 7.25 (m, 5 H, phenyl); mass spectrum, m/e 193, 166 (M-HCN)⁺, 115 (C₆H₅CCN)⁺; exact mass calcd for C₁₄H₁₁N, 193.089144, obsd 193.089668; Anal. Calcd for C₁₄H₁₁N: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.75; H, 6.01; N, 7.28.

The third fraction collected was identified as trans-9,10-dicyano-9,10-dihydrophenanthrene (249, 99 mg, 8%); mp(benzene) 202-204°C (lit. mp 199-204°C); IR(KBr) 3080, 3022, 2948, 2886, 2240, 1440, 1010 cm⁻¹; NMR(DMSO/D₆) δ 5.30 (s, 2 H, -CHCN), 7.70-6.82 (m, 8 H, phenanthrene); mass spectrum, m/e calcd for C₁₆H₁₀N₂, 230.089451, obsd 230.089943.

The fourth product eluted was 9,10-dicyanophenanthrene (250, 0.21 g, 11%): mp(benzene) 289-291°C (lit. mp 296-298°C); IR(KBr) 2220, 1600, 1560, 1500, 1480, 1450 cm⁻¹; NMR(CDCl₃) δ 7.89-8.26 (m, phenanthrene H); mass spectrum, m/e 228, 201 (M-HCN)⁺; exact mass calcd for C₁₆H₈N₂, 228.087632, obsd 228.087985.

The fifth product was a bis-adduct of phenylcyanocarbene and benzene 251 (0.13 g, 6%): mp(ethyl acetate/hexane)
278-280°C; IR(KBr) 3040, 2215, 1590, 1445, 1010, 760, 680 cm⁻¹; NMR(CDC₁₃, 300 mHz) δ 7.65 (m, 4 H), 7.40 (m, 8 H), 7.09 (m, 2 H), 6.85 (m, 2 H); mass spectrum calcd for C₂₂H₁₆N₂, m/e 308, 281 (M-HCN)+, 231 (M-C₆H₅)+, 196 (M-C₆H₅CCN)+.

Further elution with benzene/ethyl acetate (8:2) yielded 4,5-diphenyl-1,2,3-triazole (246, 0.19 g, 13%): white solid; mp (benzene) 135-137°C (lit. mp 138°C); the spectral data are identical with that reported for 246.

Photolysis of 4-Diazo-5-phenyl-1,2,3-triazole (102) in Toluene. A suspension of 102 (1.16 g, 6.8 mmol) in toluene (125 mL) was irradiated for 3 h. The nitrogen evolved totalled 145 mL. Toluene was removed by vacuum distillation and the yellow oil residue was chromatographed on a silica gel column with benzene/ethyl acetate (9:1). The first product isolated was a bis-adduct of phenylcyanocarbene and toluene 263 (0.78 g, 33%): yellow solid; mp 204-205°C; IR(KBr) 3060, 2210, 1494, 1450, 750, 680 cm⁻¹; NMR(DMSO/D₆) δ 2.25, 2.52 (s, 3 H, CH₃), 6.91 (m, 1 H), 7.08 (m, 1 H), 7.40 (m, 8 H), 7.60 (m, 5 H); mass spectrum, m/e 322, 307 (M-CH₃)+, 295 (M-HCN)+, 280 (M-CH₃-HCN)+, 245 (M-C₆H₅)+, 206 (M-C₆H₅CCN)+.

The second fraction eluted from the column was a viscous yellow oil which vacuum distilled (140-145°C at 0.35 mm Hg) to give isomeric methyl-7-cyano-7-phenylnorcar-
dienes 262a-c (0.24 g, 17%). Preparative GLC of this mixture at 180°C (25% SE-30 on chromosorb W-AW-DCMS 0.25" x 12") separated it into three components in the ratio of 55:45:5 = 262 a:b:c; the spectral data for the mixture of 3 compounds are: IR(neat) 3060, 1585, 1500, 1460, 1208, 830, 750(vs), 700, 690 cm⁻¹; NMR(CDC13) δ

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1.98 (s, CH3, ca. 45%, I),
2.03 (s, CH3, ca. 55%, II),
2.32 (s, CH3, ca. 5%, III),
3.07 (m, g), 6.10 (m, vinyl H), 7.30 (m, 5 H, phenyl);
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mass spectrum, m/e calcd for C₁₅H₁₃N, 207.104794, obsd 207.105262;

Found : C, 86.91; H, 6.62.

The third product eluted from the column was identified as 4-phenyl-5-(4-methylphenyl)-1,2,3-triazole (261, 0.13 g, 8%): white solid; mp(ethyl acetate/hexane) 192-193°C; IR(KBr) 3160, 3110, 3075, 3020, 2970, 2880, 1470, 1350, 1082, 1000, 985, 760, 692 cm⁻¹; NMR(DMSO/D₆) δ 2.48

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(s, CH₃), 7.18 (d, J = 9.2 Hz, H₁), 7.32 (m, 3 H, phenyl), 7.65 (d, J = 9.2 Hz, H₂), 7.88 (m, 2 H, phenyl); mass spectrum, m/e 235, 220 (M-CH₃)⁺, 160
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(M-C\(_6\)H\(_5\))^+ , 145 (M-CH\(_3\)C\(_6\)H\(_5\))^+; exact mass calcd for C\(_{15}\)H\(_{13}\)N\(_3\),
235.087465, obsd 235.087937.

Thermolysis of 4-Diazo-5-phenyl-1,2,3-triazole (102) in
Toluene. A suspension of 102 (0.62 g, 6.8 mmol) in toluene
(100 mL) was heated at 95-100 °C for 60 h. The slightly
brown oily residue was decolorized with activated charcoal
and chromatographed on a silica gel column with benzene.

The first product eluted was a yellow oil which
vacuum distilled (140-145 °C at 0.35 mm Hg, bulb to bulb)
to yield isomeric methyl-7-phenyl-7-cyanonorcaradienes
262a,b,c (0.76 g, 54%). GLC analysis of this mixture at
180 °C (25%, SE-30 on chromosorb W-AW-DCMS 0.25" X 12')
separated it into three components in the ratio of
50:50:0.5; The spectral data of the mixture are as follows:
IR(neat) 3060, 3030, 2960, 2930, 2860, 2235, 1730, 1600,
1580, 1500, 1460, 1200, 835, 750, 700 and 690 cm\(^{-1}\);
NMR(CDC\(_3\)) \& 1.98 (s, CH\(_3\), 50%, I), 2.03 (s, CH\(_3\), 50%, II),
3.07 (m, H\(_1,6\), 2 H), 6.10
(m, H\(_2,3,4,5\), 3 H), 7.30
(m, 5 H, phenyl); mass
spectrum , m/e calcd for
C\(_{15}\)H\(_{13}\)N, 207.104794,
obsd 207.105132.
The second elutant was 4-phenyl-5-(4-methylphenyl)-1,2,3-triazole (261, 0.38 g, 24%): mp 187-190°C. Spectral data indicate that 261 is identical with that obtained from photolysis of 102 in toluene. The product might be contaminated with a trace amount of the o-substituted isomer.

Photolysis of 4-Carbethoxy-5-diazo-1,2,3-triazole (103) in Benzene. 4-Amino-5-carbethoxy-1,2,3-triazole (108, 0.42 g, 2.7 mmol) was diazotized as previously described to give 4-carbethoxy-5-diazo-1,2,3-triazole (103, 0.32 g, 72%).

A suspension of 103 (0.32 g, 1.9 mmol) in benzene (125 mL) was irradiated 3 h. Upon removal of the benzene under vacuum, TLC showed that the yellow residue contained only one product. Elution of the residue through a silica gel column with benzene afforded first a yellow liquid identified as ethyl phenylcyanoacetate (270, 0.21 g, 58%); IR(neat) 3090, 3080, 2960, 2930, 2870, 1730, 1250, 1030, 740, 690 cm⁻¹; NMR(CDCl₃) δ 1.20 (t, J = 7.5 Hz, CH₂CH₃), 4.20 (q, J = 7.5 Hz, CH₂), 4.70 (s, t-CH), 7.35 (s, 5 H, phenyl); mass spectrum, m/e 189, 117 (M-COOC₂H₅)+, exact mass calcd for C₁₁H₁₁NO₂, 189.078973, obsd 189.078549.

The second product off the column was a yellow solid. Recrystallization from acetonitrile afforded 7-carbethoxy-7-cyanonorcaradienes (269a-b, 84.5 mg, 23%): colorless crystals; mp(acetonitrile) 175-176°C; IR(KBr) 3050, 3020,
2980, 2960, 2920, 2840, 2240, 1725, 1250, 1110, 1000, 740 cm⁻¹;  

$$\text{NMR(CDC}_3\text{)}; \delta 1.36 \ (t, 3 \text{ H}, J = 7.14 \text{ Hz},$$
$$\text{CO}_2\text{CH}_2\text{CH}_3; 3.24 \ (4 \text{ lines}, \text{ H}_1,\text{ H}_6;$$
$$J_{12} = 3.0 \text{ Hz}), 4.31 \ (q, J = 7.1 \text{ Hz},$$
$$\text{COOCCH}_3; 6.22 \ (8 \text{ lines}, \text{ H}_2,\text{ H}_5;$$
$$J_{21} = 3.0 \text{ Hz}), 6.43 \ (4 \text{ lines},$$
$$\text{H}_3,\text{ H}_4; J_{32} = 2.8 \text{ Hz});$$

UV(cyclohexane) λ max 271 nm; mass spectrum, m/e 189,
161 (M–HCN)+, 143 (M–C₂H₅OH)+, 116 (M–CO₂C₂H₅)+, 90 (C₇H₈)+,
78 (M–NCCO₂C₂H₅)+; exact mass calcd for C₁₁H₁₁NO₂,
189.078973, obsd 189.079563.

**Anal.** Calcd for C₁₁H₁₁NO₂: C, 69.83; H, 5.86; N, 7.40.

**Found:** C, 69.67; H, 6.22; N, 7.08.

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**Photolysis of 4-Cyano-5-diazo-1,2,3-triazole (103) in Benzene.**

4-Amino-5-cyano-1,2,3-triazole (107, 0.55 g, 5 mmol) was diazotized by the previously described method to give 4-cyano-5-diazo-1,2,3-triazole (104, 0.37 g, 62%).

A suspension of 104 (0.37 g, 3.1 mmol) in benzene (125 mL) was photolyzed for 3 h. The reaction mixture was concentrated and eluted through a silica gel column with benzene. The first eluant was identified as phenylmalononitrile (277, 0.19 g, 24%): white crystals; mp 69–70 °C
(lit. 82b mp 67 °C); IR(KBr) 3060, 3050, 3030, 2980, 2960, 2255, 1620, 1510, 1460, 820 cm⁻¹; NMR(CDC₃) δ 5.01 (s, t–CH),

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7.32 (m, 5 H, phenyl).

The second elutant was identified as 7,7-dicyano-norcaradiene (276, 0.12 g, 28%): colorless crystals; mp (cyclohexane) 96-98 °C (lit. mp 97-98 °C); IR (KBr) 3100, 3070, 3030, 2243, 1250, 1000, 740 cm⁻¹; NMR (CDCl₃)

\[
\begin{align*}
\text{NC} & \quad \text{CN} \\
6 & \quad 1 \\
5 & \quad 2 \\
4 & \quad 3
\end{align*}
\]

3.47 (d, J₁₂ = 3.1, H₁,6), 6.28 (m, H₂,5), 6.62 (d, J₃₂ = 2.8 Hz, H₃,4); mass spectrum, m/e calcd for C₉H₆N₂ 142.077493, obsd 142.077933.


Reaction of 4-Cyano-5-diazo-1,2,3-triazole (104) with Anisole.

A solution of 4-cyano-5-diazo-1,2,3-triazole (104, 0.37 g, 3.1 mmol) in anisole (50 mL) was stirred and heated at 60-65 °C for 5 h. The solvent was removed under reduced pressure and the product mixture was eluted through a silica gel column with dichloromethane. The first elutant was identified as 4-cyano-5-phenoxy-1,2,3-triazole (280, 69 mg, 12%): colorless prisms; mp (aq ethanol) 109-111 °C; IR (KBr) 3430, 3200, 3010, 2242, 1720, 1600, 1550, 1350, 1030 cm⁻¹; NMR (DMSO/D₆) δ 7.31 (m, 3 H, phenyl), 7.90 (m, 2 H, phenyl), 8.32 (br s, N-H); mass spectrum, m/e calcd for C₉H₆N₄O, 186.062356, obsd 186.062782.
The second elutant was a yellow oil which crystallized on standing to a white crystalline product identified as a mixture of o- and p-methoxyphenyltriazoles (278 and 279, 0.29 g, 47%). Integration of the O-CH₃ signal indicated that the p- and o-substituted products exist in a 3:2 ratio. Careful separation by column chromatography led to isolation of the two isomers in pure form: (1) 4-cyano-5-(2-methoxyphenyl)-1,2,3-triazole: mp 116-118°C; IR(KBr) 3260, 3050, 2985, 2245, 1600, 1460, 825 cm⁻¹; NMR(DMSO/D₆) 3.90 (s, OCH₃), 7.09 (d, J = 8.7 Hz, phenyl), 7.55 (m, 3 H, phenyl), 8.15 (s, N-H); mass spectrum, m/e calcd for C₁₀H₇N₄O, 200.069806, obsd 200.070258. Anal. Calcd for C₁₀H₇N₄O: C, 59.99; H, 4.03. Found: C, 59.65; H, 4.19.

(2) 4-cyano-5-(4-methoxyphenyl)-1,2,3-triazole: mp(ethyl acetate/hexane) 196-198°C (lit. 196°C); IR(KBr) 3263, 3050, 2985, 2250, 1610, 1475, 1260, 760 cm⁻¹; NMR(DMSO/D₆) 3.83 (s, 3 H, OCH₃), 7.09 (d, J = 8.7 Hz, 2 H, phenyl), 7.83 (d, J = 8.7 Hz, 2 H, phenyl), 8.12 (br s, N-H); mass spectrum, m/e calcd for C₁₀H₈N₄O, 200.069806, obsd 200.070345.
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