

STRUCTURE AND REACTIVITY

OF ARYNES

A Thesis submitted for the degree of
Doctor of Philosophy in the Faculty of Science of the
University of Leicester.

by

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STATEMENT

The work described in this Thesis was carried out by the author in the Department of Chemistry of the University of Leicester under the supervision of Professor C.W. Rees, and is not concurrently being submitted for any other degree.

September 1966

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June 1969

Signed

R.W. Atkin

R.W. Atkin

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To Professor C.W. Rees for his excellent supervision, constant help and provision of research facilities.

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To my friend and long-suffering typist, June, for her patience.

SUMMARY

Known methods of generating arynes, and their chemical reactions, have been classified, and some new syntheses and reactions are described.

A series of substituted 1-aminobenzotriazoles were synthesised from the corresponding o-nitroanilines by considerable modification of the literature method. These compounds were also synthesised by the amination of the corresponding benzotriazoles, using hydroxylamine-O-sulphonic acid. This reaction afforded the isomeric 2-aminobenzotriazole in the unsubstituted case only. Oxidation of the substituted 1-aminobenzotriazoles with lead tetra-acetate was accompanied by elimination of nitrogen from the nitrene initially formed, to yield the free aryne. The degree of dimerisation of the arynes, to give the corresponding biphenylenes, was found to vary with the substitution of aryne. 3-Nitrobenzyne afforded no dimer, forming instead 3-nitrophenyl acetate.

Benzyne and 4-methoxybenzyne were shown to react as a symmetric singlet by the stereospecificity of the reaction with trans,trans-hexa-2,4-diene. Evidence for the existence of 3-nitrobenzyne in this electronic state was also found; semi-empirical calculations predicted benzyne, 4-nitrobenzyne and 3-nitrobenzyne to exist in the singlet ground state.

The reactivities of several arynes were compared by the relative degree of 2 + 2 cycloaddition to vinyl acetate.

3-Nitrobenzyne was found to be highly reactive; semi-empirical calculations showed that this species had an unusually high dipole

moment, and the reactivity was explained in terms of the polarity between the non-bonded σ -orbitals.

Evidence for the intermediacy of 2,2'-dehydrobiphenyl in the dimerisation of benzyne was found.

Certain arynes cleaved dialkyl ethers to give the phenyl alkyl ether. The "ene" reaction was extended to acetylenes, phenyl allenes being the products. Evidence for the existence of a transient ruthenium-benzyne complex was found, as was evidence of interaction between benzyne and silver or mercury.

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INTRODUCTION

The chemistry of the short lived reactive intermediate, benzyne (o-dehydrobenzene), has been intensively studied over the last fifteen years, but postulates regarding the precise nature of the bonding in this intermediate have been the result of speculation, as no experiment has yet been performed to test the validity of these postulates.

The generation and reactions of this and related intermediates have been extensively reviewed¹⁻¹¹, and so only the barest outlines of the chemistry of benzyne are given in this Introduction. Only synthetically important methods of generating benzyne are covered here; these may be classified as:

- 1) dehydrohalogenation of aryl halides,
- 2) treatment of 2-fluorobromobenzenes with lithium amalgam or magnesium,
- 3) elimination of stable molecules from ortho-disubstituted benzenes, and
- 4) degradation of heterocyclic rings, ortho-fused to benzene.

Next, the reactions of benzyne are described in outline; the classification of these reactions is:

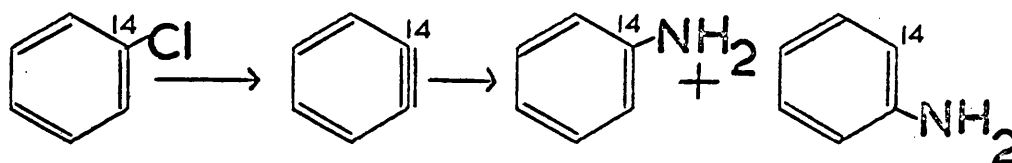
- 1) dimerisation and trimerisation,
- 2) Diels-Alder reactions,
- 3) the "ene" reaction,
- 4) 1,2 addition,
- 5) reaction with 1,3 dipolar species,
- 6) reaction with nucleophiles, and
- 7) reaction with electrophiles.

This is followed by a synopsis of attempts to isolate or detect the benzyne intermediate and finally, a review of the theoretical postulates concerning the nature of benzyne.

THE GENERATION OF BENZYNE

1. Dehydrohalogenation of aryl halides

Roberts¹² first authenticated the intermediacy of benzyne in the reaction of chlorobenzene with potassamide in liquid ammonia. $[1-^{14}\text{C}]$ -Chlorobenzene was treated with potassamide in liquid ammonia and equal amounts of $[1-^{14}\text{C}]$ -aniline and $[2-^{14}\text{C}]$ -aniline were formed. Hence the reaction was shown to proceed via a symmetrical intermediate which he termed "benzyne".



Roberts¹³ observed that *o*-deuterated halobenzenes reacted more slowly than their protium analogues. Hence removal of the ortho-proton is involved in the rate determining step. The rate of reaction was further shown to be independent of the nature of the halogen atom, and so the slow, rate-determining, loss of a proton must be followed by a fast loss of the halide ion. This method is a very general route to arynes, but obviously has synthetic disadvantages. However, lysergic acid has recently been prepared by this method¹⁴.

Potassium *t*-butoxide in dimethyl sulphoxide may be used as an alternative method of dehydrohalogenation, benzyne being generated at room temperature¹⁵.

2. Treatment of 2-fluorobromobenzenes with lithium amalgam or magnesium

Wittig found that 2-fluorobromobenzene, when treated with lithium amalgam¹⁶ or magnesium turnings¹⁷ in either diethyl ether or tetrahydrofuran, gave benzyne which could be intercepted with furan¹⁷, anthracene¹⁷ or with acyclic dienes¹⁸ in reasonable yields. Side reactions leading to the stepwise formation of polyaromatic compounds often interfere with this reaction, thus lowering the efficiency of benzyne generation. The most serious drawback, however, is the high reactivity of the organo-metallic intermediates which may be intercepted before they decompose to benzyne. This limits the types of compound that may be present in the reaction mixture and thus reduces the synthetic usefulness of the route.

3. Elimination of stable molecules from ortho-disubstituted benzenes

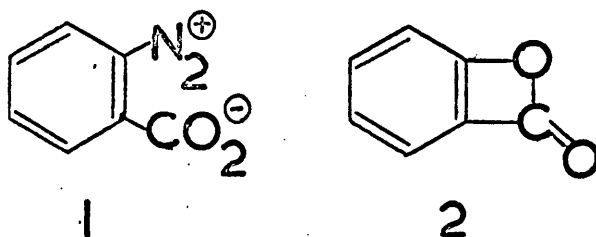
There are only two synthetically useful methods in this category:

- i) the thermal decomposition of benzenediazonium 2-carboxylate
- and ii) the thermal decomposition of diphenyliodonium 2-carboxylate.

i) thermal decomposition of benzenediazonium 2-carboxylate

In 1960, Stiles¹⁹ generated benzyne by decomposing benzenediazonium 2-carboxylate (1) in refluxing organic solvents, and adducts with anthracene (30%) and furan (55%) were obtained. Friedmann²⁰ showed that the hazardous isolation of (1) was unnecessary, since it could be generated in situ by aprotic diazotisation of anthranilic

acid in a refluxing organic solvent. Friedmann²¹ developed



a further procedure to avoid the isolation of (1).

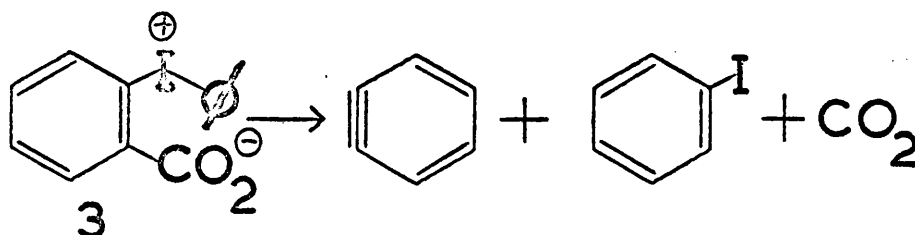
Benzenediazonium chloride 2-carboxylic acid (a much more stable compound) was decomposed in a refluxing organic solvent in the presence of propylene oxide and a catalytic amount of trichloroacetic acid. These methods all appear to involve (1) as an intermediate. The decomposition of (1) is thought not to be a concerted reaction. Stiles¹⁹ found that whereas evolution of nitrogen was quantitative, the yield of carbon dioxide was only 59%. Had the carbon dioxide and the nitrogen been lost simultaneously, then one would have expected nearly equal amounts of these gases to have been evolved. Gompper²² has shown, by decomposition of this precursor in mixtures of furan and water and alcohols, that the intermediate in this non-concerted reaction was nitrogen free, and probably is (2).

All three methods of generating benzyne by this route give good yields.

ii) thermal decomposition of diphenyliodonium 2-carboxylate

LeGoff²³ pyrolysed diphenyliodonium 2-carboxylate (3) in refluxing diglyme in the presence of tetraphenylcyclopentadienone (tetracyclone) and obtained a 68% yield of 1,2,3,4-tetraphenylnaphthalene. This method has the synthetic

disadvantage in that it requires a temperature of over 160°



to effect decomposition of the betaine. This, however, could be turned to advantage if benzyne was needed to react in the melt of some compound.

4. Degradation of heterocyclic rings, ortho-fused to benzenes

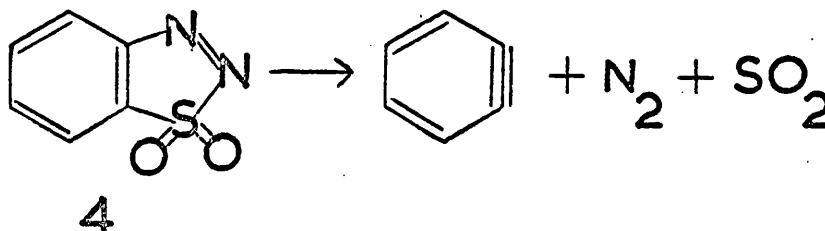
There are only two methods in this category that are important synthetically:

- i) thermolysis of 1,2,3-benzothiadiazole-1,1-dioxide, and
- ii) cleavage of benzotriazoles.

i) thermolysis of 1,2,3-benzothiadiazole-1,1-dioxide

Wittig^{24,25} prepared 1,2,3-benzothiadiazole-1,1-dioxide

(4) and showed that this thermally unstable compound readily formed benzyne in organic solvents at room temperature, although better yields were obtained at

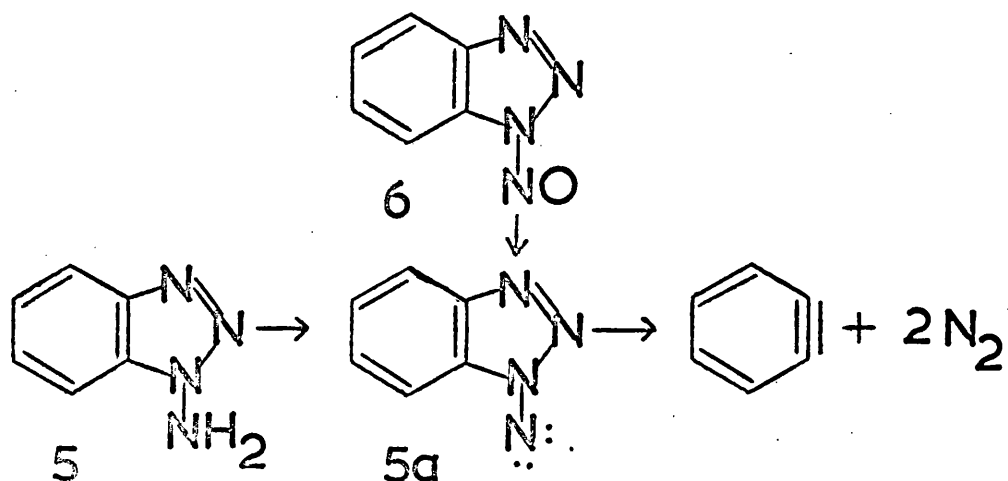


about 40°. The benzyne produced was detected in the usual manner.

R.W. Hoffmann²⁶ has shown that the loss of nitrogen and sulphur dioxide is essentially a concerted process. Initially nitrogen and sulphur dioxide are evolved at the same rate, but the rate of evolution of sulphur dioxide drops rapidly as the reaction proceeds. Hoffmann thought that this phenomenon was due to attack of benzyne on the sulphur dioxide before it could escape from the reaction vessel; he found that, upon purging the vessel with carbon dioxide, the yield of sulphur dioxide rose. Hoffmann further found that the rate of decomposition of this precursor was insensitive to changes of environment. Hence Hoffmann's theory was verified and the reaction proceeds via a concerted pathway.

ii) cleavage of benzotriazoles

In 1964, Rees and Campbell²⁷ found that oxidation of 1-aminobenzotriazole⁽⁵⁾ with lead tetra-acetate in an organic solvent gave benzyne in abnormally high yield as its dimer, biphenylene (70-80%) or, in the presence of tetracyclone, tetraphenylnaphthalene (95%). Nitrogen was evolved from the reaction mixture extremely rapidly. The oxidative procedure generates the nitrene (5a), which then loses two molecules of nitrogen to give benzyne. Support



for the intermediacy of (5a) has been given by Cadogan²⁸, who generated this intermediate by deoxygenation of 1-nitrosobenzotriazole (6), and found that benzyne was also formed.

Further chemistry of the oxidation of 1-aminobenzotriazoles is found in the Experimental and Discussion parts of this thesis.

REACTIONS OF BENZYNE

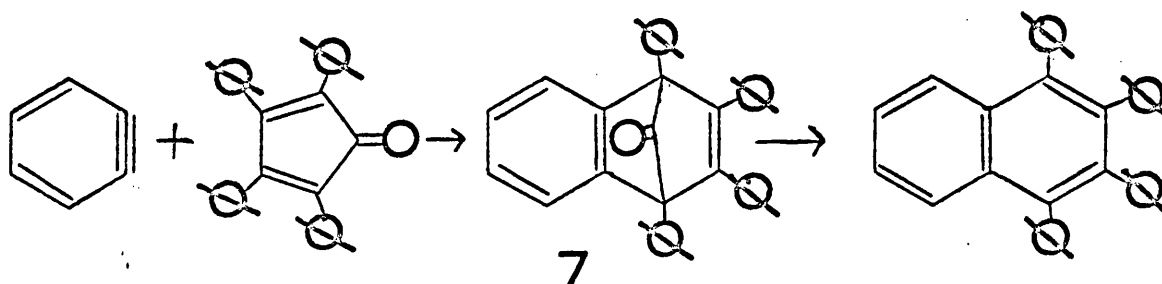
1. Dimerisation and trimerisation

The highest yield (83%) of the dimer, biphenylene, was obtained by Campbell and Rees^{27a,b} in the oxidation of 1-aminobenzotriazole with lead tetra-acetate in benzene. The dimerisation in this case is far higher than for any other precursor. Decomposition of benzenediazonium chloride 2-carboxylic acid in 1,2-dichloroethane in the presence of propylene oxide gives 25-30% biphenylene²⁹. Smaller yields (3-10%) of biphenylene are obtained from the reaction between o-dihalobenzenes and lithium amalgam^{16,30}.

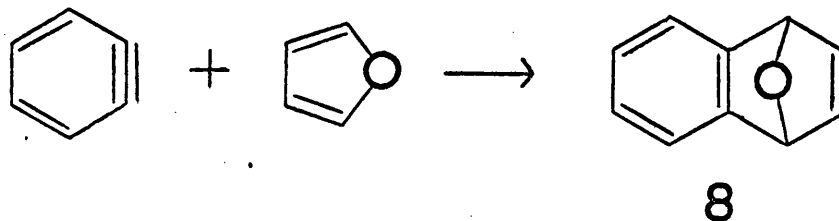
A small quantity of the trimer, triphenylene, was obtained by Campbell and Rees from the oxidation of 1-aminobenzotriazole with lead tetra-acetate in organic solvents, but the yield was never above 0.5%. This yield was probably due to genuine three collision trimerisation of benzyne. High yields of triphenylene are obtained from organometallic sources, but this has been shown to be due to stepwise elimination between different molecules of the benzyne precursor^{11a}.

2. Diels-Alder reactions

Benzyne is a powerful dienophile, and reacts with tetracyclone to give good yields of tetraphenylnaphthalene.



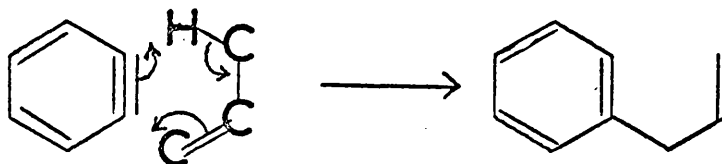
The first step is a Diels-Alder reaction, giving the primary adduct (7), which then spontaneously decarbonylates to give the tetraphenyl-naphthalene. Benzyne also reacts with furan^{27c,17} to give 1,4-dihydro-1,4-oxido-naphthalene (8) and with anthracene^{17,27c} to yield triptycene.



Benzyne also reacts with acyclic dienes. Thus Wittig¹⁸ obtained 1,4-dihydronaphthalene (10%) by reaction between benzyne and butadiene. This reaction was repeated by Hatch and Peter³¹ (9%).

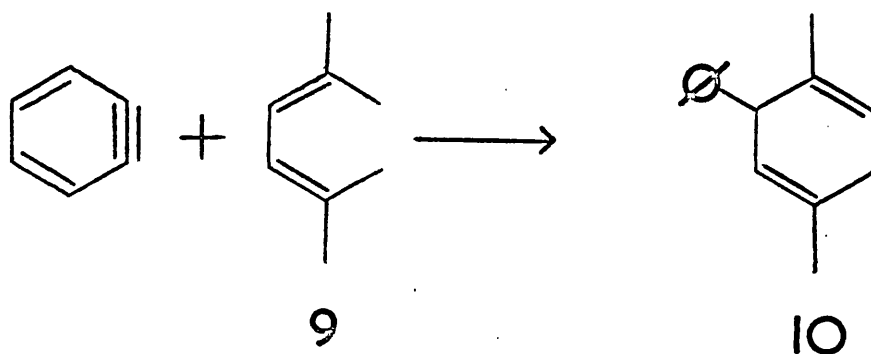
3. The "ene" reaction

This is a Diels-Alder type of reaction with the diene replaced by a mono-ene which is part of an allylic system. With benzyne, it proceeds as follows:



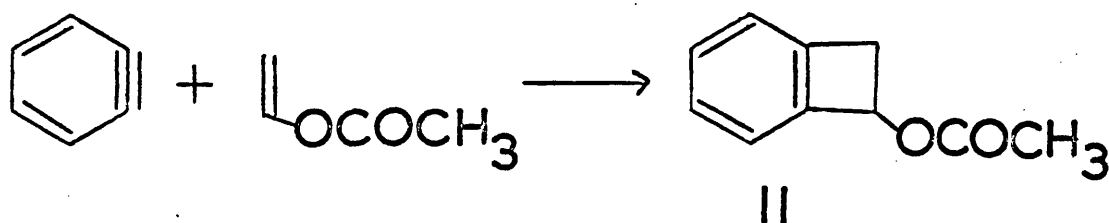
Hence there is a double bond shift onto the allylic carbon atom concerted with attack of benzyne at the site of the original double bond and shift of the allylic hydrogen onto benzyne. In some cases, the products from this type of reaction appear to be insertion of a phenyl ring into the allylic carbon-hydrogen bond. Thus reaction

between benzyne and isoprene gave, inter alia, 2-benzylbutadiene by an "ene" reaction¹⁸. In other cases, the double bond movement is more obvious. Hence reaction between benzyne and 2,5-dimethylhexa-2,4-diene (9) gave 2,5-dimethyl-3-phenylhexa-1,4-diene (10) (11%)³².



4. 1,2-Addition reactions

Benzyne does not normally add in very high yield to mono-enes, and the addition appears to some extent to depend on the method of generating the benzyne. Hence Campbell and Rees^{27c} found that benzyne from 1-aminobenzotriazole only added to vinyl acetate to give only a trace yield of benzocyclobutenyl acetate (11), whereas



Wasserman and Solodar³³ obtained a much higher yield of (11) from benzenediazonium 2-carboxylate. In general, benzyne reacts with electron-rich olefins more readily than with electron-poor olefins. Also, as expected, it reacts better with strained olefins. Thus norbornene³⁴, norbornadiene³⁴ and trans-cyclooctene³⁵ all show

abnormal reactivity towards benzyne.

The stereochemistry of benzyne addition to mono-enes has been investigated^{36,37;38,39}; the reactions are stereoselective but not stereospecific. Further consequences of this reaction can be found in the Discussion part of this Thesis.

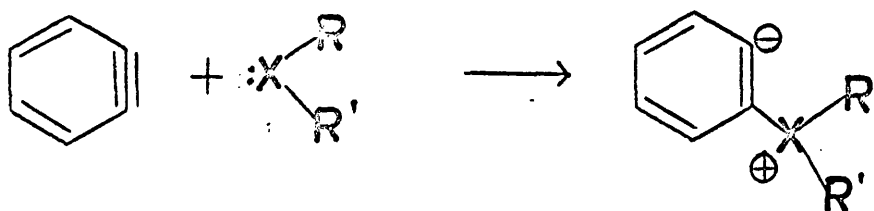
Under certain circumstances, benzyne can react with acetylenes for form benzocyclobutadienes. Stiles⁴⁰ reacted benzyne with phenyl acetylene and obtained, inter alia, diphenyl-dibenzocycloöctatetraene (29%). This product presumably arose from dimerisation of the primary adduct, 1-phenylbenzocyclobutadiene. Other acetylenes may also be induced to undergo this type of reaction^{11b}.

5. Reactions with 1,3-dipolar species

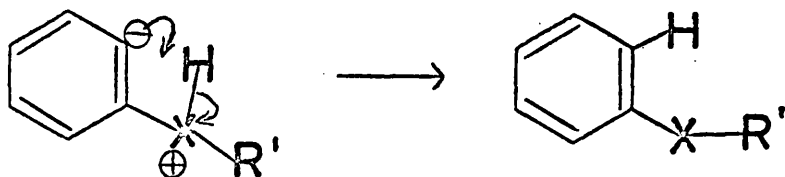
Benzyne reacts with 1,3-dipolar species to give high yields of 2+3 adducts^{11c}. Thus benzyne reacts with azides to yield benzotriazoles, with diazomethanes to give indazoles, and with nitrileoxides to give benzoxazoles.

6. Reactions with nucleophiles

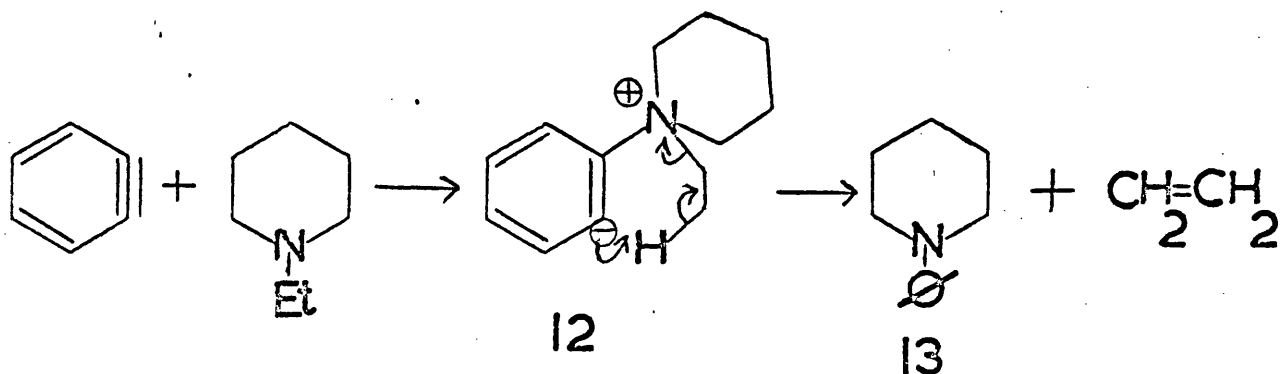
Reaction of benzyne with nitrogen, sulphur, oxygen, and phosphorus nucleophiles and with carbanions has been reviewed by Hoffmann¹¹. Initial attack is at the hetero-atom (or at the charged carbon in the case of a carbanion), and the nucleophilic atom becomes positively charged, and the benzyne acquires a negative charge, as follows:



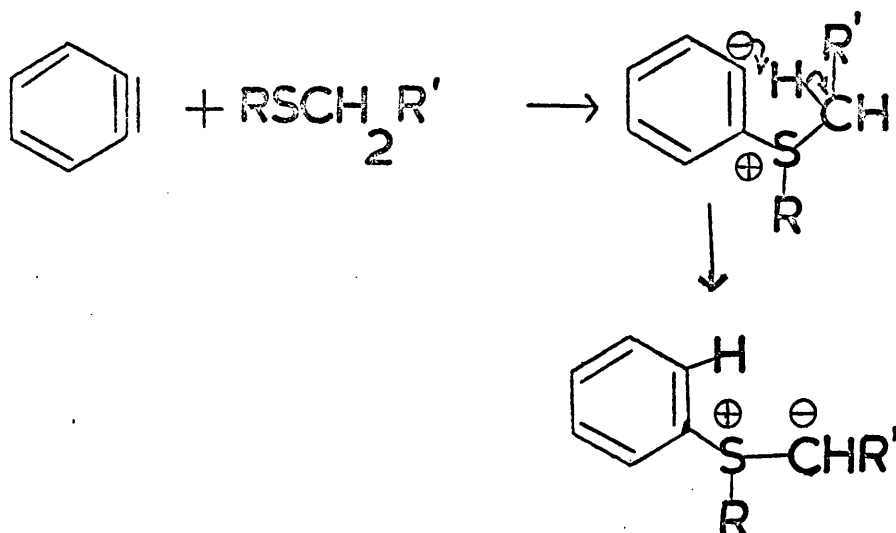
The second stage of the reaction is governed by the nature of R and R'. If R = H, then the next step in the reaction will be transfer of a proton from X to the o-carbanion:



and thus benzyne and ethanol give phenetole by this mechanism. If R is alkyl, sometimes a proton is abstracted from the β -carbon of the alkyl group to give an olefin as in the reaction between 1-ethylpiperidine and benzyne^{11d}. The betaine (12) decomposes to give 1-phenylpiperidine (13) and ethylene:



Sometimes a proton is abstracted from the α -position to form an ylid, especially if X is sulphur:

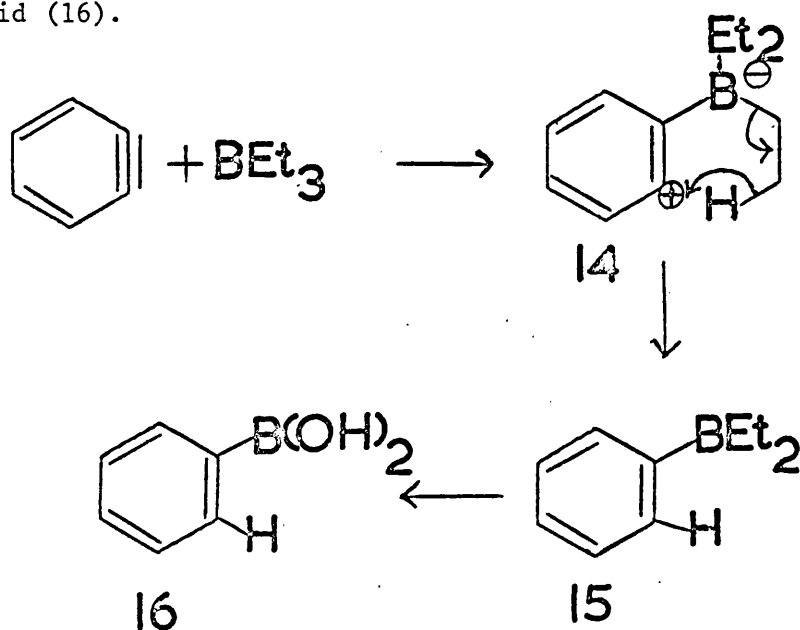


This ylide will then undergo the usual reactions of that species.

In general, benzyne does not cleave ethers.

7. Reactions with electrophiles

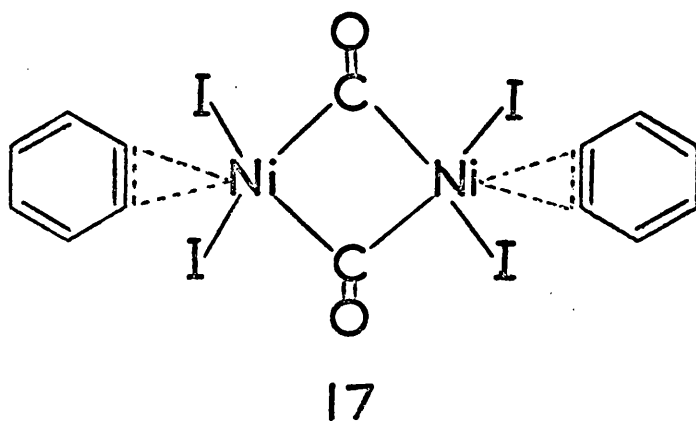
Only very powerful electrophiles will attack benzyne, since benzyne is a powerful electrophile itself. Wittig⁴¹ reacted benzyne with triethyl boron and obtained phenylboronic acid (16) (6%) after workup. Electrophilic attack on benzyne by the hetero-atom gives the intermediate (14) which then eliminates ethylene to give diethylphenyl boron (15), which is hydrolysed to phenylboronic acid (16).



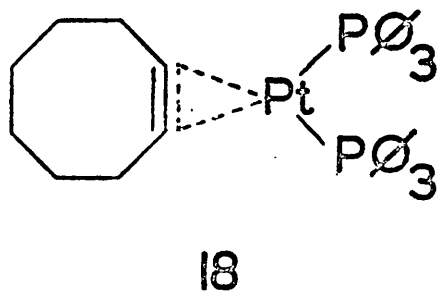
Benzyne is also attacked by mercury, tin and silicon
electrophiles^{11e}.

THE ISOLATION AND DETECTION OF THE BENZYNE INTERMEDIATE

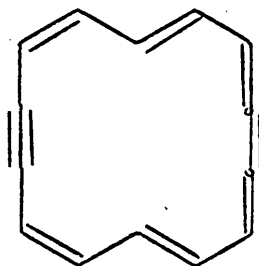
Isolation of the short-lived benzyne intermediate could only be carried out if it were stabilised by some other entity. Attempts to isolate a transition metal-benzyne complex have been unsuccessful⁴² except for the example reported by Kettle⁴³: o-diiodobenzene and tetracarbonyl nickel were reacted together in pentane, and II-benzyne-diiodo-μ-carbonylnickel dimer (17) was obtained as black needles.



Some evidence for the existence of a platinum-benzyne complex in solution has been found by Graveling⁴². The very reactive strained acetylene, cycloöctyne was obtained as a stable complex with platinum [0] (18) by Gilchrist, Graveling and Rees⁴⁴, showing that, in principle, this method was feasible for the stabilisation of benzyne.



Large ring arynes have been isolated by Sondheimer *et alia*, and show abnormal stability. Thus Sondheimer⁴⁵ prepared 1,8-bisdehydro[14]-annulene (19), which was a blood-red solid stable to light and air indefinitely.



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Evidence^{46a} for the existence of benzyne in the gas phase was obtained by flash photolysis of benzenediazonium 2-carboxylate and examination of the ultraviolet spectrum of the products. Before the appearance of the biphenylene spectrum, a transient continuum was observed. This had the following features:

- (a) > 270 nm., very weak
- (b) 270 - 255 or 250 nm., slightly stronger
- (c) 250 - 235 nm., distinctly stronger ($\lambda_{\text{max}}^{\text{46b}} = 242 \pm 3 \text{ nm.}$)
- (d) beyond 230 nm., very strong.

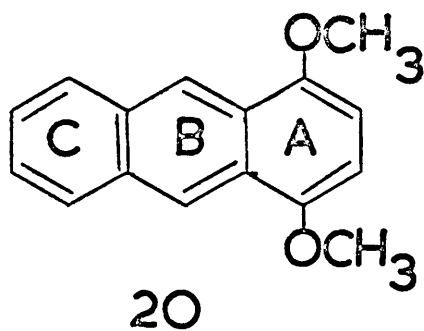
(a) and (b) were assigned to the $n \rightarrow \pi$ transitions and the region around 240 nm. was assigned to the $\pi \rightarrow \pi^*$ transitions.

o-Iodophenylmercuric iodide also gave the same transient continuum, but with lower extinction coefficients due to interference by mercury compounds^{46b}. The emission spectrum of benzyne has been obtained by Schöler and Lutz⁴⁷. Flash photolysis of benzenediazonium 2-carboxylate, followed by time-resolved mass spectroscopy, gives further evidence for the existence of the benzyne intermediate⁴⁸.

Within 50 μ sec, masses 28(N₂), 44(CO₂) and 76(C₆H₄) appeared simultaneously at or near their maximum intensities. The biphenylene peak (152) also appeared, but at only one quarter of its maximum intensity. The disappearance of the C₆H₄ peak corresponded with the increase in the biphenylene peak, the 76 peak lasting for about 250 - 300 μ sec. The correlation with the ultraviolet spectrum was good, the 76 peak persisting for as long as the continuum in the absorption spectrum. In addition, mass spectral analysis showed no evidence for partially decomposed intermediates. A rate constant for the dimerisation of gaseous benzyne has been estimated⁴⁹.

Further support for the existence of benzyne is given by the fact that different precursors give an intermediate which is identical in each case. Huisgen⁵⁰ generated benzyne by four different methods [decomposition of benzenediazonium 2-carboxylate and 1,2,3-benzothiadiazole-1,1-dioxide and treatment of 2-fluorobromobenzene with lithium amalgam and with magnesium] in the presence of an equimolar mixture of furan and cyclohexadiene. Each precursor gave a similar ratio of adducts of benzyne, and so it could be concluded that all the precursors gave an identical intermediate. Klanderman and Criswell⁵¹ generated benzyne from six different precursors [decomposition of benzenediazonium 2-carboxylate (2 methods), diphenyliodonium 2-carboxylate and 1,2,3-benzothiadiazole-1,1-dioxide, treatment of 2-fluorobromobenzene with magnesium, and oxidation of 1-aminobenzotriazole with lead tetra-acetate] in the presence of 1,4 dimethoxyanthracene (20). Each different source of benzyne gave the same ratio of adducts of ring A and ring B, except for diphenyliodonium 2-carboxylate. For this case, Klanderman showed that the iodobenzene produced during the decomposition of the precursor

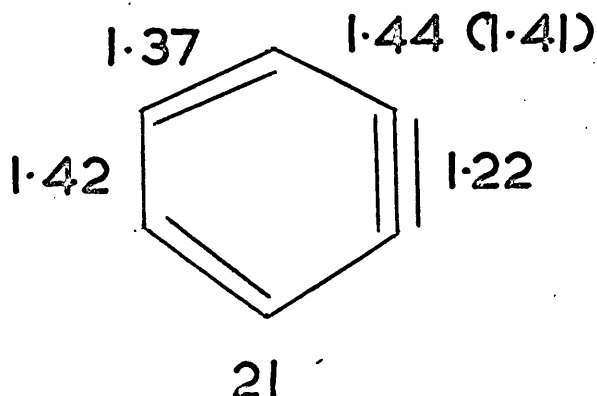
formed a weak Π -complex with the dimethoxy-anthracene which affects



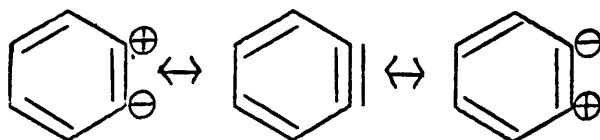
the relative reactivities of ring A and ring B. Hence it was verified that benzyne from different precursors had the same properties.

THEORETICAL POSTULATES REGARDING THE NATURE
OF BENZYNE

In 1954, Ingold⁵² considered that benzyne was analogous with a cis-bent acetylene and commented that the triple bond must be "opened" to some extent. Coulson⁵³ calculated a geometry for benzyne. He assumed a singlet ground state, and carried out a simple molecular orbital treatment for π electrons using four different resonance integrals for the four different bonds in the C_{2v} structure.

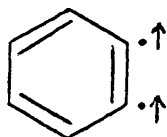


A starting geometry was assumed and the calculation made iteratively until the bond lengths gave an energy minimum. The bond lengths at minimum energy are shown in (21). Wittig³⁰ considered benzyne to be a hybrid of three resonating structures:

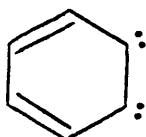


Two ortho-hydrogens were removed from benzene and the two remaining sp^2 hybrids were free to overlap. This overlap must be small due to "strain" in the benzyne ring, and this explained the reactivity of benzyne. Substituents would affect this resonance and so approaching reagents would polarise this bond into one of the charged structures.

Wittig dismissed the triplet diradical²⁵ (22) and the biscarbene¹⁸ (23) structures for benzyne.



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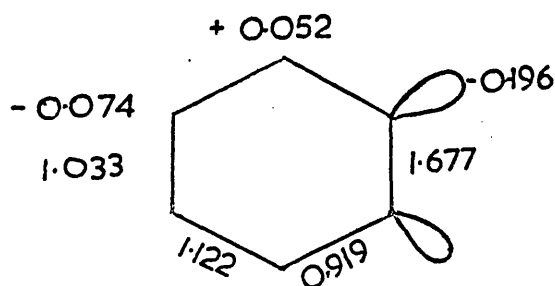


23

Simmons⁵⁴ assumed that benzyne was a resonance hybrid similar to that of Wittig³⁰, and derived a geometry for benzyne in the same way as Wittig³⁰. It was assumed that the dehydro-orbitals were part of the σ framework and were orthogonal to the π system of the ring, which was negligibly perturbed.

Using simple valence bond methods, Simmons calculated that the overlap integral of the approximately non-bonding σ orbitals, $S_{\sigma\sigma} = 0.125$. This corresponds to about one quarter of a pure π bond. The polar resonance contributors were about 4.8 eV higher in energy than the non-polar form.

Fukui et al⁵⁵ first applied the extended Hückel method to benzyne. He assumed the geometry calculated for benzyne by Coulson⁵³, and calculated separately the σ and π electron contributions to the electronic structure of the intermediate. The atomic charges and overlap populations in the singlet state is given in the molecular diagram (23a).



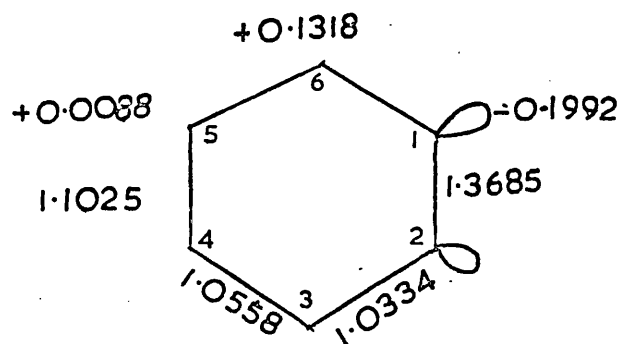
23a

Hoffmann⁵⁶ also treated benzyne by an extended Hückel method.

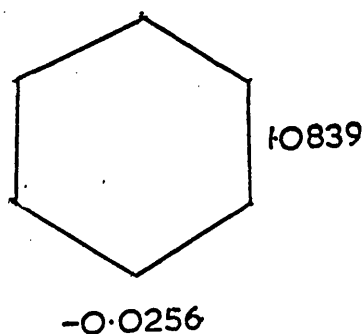
Assuming a benzene starting geometry, he removed two ortho-hydrogens to leave two orbitals with, formally, one electron in each. The precise hybridisation of these orbitals was not known and was irrelevant to the calculation. These two orbitals were represented by two wave functions: n_1 and n_2 . By considering the two-fold symmetry axis interchanging n_1 and n_2 as a classifying symmetry element, symmetry adapted (but unnormalised) combinations could be formed to describe the transformation properties. These were $n_1 + n_2$, called "symmetric" (S) and $n_1 - n_2$, called "antisymmetric" (A). If there were no interaction between n_1 and n_2 then A and S would be degenerate; if n_1 and n_2 did interact, then there would be a splitting

$$\Delta = E(A) - E(S)$$

which would be a measure of this interaction. Hoffmann found that A was higher than S by 1.52eV. Hence benzyne is probably a singlet with both electrons in S, as Hoffmann⁵⁷ has put an upper limit of about 1eV. on the difference on energies of the A and S levels. Hoffmann⁵⁶ calculated the Mulliken overlap populations and atomic charges for benzyne in the symmetric singlet state (24). Benzene (25) was given for comparison.

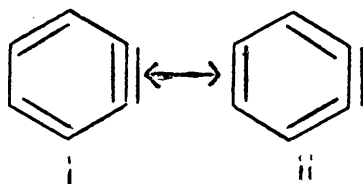


24



25

Hoffmann noted that the overlap population along the 4,5-bond in benzyne was higher than that in benzene. Thus, in valence bond terms, resonance contributor (ii) must play a large part in the resonance hybrid, and the molecule must suffer a compression along



both the 1,2- and 4,5-bonds relative to benzene.

Yonezawa⁵⁸ used a semi-empirical self consistent field-molecular orbital method to calculate the "triple" bond length and lowest transition energies of benzyne and some hetarynes. Using the method of complete neglect of differential overlap (CNDO), they found, using the usual iterative procedure, that the "triple" bond length was $1.29\overset{\circ}{\text{\AA}}$, much shorter than the bond length in benzene ($1.39\overset{\circ}{\text{\AA}}$) but longer than that of the stable aryne, 1,8-bisdehydro[14]annulene ($1.20\overset{\circ}{\text{\AA}}$)⁵⁹. The singlet-triplet transition energy was found to be 1.65eV.

EXPERIMENTAL

INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES

1. Infrared (i.r.) spectra were run in the range $4000-650\text{ cm}^{-1}$ on Perkin-Elmer 137 and 237 and Unicam SP 200 spectrophotometers with sodium chloride optics. Spectra of solids were taken as Nujol mulls or potassium bromide discs, and liquids as capillary films. Absorption peaks for new compounds were corrected with reference to polystyrene.
2. Ultraviolet (u.v.) spectra were run in ethanol in the range 200-450 nm. on a Unicam SP 800 spectrophotometer.
3. Nuclear magnetic resonance (n.m.r.) spectra were run on a Varian A60 instrument, in a variety of solvents, using tetramethylsilane as an internal standard.
4. Mass spectra were measured on an Associated Electrical Industries M.S.9 spectrometer.
5. Thin layer chromatography (t.l.c.) was used extensively for qualitative analysis of reaction products and for testing the purity of compounds. Samples were eluted with suitable solvent mixtures on glass plates coated with a 250μ thickness of Kieselgel G (MERCK).
6. Column chromatography was carried out using silica gel (BDH or Koch-Light's 100-200 mesh) or basic aluminium (Spence type H). All columns were packed under petrol and the eluant gradually replaced by more polar solvents.
7. Solvents used in benzyne generation experiments.

Benzene (A.R.) was dried with and kept over sodium wire.

Methylene chloride was refluxed over and distilled from calcium.

hydride, and stored over molecular sieves (type 4A).

Anhydrous ether and tetrahydrofuran were stored over sodium wire.

Bromotrichloromethane (KODAK) was dried with anhydrous magnesium sulphate and then fractionally distilled from a spinning band column.

The fraction boiling at 106.5° was collected, and stored over anhydrous magnesium sulphate.

Ethanol was refluxed over, and distilled from calcium hydride, and stored over fresh calcium hydride. The dry solvent was distilled directly from the storage vessel into the reaction vessel.

Petrol refers to light petroleum b.p. $40-60^{\circ}$.

Ether, chloroform and methylene chloride extracts were dried over anhydrous sodium sulphate.

Solvents were removed under reduced pressure on a rotary film evaporator.

8. Oxidants used in benzyne experiments:

Lead tetra-acetate (BDH) was dried by filtration from acetic acid and stored over sulphuric acid.

Nickel peroxide was prepared by the method of Nakagawa⁶⁰ and stored in an airtight jar in the dark. This material was of much higher activity than a sample from BDH.

9. Melting points (m.p.) were taken on a Kofler block using uncorrected thermometers.

10. Reaction products were, where possible, identified by direct comparison of i.r. spectra with authentic material and by mixed melting point determination. Literature m.p. or b.p. values are given with literature references, except for common or well-authenticated compounds, when the values are taken from "The Dictionary of Organic Compounds" (4th Edition) or from Beilstein.

11. Microdistillations were carried out under reduced pressure using a sublimation tube in which indentations had been blown. The liquid was absorbed into cotton wool at the bottom of the sublimation tube, and the tube placed in an electrically heated block. The oil was then fractionally distilled into the indentations. Very small amounts of liquids (c. 20mg.) could be purified by this method.

SECTION 1.

Preparation of 1-aminobenzotriazoles

1. From o-nitroanilines and diethyl malonate.

1-Aminobenzotriazole

- a) o-Nitroaniline (0.3 mole) was stirred with concentrated hydrochloric acid (90 ml.) until all the amine was converted into its almost white hydrochloride. Water (200 ml.) was added, and to the well-stirred suspension at 0°, sodium nitrite (0.35 mole) in water (50 ml.) was added, keeping the temperature below 5°. The resulting diazonium solution was filtered and added dropwise to a vigorously stirred suspension of diethyl malonate (0.3 mole) in water (200 ml.) at 5°. Sodium acetate (c. 100 g.) was added in portions during the reaction to buffer the solution. When the addition was complete, the mixture was stirred for one hour, and the orange-brown solid filtered off, washed with water and dried in vacuo. Crystallisation from methanol (charcoal) gave diethyl mesoxalate 2-nitrophenylhydrazone (50%), yellow needles, m.p. 70-2° (lit.⁶¹ m.p. 74%).

- b) The hydrazone (0.1 mole) was suspended in methanol and 10% palladium on charcoal (1.5 g.) added. The mixture was hydrogenated at 25°, and the theoretical amount of hydrogen was taken up in c. three hours. The mixture was filtered through Kieselguhr, and the dark red solution was reduced to one-third of its volume. Sodium nitrite (0.11 mole) in water (30 ml.) was added to the methanolic solution, and this mixture was added dropwise to a stirred solution of concentrated hydrochloric acid (25 ml.) in water (100 ml.) at 5°. The pale brown solid was filtered off, washed with water and dried in vacuo. Crystallisation from

ethanol (charcoal) gave diethyl (benzotriazol-1-yl)-iminomalonate (80%), large prisms, m.p. 96-8° (lit.^{27b} m.p. 99-100°).

- c) The finely powdered ester (0.05 mole) was heated on a water bath with concentrated hydrochloric acid (150 ml.) until the solution was homogeneous (c. 3 hours). Water (150 ml.) was added, and the solution thoroughly extracted with ether, and the ether layer discarded. The aqueous layer was neutralised with sodium carbonate, and extracted with ether. Evaporation of the ether layer gave a light yellow semi-solid which, after chromatography on basic alumina, gave 1-aminobenzotriazole (30%), needles, m.p. 82° (from benzene-petrol (60-80)) (lit.⁶² m.p. 82°).

5-Chloro- and 5-trifluoromethyl-1-aminobenzotriazoles were prepared by analogous routes, except that hydrogenation was performed with Adams' catalyst in glacial acetic acid.

The intermediates and products are given below:

Diethyl mesoxalate 4-chloro-2-nitrophenylhydrazone,

large yellow-brown blades, m.p. 107° (from ethyl acetate-petrol (60-80)).
(Found: C, 45.4; H, 4.1; N, 12.2. $C_{13}H_{14}N_3O_6Cl$ requires C, 45.5; H, 4.1; N, 12.5%), ν max 3200, 3100 (NH), 1728 (C=O), 807, 730 cm^{-1} .

Diethyl mesoxalate 2-amino-4-chlorophenylhydrazone,

orange-yellow microprisms, m.p. 84° (from ether-petrol), (Found: C, 49.8; H, 5.2; N, 13.4. $C_{13}H_{16}N_3O_4Cl$ requires C, 49.8; H, 5.1; N, 13.8%), ν max 3465, 3340 (NH₂), 1680 (C=O), 800, 780 cm^{-1} .

Diethyl(5-chlorobenzotriazol-1-yl)-iminomalonate,

uncrystallisable brown tar, one spot on t.l.c. Carried on to next stage.

1-Amino-5-chlorobenzotriazole,

(31% from 4-chloro-2-nitroaniline), long buff microneedles, m.p. 152-3°

(from ethyl acetate-petrol (60-80)), (Found: C, 42.5; H, 3.1; Cl, 20.8. $C_6H_5N_4Cl$ requires C, 42.7; H, 3.0; Cl, 21.1%), ν max 3280, 3190 (NH_2), 930, 880, 823, 801 cm^{-1} .

Diethyl mesoxalate 2-nitro-4-trifluoromethylphenylhydrazone,

long yellow needles, m.p. 62° (from methanol-water), (Found: C, 44.2; H, 3.4; N, 11.2. $C_{14}H_{14}N_3O_6F_3$ requires C, 44.6; H, 3.7; N, 11.1%), ν max 1728 (C = O), 1512, 1320 (NO_2), 920, 904, 865, 848, 808, 762, 700 cm^{-1} .

Diethyl mesoxalate 2-amino-4-trifluoromethylphenylhydrazone,

long yellow blades, m.p. 112° (from ethanol-water), (Found: C, 48.1; H, 4.1; N, 12.3. $C_{14}H_{16}N_3O_6F_3$ requires C, 48.5; H, 4.6; N, 12.1%), ν max 3450, 3348 (NH_2), 3200, 3130 (NH), 1692 (C = O), 1170, 1107 (CF), 940, 916, 867, 837, 803, 799, 750, 728 cm^{-1} .

Diethyl (5-trifluoromethylbenzotriazol-1-yl)-iminomalonate,

yellow-brown oil (contaminated with an azide). This compound could not be obtained free from impurities. ν max 1750 (C = O), 1170, 1130, 1100 (CF), 940, 900, 865, 828, 770 cm^{-1} .

1-Amino-5-trifluoromethylbenzotriazole,

(20% from 2-nitro-4-trifluoromethylaniline), long needles, m.p. 145° (from methylene chloride-petrol), (Found: C, 41.5; H, 2.2; N, 27.5. $C_7H_5N_4F_3$ requires C, 41.6; H, 2.5; N, 27.8%), ν max 3320, 3220 (NH_2), 1220, 1190, 1178, 1160, 1115 (CF), 1050, 900, 821, 723 cm^{-1} .

2. From o-nitroanilines and methyl cyanoacetate.

The procedure followed was identical to that used for 1-amino-5-chlorobenzotriazole except that methyl cyanoacetate replaced diethyl malonate in the synthesis. The intermediates and products are given below:

Methyl 2-nitrophenylhydrazonocyanoacetate,

yellow microcrystals, m.p. $186-7^{\circ}$ (from acetone-methanol), ν max 3215 (NH), 2240 ($C \equiv N$), 1710 ($C = O$), 860, 820, 800, 790, 760 cm^{-1} .

Methyl 2-amino phenylhydrazonocyanoacetate,

yellow-orange needles, m.p. 160° (from acetone-petrol (60-80)) (lit.⁶² m.p. 160°) ν max 3400, 3340 (NH_2), 3180 (NH), 2240 ($C \equiv N$), 1690 ($C = O$), 770, 728 cm^{-1} .

Methyl (benzotriazol-1-yl)-iminocyanoacetate, α form,

yellow needles, m.p. 166° (from ethyl acetate-petrol (60-80)) (lit.⁶² m.p. $162-4^{\circ}$) ν max 2240 ($C \equiv N$), 1750 ($C = O$), 1010, 848, 788, 775, 760 cm^{-1} .

Treatment of the above compound with concentrated nitric acid in glacial acetic acid gave:

Methyl (benzotriazol-1-yl)-imino cyanoacetate, β form,

long feathery needles, m.p. 179° (from ethyl acetate-petrol (60-80)), (Found: C, 52.2; H, 3.0; N, 30.0. $\text{C}_{10}\text{H}_7\text{N}_5\text{O}_2$ requires C, 52.4; H, 3.0; N, 30.6%), ν max 1760 ($C = O$), 1255, 1000, 830, 790, 770, 750 cm^{-1} .

Both of the above compounds gave, on hydrolysis, 1-Aminobenzotriazole (56% from o-nitroaniline), needles, m.p. and mixed m.p. 82° (from benzene-petrol (60-80)) (lit.⁶² m.p. 82°).

Methyl 4-methoxy-2-nitrophenylhydrazonocyanoacetate,

bright yellow tablets, m.p. $171-2^{\circ}$ (from ethyl acetate-petrol (60-80)), (Found: C, 47.3; H, 3.6; N, 20.1. $\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}_5$ requires C, 47.5; H, 3.6; N, 20.1%), ν max 3210 (NH), 2220, 2200 ($C \equiv N$), 1740 ($C = O$), 875, 840, 810, 800, 755, 732 cm^{-1} . τ (CDCl_3), 1.9-2.8 (m, 3H), 6.02 (s, 3H), 6.08 (s, 3H).

Methyl 2-amino-4-methoxyphenylhydrazonocyanoacetate,

orange-red crystals, m.p. 127-9° (from ethyl acetate-petrol (60-80)),

(Found: C, 53.5; H, 4.6; N, 22.1. $C_{11}H_{12}N_4O_3$ requires C, 53.2; H, 4.8; N, 22.6%), ν max 3460, 3340 (NH_2), 3200 (NH), 2205 ($C \equiv N$), 1680 ($C = O$), 870, 830, 770 cm^{-1} .

Methyl (5-methoxybenzotriazol-1-yl)-iminocyanoacetate,

orange-brown crystals, m.p. 186-8° (from ethyl acetate/petrol (60-80)),

(lit.⁶² m.p. 151-2°), ν max 2242 ($C \equiv N$), 1735 ($C = O$), 887, 852, 840 cm^{-1} . τ ($CDCl_3$), 2.1-2.8 (m, 3H), 5.9 (s, 3H), 6.1 (s, 3H).

1-Amino-5-methoxybenzotriazole,

(90% from 4-amino-3-nitroanisole), long blades, m.p. and mixed m.p.

131° (from ether-petrol) (lit.⁶² m.p. 121°).

If the hydrogenation was attempted using a solvent other than glacial

acetic acid, the corresponding azoxy-compound was obtained, (70%),

blood red microneedles, m.p. 252° (dec) (from ethyl acetate),

(Found: C, 52.6; H, 3.8; N, 22.2. $C_{22}H_{20}N_8O_7$ requires C, 52.0; H, 3.9; N, 22.0%), ν max 2220 ($C \equiv N$), 1680 ($C = O$), 930, 871, 861, 825, 815, 785 cm^{-1} .

Methyl 4-chloro-2-nitrophenylhydrazonocyanoacetate,

long lemon-yellow needles, m.p. 206° (from benzene-petrol (60-80)),

(Found: C, 42.5; H, 2.5; N, 19.8. $C_{10}H_7N_4O_4Cl$ requires C, 42.5; H, 2.5; N, 19.8%). ν max 3240 (NH), 2220 ($C \equiv N$), 1750 ($C = O$), 900, 885, 840, 820, 765, 758, 654 cm^{-1} . τ ($CDCl_3$), -2.1 (s, 1H), 1.7-2.7 (m, 3H), 6.0 (s, 3H).

Methyl 2-amino-4-chlorophenylhydrazonocyanoacetate,

(60% from 4-chloro-2-nitroaniline), orange needles, m.p. 212° (from chloroform-petrol), (Found: C, 46.8; H, 3.4; N, 20.9.

$C_{10}H_9N_4O_2Cl$ requires C, 46.7; H, 3.6; N, 22.2%). ν max 3465, 3400,

3358, 3320 (NH_2), 3200, 3160 (NH), 2220 ($\text{C} \equiv \text{N}$), 1720, 1680 ($\text{C} = \text{O}$), 980, 930, 905, 870, 777, 760, 720 cm^{-1} .

Methyl (5-chlorobenzotriazol-1-yl)-iminocyanoacetate,

red-brown crystals. ν max 2222 ($\text{C} \equiv \text{N}$), 1740 ($\text{C} = \text{O}$). Impure.

This compound was inert to hydrolysis with acid.

Methyl 2,4-dinitrophenylhydrazonocyanoacetate,

(70% from 2,4 dinitroaniline), orange-buff leaflets and granules, m.p. 170° (from ethanol-ethyl acetate), (Found: C, 40.6; H, 2.5; N, 23.1. $\text{C}_{10}\text{H}_7\text{N}_5\text{O}_6$ requires C, 41.0; H, 2.4; N, 23.9%), ν max 3245 (NH), 2240 ($\text{C} \equiv \text{N}$), 1730 ($\text{C} = \text{O}$), 920, 860, 840, 770, 748, 710, 687 cm^{-1} . This compound gave only intractable red solids when subjected to mono-reduction conditions.

3. Attempted preparations of 1-amino-5nitrobenzotriazole,

- a) Benzaldehyde 2,4-dinitrophenylhydrazone (2.0g.; 6.8 mmole.) was suspended in ethanol, and ammonia solution (20ml.; $d = 0.88$) added. Hydrogen sulphide gas was passed for three hours, after which time the solution had turned deep red. Water (60ml.) was added, and the resulting red precipitate was filtered off, washed with water and dried in vacuo. Recrystallisation from ethyl acetate-petrol (60-80) gave benzaldehyde 2-amino-4-nitrophenylhydrazone (80%), copper needles, m.p. $167-9^\circ$, (Found: C, 60.9; H, 4.6; N, 22.0. $\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_2$ requires C, 60.9; H, 4.7; N, 21.9%), ν max 3555, 3390 (NH_2), 3335, 3250 (NH), 875, 805, 785, 740, 735, 685 cm^{-1} .
- b) The amine (1.0g.; 3.8 mmole.) was dissolved in methanol (40ml.). Concentrated hydrochloric acid (10ml.) was added to the methanolic solution, which instantly precipitated the deep yellow hydrochloride. The suspension was cooled to 0° , and sodium nitrite (4.5 mmole.) in water (10ml.) was added. The solution was stirred at 0° for twenty minutes, and then water (150ml.)

was added, and the solution filtered. The light yellow residue was washed successively with water (10ml.), sodium carbonate solution (0.5N; 2 × 20ml.), water (10ml.), ethanol (5ml.) and petrol (3 × 30ml.). The resulting light yellow solid was recrystallised from ethyl acetate-petrol (60-80) to give 1-benzylideneamino-5-nitrobenzotriazole (99%), yellow-buff cubes, m.p. 222°, (Found: C, 58.0; H, 3.3; N, 25.8.

$C_{13}H_9N_5O_2$ requires C, 58.4; H, 3.4; N, 26.2%), ν max 1528, 1340 (NO₂), 980, 900, 820, 800, 760, 735, 690 cm⁻¹.

- c) The benzylidene derivative (5.3g.; 20 mmole.) was suspended in hydrobromic acid (48-50%; 10ml.) and heated at 100° for forty hours. The dark reaction mixture was poured into water (500ml.) and unchanged starting material was filtered off. (65% recovery of starting material.) The clear red filtrate was neutralised with solid sodium carbonate and extracted with chloroform (3 × 150ml.). The chloroform extracts were dried, and evaporation gave an orange-red gum (c. 500mg.) which gave, after repeated crystallisations from ether-petrol, light yellow microneedles m.p. 144-5°, (Found: C, 51.6; H, 3.3; N, 27.5%). ν max 3340, 820, 800, 737cm⁻¹.
- d) The benzylidene derivative (300mg.; 1.1mmole.) was suspended in hydrobromic acid (48-50% 10ml.) and acetone (100mg.; 1.7mmole.) added. The mixture was heated at 100° for forty-eight hours. The black solution was poured into water (50ml.) and extracted with chloroform (3 × 50ml.). The chloroform layer was dried, and evaporation gave a buff solid which upon repeated crystallisation from petrol gave 1-isopropylideneamino-5-nitrobenzotriazole (30%), m.p. 137-8°, (Found: C, 48.8; H, 4.1; N, 31.4. $C_9H_9N_5O_2$

requires C, 49.3; H, 4.1; N, 31.9%), ν max 1530, 1350 (NO_2), 1070, 1040, 940, 832, 820, 804, 760, 740cm^{-1} . $\frac{m}{e}$ 219(P), 163, 117, 115.

The aqueous layer was neutralised with solid sodium carbonate and extracted with chloroform (3 × 50ml.). The chloroform extracts were dried, and evaporated to give a red solid. Sublimation at $180^\circ/\text{mm}$ gave 4-nitro-o-phenylenediamine, (20%), m.p. 196° , mixed m.p. 199° (lit. m.p. 198°).

4. From hydroxylamine O-sulphonic acid (HOS) and benzotriazoles.

Hydroxylamine O-sulphonic acid was prepared by the method of Gösl and Meuwsen⁶³, and dried in vacuo before use.

Amination of benzotriazole

Benzotriazole (BDH; 10g.; 0.083mole) was dissolved in a solution of anhydrous sodium carbonate (80g.) in water (300ml.) at 60° . HOS(30g.) was added and the temperature was moderated at $60-65^\circ$ by the addition of ice. The solution was allowed to cool, and the buff-brown precipitate was filtered off. The residue was washed with water, and dried in vacuo. Recrystallisation from ether/petrol (charcoal) gave 2-aminobenzotriazole (2.5g.).

The aqueous layer was ether extracted (4 × 200ml.) and the residue from the ether extracts was chromatographed on basic alumina. Elution: with ether-petrol (25%) gave 2-aminobenzotriazole (0.5g.), followed by a mixture of 1- and 2-aminobenzotriazoles (0.1g.).

Elution with ether gave 1-aminobenzotriazole (7g.; 63%) m.p. and mixed m.p. 82° (lit.⁶² m.p. 82°). The total yield of 2-aminobenzotriazole was 3g. (27%), m.p. and mixed m.p. $121-2^{\circ}$ (lit.^{27b} m.p. $121-2^{\circ}$).

Preparation of 1-amino-4-nitrobenzotriazole and 1-amino-7-nitrobenzotriazole

- a) 2-Nitro-o-phenylenediamine (Aldrich; 10g.; 0.065mole.) was suspended in a mixture of glacial acetic acid (30ml.) and water (30ml.), and cooled to 0° . Sodium nitrite (0.075mole.) in water (10ml.) was added, and the reaction mixture immediately removed from the ice-bath. The temperature rose to 50° . After the reaction had subsided, water (500ml.) was added, and the light yellow triazole filtered off, washed with water, and dried in vacuo. Recrystallisation from ethanol gave 4-nitrobenzotriazole (90%), light yellow needles, m.p. 236° (lit. m.p. 236°).
- b) Benzotriazole (10g.; 0.083mole.) was dissolved in concentrated sulphuric acid (50ml.) and cooled to -10° (ice-methanol bath). A mixture of fuming nitric acid (10ml.) was added, keeping the temperature below 0° . The addition took c. two hours.

The mixture was stirred for a further hour, and then poured onto ice (500g.). The light yellow precipitate was filtered off, washed with water, and dried in vacuo. Recrystallisation from ethanol gave 4-nitrobenzotriazole (60%), light yellow needles, m.p. 236° (lit. m.p. 236°).

- c) 4-Nitrobenzotriazole (8g.; 0.048mole.) was aminated using the same technique as that used to aminate benzotriazole. The cooled reaction mixture was extracted with chloroform ($2 \times 250\text{ml.}$), the extracts dried, and the residual oil from evaporation of the solvent was chromatographed on silica gel. Elution with ether-petrol (50%) gave:

1-amino-7-nitrobenzotriazole (5-15%),

yellow needles, m.p. 100-110°, ν max 3360 (NH₂), 1536, 1345 (NO₂), 820, 805, 738cm⁻¹. τ (DMSO), 1.3-2.7 (m, 3H), 2.86 (s, 2H). $\frac{m}{e}$, 179 (P), 151, 77. This compound could not be obtained pure enough for analysis. Elution with ether gave:

1-amino-4-nitrobenzotriazole (5-20%),

long yellow needles, m.p. 128-9° (from ether-petrol), (Found: C, 39.9; H, 3.0; N, 38.8. C₆H₅N₅O₂ requires C, 40.2; H, 2.8; N, 39.1%). ν max 3300, 3160 (NH₂), 1510, 1335 (NO₂), 805, 790, 740, 727 cm⁻¹. τ (DMSO), 1.6-2.3 (m, 3H), 2.63 (s, 2H). $\frac{m}{e}$, 179 (P), 151, 150, 149, 122.

Preparation of 1-amino-5-nitrobenzotriazole and 1-amino-6-nitrobenzotriazole.

- a) Benzotriazole (10g.; 0.083mole) was added to a mixture of nitric acid (50ml.) and concentrated sulphuric acid (50ml.), and then heated on a water bath for thirty minutes. The reaction mixture was poured onto ice (800g.), and the light yellow solid filtered off, washed with water, and dried in vacuo. Recrystallisation firstly from ethanol and then from benzene gave 5-nitrobenzotriazole (50%), light yellow blades, m.p. 211° (lit.⁶⁴ m.p. 211°).
- b) 5-Nitrobenzotriazole (8g.; 0.048mole) was aminated by the same technique as for 4-nitrobenzotriazole. Chromatography on basic alumina gave an inseparable mixture of 1-amino-5-nitrobenzotriazole and 1-amino-6-nitrobenzotriazole (5-50%), long yellow needles, m.p. 168-9° (from methylene chloride-petrol), (Found: C, 40.2; H, 2.8; N, 38.7. C₆H₅N₅O₂ requires C, 40.2; H, 2.8; N, 39.1%), ν max 3320, 3200 (NH₂), 1520, 1320 (NO₂), 880, 840, 800, 731 cm⁻¹.

Benzylidene derivative, buff blades, m.p. 148-9° (from ethanol),

(Found: C, 57.5; H, 3.3; N, 25.8. C₁₃H₉N₅O₂ requires C, 58.4; H, 3.4; N, 26.2%). ν max 1530, 1350 (NO₂), 1070, 1050, 820, 805, 768, 732, 698cm⁻¹.

This derivative was not the same as the benzylidene derivative of 1-amino-5-nitrobenzotriazole (see p.32) by i.r. comparison and mixed melting point. Thus this mixture is nearly all the 6-nitro isomer, and for the purposes of experiment, it was treated as if it were all the 6-nitro isomer.

Also obtained from the basic alumina column was 4-nitro-o-phenylenediamine (1%), blood-red microplates, m.p. 192-5°, mixed m.p. 197-8° (after sublimation) (lit. m.p. 198°), (Found: C, 46.9; H, 4.4; N, 27.5. $C_6H_7N_3O_2$ requires C, 47.1; H, 4.6; N, 27.4%), ν max 3439, 3380, 3340, 3220 (NH_2), 868, 795, 742 cm^{-1} .

Preparation of 1-amino-5-methoxybenzotriazole and 1-amino-6-methoxybenzotriazole.

- a) 5-Methoxybenzotriazole was prepared by the method of Scalera and Adams⁶⁵ in 1-10% yield based on 4-methoxy-o-phenylenediamine. m.p. 126° (from water) (lit.⁶⁵ m.p. 126.8-127.2°), ν max 1630, 1610, 995, 830, 810 cm^{-1} .
- b) 5-Methoxybenzotriazole (3g.; 0.02mole) was dissolved in a solution of sodium hydroxide (4g.) in water (25ml.) at 60° and HOS (3g.) added. The temperature was regulated at 60-6° by the addition of ice. The reaction mixture was allowed to cool, and then was extracted with ether (2 × 50ml.). The ether layer was dried, and evaporated to small bulk (c. 10ml.). A yellow-buff solid crystallised out, and was filtered off. Recrystallisation of the residue from methylene chloride-petrol gave 1-amino-6-methoxybenzotriazole (3.5%), needles, m.p. 165°, (Found: C, 51.3; H, 5.2; N, 33.8. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.1%), ν max 1650, 970, 940, 854, 820, 785, 700 cm^{-1} .

Addition of petrol (40ml.) to the filtrate gave a buff precipitate, which was filtered off and recrystallised from methylene chloride-petrol to give 1-amino-5-methoxybenzotriazole (10%), needles, m.p. 131° , (Found: C, 51.3; H, 4.9; N, 33.5. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.1%), ν max 3305, 3190 (NH_2), 1610, 855, 805 cm^{-1} . $\tau(CDCl_3)$, 2.0-3.1 (m, 3H), 4.3 (s, 2H), 6.1 (s, 3H). This compound was identical with a sample prepared by an unambiguous route (see p.30).

5. From other 1-aminobenzotriazoles.

Preparation of 1,7-diaminobenzotriazole, and stabilisation as an isopropylidene derivative.

1-amino-7-nitrobenzotriazole (250mg.; 1.4mmole.) was dissolved in ethyl acetate (10ml.) and 10% palladium on charcoal (50mg.) added. The mixture was hydrogenated at 23° ; 5.2mmole. of hydrogen were consumed. The mixture was filtered under nitrogen to prevent decomposition of the extremely air-sensitive diamino compound, and the ethyl acetate was removed at 20° in vacuo. The light yellow residue was dissolved in "Analar" acetone (10ml.) and passed down a basic alumina column, to give 7-amino-1-isopropylideneaminobenzotriazole (27%), cubes, m.p. 120° (from petrol (60-80)), (Found: C, 57.3; H, 6.0; N, 37.3. $C_9H_{11}N_5$ requires C, 57.1; H, 5.9; N, 37.0%), ν max 3330, 3230 (NH_2), 1610, 880, 788, 740 cm^{-1} . $\tau(CDCl_3)$, 2.5-3.5 (m, 3H), 5.17 (s, 2H), 7.60 (s, 3H), 7.71 (s, 3H).

This compound did not give a gas with lead tetra-acetate in methylene chloride.

Preparation of 1,4-diaminobenzotriazole, and stabilisation as an isopropylidene derivative.

1-amino-4-nitrobenzotriazole (310mg.; 1.7mmole.) was treated in the

same manner as for 1-amino-7-nitrobenzotriazole to give

4-amino-1-isopropylideneaminobenzotriazole, (10%)

yellow plates, m.p. $71-2^{\circ}$ (from petrol (60-80)), (Found: C, 56.9;

H, 6.0; N, 36.9. $C_9H_{11}N_5$ requires C, 57.1; H, 5.9; N, 37.0%), ν max
3340, 3220 (NH_2), 1630, 1604, 860, 840, 785, 740 cm^{-1} . $\tau(CDCl_3)$,

2.6-3.7 (m, 3H), 5.2 (s, 2H), 7.69 (s, 3H), 7.79 (s, 3H).

This compound did not give a gas with lead tetra-acetate in methylene
chloride.

SECTION 2

Oxidation of 1-aminobenzotriazoles with no benzyne "trap".

1. Oxidations with lead tetra-acetate.

All reactions were performed in a 3-necked 250ml. round-bottomed flask fitted with a magnetic stirrer. The 1-aminobenzotriazole was dissolved in the solvent, and solid lead tetra-acetate (1.5 equivalents) was added in portions. Excess of oxidant was destroyed by the addition of glycerol, and the lead salts were precipitated by addition of diethyl ether. The reaction mixture was then filtered and the filtrate chromatographed on silica gel.

The list below names first the precursor, then the quantity of the precursor, then the solvent. The products are listed after the heading.

Oxidation of 1-amino-5-methoxybenzotriazole, (3mmole.) in methylene chloride.

- i) 2,6- and 2,7-dimethoxybiphenylenes (mixture) (5%), yellow prisms
m.p. 70-85° (after sublimation), (Found: C, 78.9; H, 6.0.
 $\text{C}_{14}\text{H}_{12}\text{O}_2$ requires C, 79.2; H, 5.7%), ν max 1612, 1600, 1580, 967,
867, 800, 790, 770, 691 cm^{-1} . λ max 245, 254, 341, 360nm.
 $\tau(\text{CDCl}_3)$, 3.4-4.1 (m, 6H), 6.35 (s, 6H). $\frac{m}{e}$, 212 (P), 197, 183,
169, 167.
- ii) 3- and 4-acetoxy anisoles (mixture) (10.5%), colourless oil with
an aniseed odour, b.p. 50°/1mm (purified by microdistillation),
 ν max 1760 (C = O), 1610, 1590, 1200 (C-O-C), 950, 900, 865, 840,
815, 778, 760, 750, 688, 670 cm^{-1} . $\tau(\text{CCl}_4)$, 2.7-3.6 (m, 4H),
6.30 (s, 3H), 7.86 (s, 3H).

Oxidation of 1-aminobenzotriazole and 1-amino-5-methoxybenzotriazole
(1.2mmole. each) in methylene chloride.

- i) biphenylene (63%), m.p. 112° (lit.⁶⁸ m.p. 110°)
- ii) 2,6- and 2,7-dimethoxybiphenylenes (41%), m.p. $\sim 65^{\circ}$ i.r. and u.v. spectra identical to previous sample.

Oxidation of 1-aminobenzotriazole and 1-amino-6-methoxybenzotriazole
(0.6mmole. each) in methylene chloride.

- i) biphenylene (32%), m.p. 112° .
- ii) 2,6- and 2,7-dimethoxybiphenylenes (20%).

Oxidation of 1-amino-6-nitrobenzotriazole (1.7mmole) in methylene chloride.

- i) 2,6- and 2,7-dinitrobiphenylenes (mixture) (1%); bright yellow prisms, m.p. $\sim 250^{\circ}$ (from petrol), ν max 1528, 1510, 1342, 1330 (NO_2), 1080, 1030, 980, 880, 851, 811, 740cm^{-1} . λ max 234, 283, 286, 345, 365 (sh), 383nm. $\frac{m}{e}$, 242 (P), 212, 196, 150.
- ii) yellow granules (35mg.), m.p. $180-260^{\circ}$ (after sublimation)
(Found: C, 55.9; H, 2.9; N, 16.1. $\text{C}_{12}\text{H}_7\text{N}_3\text{O}_4$ requires C, 56.0; H, 2.7; N, 16.3%), ν max 1580, 1520, 1340 (NO_2), 1106, 810, 728cm^{-1} .

Oxidation of 1-amino-6-nitrobenzotriazole (3.1mmole.) in acetonitrile.

3- and 4-nitrophenyl acetates (mixture) (16%), light yellow oil, ν max 3100, 1780 (C = O), 1540, 1360 (NO_2), 1200 (C-O-C), 1028, 950, 920, 872, 860, 820, 807, 752, 745, 707cm^{-1} . $\tau(\text{CCl}_4)$, 1.6-2.8 (m, 4H), 7.7 (s, 3H).
Identical with authentic samples by i.r. comparison.

Oxidation of 1-aminobenzotriazole and 1-amino-6-nitrobenzotriazole
(1.2mmole. each) in methylene chloride.

- i) biphenylene (18%), m.p. 112° .
- ii) 2-nitrobiphenylene (9%), long deep yellow needles, m.p. $106-7^{\circ}$

(after sublimation) (lit.⁶⁶ m.p. 107-8°), ν max 1598, 1515, 1340, 1325, 970, 930, 880, 860, 843, 752, 731 cm^{-1} . λ max 232(log ϵ , 4.20), 239 (4.20), 265 (4.15), 328 (3.19), 347 (3.33), 364 (3.50), 400nm. (3.44). $\frac{m}{e}$, 197 (P), 167, 151, 150.

Oxidation of 1-amino-4-nitrobenzotriazole (3.3mmole.) in methylene chloride (-80°).

3-nitrophenyl acetate (23%), light yellow needles, m.p. and mixed m.p. 53° (from petrol) (lit. m.p. 54-5°), ν max 1765 (C = O), 1520, 1350 (NO_2), 1190 (C-O-C), 1009, 936, 890, 850, 803, 730, 690, 660 cm^{-1} .

Oxidation of 1-amino-7-nitrobenzotriazole (0.8mmole.) in benzene.

3-nitrophenylacetate (18%), m.p. 53-4°.

Oxidation of 1-amino-4-nitrobenzotriazole (1.1mmole.) in methylene chloride in the presence of anhydrous potassium carbonate (4g.).

3-nitrophenyl acetate (27%), m.p. 53°.

Oxidation of 1-aminobenzotriazole and 1-amino-4-nitrobenzotriazole (1.2mmole. each) in methylene chloride.

- i) biphenylene (13%), m.p. 110°.
- ii) 3-nitrophenyl acetate (30%), m.p. 53°.

Oxidation of 1-aminobenzotriazole and 1-amino-7-nitrobenzotriazole (0.6mmole. each) in methylene chloride.

- i) biphenylene (21%), m.p. 110°.
- ii) 3-nitrophenyl acetate (26%), m.p. 53-4°.

Oxidation of 1-amino-5-methoxybenzotriazole and 1-amino-4-nitrobenzotriazole (1.6mmole. each) in methylene chloride.

3-nitrophenyl acetate (54%), m.p. 54°.

Oxidation of 1-aminonaphtho[1,8-de]triazine and 1-amino-4-nitrobenzotriazole (1.7mmole. each) in methylene chloride.

- i) naphthalene (8%) contaminated with 1-chloronaphthalene, m.p. 55-60°. Identical by i.r. comparison with mixture supplied by Dr. R.C. Storr.
- ii) 3-nitrophenyl acetate (14%), m.p. 54°.

Oxidation of 1-amino-5-chlorobenzotriazole (3.1mmole.) in ethyl acetate.

- i) 2,6- and 2,7-dichlorobiphenylenes (mixture) (18%),
light yellow prisms, m.p. 108-30° (after sublimation), (Found: C, 65.0; H, 2.7. $C_{12}H_6Cl_2$ requires C, 65.1; H, 2.7%), ν max 1575, 1422, 1230, 980, 862, 825, 815, 800, 700 cm^{-1} .
- ii) Dichloro-1-phenylbenzotriazoles (mixture) (5%),
light yellow crystals, m.p. 122-138° (after sublimation),
(Found: C, 53.9; H, 2.5; N, 15.8. $C_{12}H_7N_3Cl_2$ requires C, 54.5; H, 2.6; N, 15.9%), ν max 1600, 1502, 1000, 940, 870, 830, 825, 720, 710 cm^{-1} . $\frac{m}{e}$ (^{35}Cl), 263 (P), 235.
- iii) 3- and 4-chlorophenyl acetates (mixture) (1%), oil, b.p. 50°/1mm (purified by microdistillation), ν max 1770 (C = O), 1597, 1490, 1375, 1200 (C-O-C), 1095, 1020, 915, 850, 800, 721, 687 cm^{-1} .
 $\tau(CCl_4)$, 2.6-3.2 (m, 4H), 7.8 (s, 3H).

Oxidation of 1-aminobenzotriazole and 1-amino-5-chlorobenzotriazole (2.0mmole. each) in benzene.

After chromatography on silica gel, the column fractions were fractionally sublimed to give:

- i) biphenylene (26%), m.p. 110°.
- ii) 2-chlorobiphenylene (19%), light yellow needles, m.p. 70°, ν max 1428, 1380, 1241, 1160, 1135, 1043, 978, 870, 820, 741 cm^{-1} .

$\frac{m}{e}$ (^{35}Cl), 186 (P), 152, 151, 150.

- iii) 2,6- and 2,7-dichlorobiphenylenes (16%), m.p. 109-142°. i.r. identical with previous sample.
- iv) 3- and 4-chlorophenyl acetate (6%), oil, i.r. identical with previous sample.

Oxidation of 1-amino-5-trifluoromethylbenzotriazole (2.0mmole.) in benzene.

- i) 2,6- and 2,7-bis(trifluoromethyl)-biphenylenes (mixture) (53%), light yellow needles, m.p. 57-90° (from ethanol-water), (Found: C, 58.1; H, 2.5. $\text{C}_{14}\text{H}_6\text{F}_6$ requires C, 58.3; H, 2.1%), ν max 1400, 1320, 1240, 1160, 1130, 1110 (C - F), 1075, 1041, 1025, 1015, 881, 830, 711, 660, 651 cm^{-1} . λ max 240, 249, 322, 327, 336, 340, 354nm.
- ii) 3- and 4-trifluoromethylphenyl acetates (mixture) (1%), oil, b.p. 80°/1mm. (purified by microdistillation), ν max 1775 (C = O), 1618, 1518, 1330, 1250, 1210, 1170, 1130 (C - F), 1060, 1048, 1021, 1015, 974, 943, 916, 858, 820, 800, 762, 731, 719, 700, 680, 662, 656 cm^{-1} . $\frac{m}{e}$, 204 (P), 188, 187, 162.

Oxidation of 1-aminobenzotriazole and 1-amino-5-trifluoromethylbenzotriazole (1.0mmole. each) in methylene chloride.

After chromatography on silica gel, the column fractions were fractionally sublimed to give:

- i) biphenylene (21%), m.p. 109°.
- ii) 2-trifluoromethylbiphenylene (3%), long very light yellow needles, m.p. 78° (after sublimation), (Found: C, 71.6; H, 3.3. $\text{C}_{13}\text{H}_7\text{F}_3$ requires C, 70.9; H, 3.2%), ν max 1412, 1320, 1248, 1170, 1152, 1130 (C - F), 1035, 845, 832, 750, 740, 711, 640 cm^{-1} . $\frac{m}{e}$, 220 (P), 201, 165, 146, 145.

- iii) Inseparable mixture of 2-trifluoromethylbiphenylene and 2,6- and 2,7-bis(trifluoromethyl)-biphenylenes (108mg.)

2. Oxidations with other oxidants.

All reactions were performed in a 3-necked 250ml. round-bottomed flask fitted with a magnetic stirrer. The 1-aminobenzotriazole was dissolved in the solvent, and the oxidant added. The solution was stirred until no more gas was evolved, and then was filtered and chromatographed on silica gel. The list below names the precursor used, the oxidant, the solvent and the products.

Oxidation of 1-amino-7-nitrobenzotriazole (0.84mmole.) with nickel peroxide (1.0g.) in methylene chloride.

3-nitrochlorobenzene (1%), light yellow crystals, m.p. 40°, mixed m.p. 41° (purified by sublimation) (lit. m.p. 46°, m.p. of authentic sample (B.D.H.), 41°), ν max 1530, 1350 (NO₂), 1130, 1067, 892, 885, 878, 800, 760, 740, 661, 651 cm⁻¹.

Oxidation of 1-amino-4-nitrobenzotriazole (1.7mmole.) with nickel peroxide (2.0g.) in methylene chloride in the presence of acetic acid (8.0mmole.).

3-nitrophenyl acetate (3%), crude oil, identified by i.r. comparison with authentic sample.

Oxidation of 1-amino-4-nitrobenzotriazole (2.0mmole.) with phenyliodosodiacetate (2.0mmole.) in methylene chloride.

- i) iodobenzene (40%), oil, i.r. identical with that of an authentic sample.
- ii) light yellow crystals (15mg.), m.p. 75-85° (purified by sublimation),

(Found: C, 42.5; H, 2.6; N, 4.0. $C_{12}H_8NIO_3$ requires C, 42.3; H, 2.4; N, 4.1%), ν max 1537, 1353 (NO_2), 1255, 1208, 840, 812, 760, 737, 706, 690. $\frac{m}{e}$, 341 (P), 168, 167, 139.

iii) 3-nitrophenyl acetate (11%), m.p. 53-4°.

Oxidation of 1-amino-4-nitrobenzotriazole (1.1mmole.) with

N-bromosuccinimide (2.2mmole.) in methylene chloride.

2,3-dibromonitrobenzene (10%), light yellow solid, m.p. 76-7° (purified by sublimation) (lit. m.p. 85°), ν max 1540, 1350 (NO_2), 1270, 1140, 1095, 1040, 873, 795, 748, 731, 716, 665 cm^{-1} .

Oxidation of 1-amino-6-nitrobenzotriazole (1.2mmole.) with

N-bromosuccinimide (2.4mmole.) in methylene chloride.

- i) 3,4-dibromonitrobenzene (27%), light yellow crystals, m.p. and mixed m.p. 53-4° (from ethanol) (lit. m.p. 58-9°), ν max 1528, 1332 (NO_2), 1120, 1009, 883, 860, 823, 818, 725 cm^{-1} .
- ii) azide oil (44mg.), ν max 2114, 2108 (N_3).

Oxidation of 1-aminobenzotriazole (2.2mmole.) with ruthenium tetroxide

(prepared by oxidation of ruthenium dioxide (3mmole.) with sodium metaperiodate) in carbon tetrachloride at 50°.

biphenylene (20%) m.p. 110°.

SECTION 3

Oxidation of 1-aminobenzotriazoles in the presence of cyclic dienes.

All reactions were performed in a 3-necked 250ml. round-bottomed flask fitted with a magnetic stirrer. The diene and 1-aminobenzotriazole were dissolved in the solvent (usually methylene chloride), and the solid oxidant was added, except for ruthenium tetroxide, which was added as a solution in carbon tetrachloride. Chromatography on basic alumina gave the products. Lead tetra-acetate (LTA) (1.5equivs.) was used as the oxidant unless otherwise stated.

TABLE I
Reactions with tetracyclone.

1-AMINO-BENZO-TRIAZOLE	MMOLE AMINE	MMOLE TRAP	OXI-DANT	MMOLE OXIDANT	PRODUCTS	YIELD
5-OCH ₃	1.2	1.2	LTA	1.8	6-methoxy-1,2,3,4-tetra-phenylnaphthalene ^a	93%
5-OCH ₃ UNSUBST	1.0 1.0	1.0	LTA	3.0	6-methoxy-1,2,3,4-tetra-phenylnaphthalene ^b 1,2,3,4-tetraphenylnaphthalene ^c biphenylene ^c	61% 34% 16%
5-OCH ₃ UNSUBST	1.0 1.0	1.0	LTA	1.0	6-methoxy-1,2,3,4-tetra-phenylnaphthalene 1,2,3,4-tetraphenylnaphthalene biphenylene	18% 27% 1%
6-OCH ₃	0.31	0.31	LTA	0.5	6-methoxy-1,2,3,4-tetra-phenylnaphthalene	83%
6-NO ₂	0.17	0.18	LTA	0.3	6-nitro-1,2,3,4-tetra-phenylnaphthalene ^d	76%
7-NO ₂	0.41	0.4	LTA	0.6	5-nitro-1,2,3,4-tetra-phenylnaphthalene ^e	24% f
5-Cl	1.0	0.9	LTA	1.5	6-chloro-1,2,3,4-tetra-phenylnaphthalene ^g	75% f
5-CF ₃	0.5	0.5	LTA	0.7	6-trifluoromethyl-1,2,3,4-tetraphenylnaphthalene ^h	92%
UNSUBST	2.4	5.0	RuO ₄	3.0	biphenylene	15%
UNSUBST	3.7	8.0	OsO ₄	2.0	1,2,3,4-tetraphenyl-naphthalene orange solid ^j	3% 1.0g
5-OCH ₃	2.1	2.5	RuO ₄	3.0	6-methoxy-1,2,3,4-tetra-phenylnaphthalene 3-methoxyphenol ^k 4-methoxyphenol ^k	5% 22% 4%

NOTES TO TABLE I

- a) new compound, octahedral prisms, m.p. $253-4^{\circ}$ (from chloroform-methanol), (Found: C, 91.0; H, 5.6. $C_{35}H_{26}O$ requires C, 91.0; H, 5.6%), ν max 1622, 1240, 1223, 1209, 1120, 1040, 850, 829, 793, 764, 749, 710, 700 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.75-3.15 (m, 23H), 6.3 (s, 3H).
- b) prisms, m.p. and mixed m.p. $204-6^{\circ}$ (from benzene-ethanol) (lit.⁶⁷ m.p. 204°).
- c) m.p. 110° .
- d) new compound, large lemon-yellow prisms, m.p. 274° (from methylene chloride-petrol), (Found: C, 85.9; H, 4.8; N, 3.0. $C_{34}H_{23}NO_2$ requires C, 85.5; H, 4.8; N, 2.9%), ν max 1527, 1342 (NO_2), 1069, 1030, 905, 835, 760, 740, 695 cm^{-1} .
- e) new compound, buff-yellow prisms with a pink reflex, m.p. 254° (from petrol), (Found: C, 85.2; H, 4.8; N, 3.1. $C_{34}H_{23}NO_2$ requires C, 85.5; H, 4.8; N, 2.9%), ν max 1510, 1340 (NO_2), 1140, 1100, 1065, 1020, 910, 805, 780, 750, 695 cm^{-1} .
- f) yield based on tetracyclone.
- g) new compound, large rosettes of hexagonal prisms, m.p. $229-30^{\circ}$ (from ethanol), (Found: C, 87.7; H, 5.2. $C_{34}H_{23}Cl$ requires C, 87.5; H, 4.9%), ν max 1600, 1065, 1025, 983, 925, 890, 875, 790, 736, 695 cm^{-1} .
- h) new compound, prisms, m.p. 244.5° (from ethanol), (Found: C, 83.6; H, 4.5. $C_{35}H_{23}F_3$ requires C, 84.0; H, 4.6%), ν max 1625, 1600, 1575, 1320, 1285, 1160, 1130 (C - F), 1071, 1065, 1021, 1000, 985, 930, 905, 835, 800, 760, 740, 721, 696, 650 cm^{-1} .
- j) orange-brown crystals, m.p. $130-160^{\circ}$ (dec.) (from chloroform-petrol), ν max 1700, 1680 (C = O), 1600, 968, 858, 819, 755, 734, 700 cm^{-1} .
- k) i.r. identical to that of an authentic sample (B.D.H.)

Oxidation of 1-aminobenzotriazole (2.5mmole.) in the presence of
4-tert-octyl-o-benzoquinone (5.2mmole.) in benzene.

2-tert-octyl-benzobicyclo[2.2.2.]octa-2,5-diene-7,8-dione (53%), lemon-yellow plates, m.p. 139° (from petrol (60-80)), (Found: C, 81.3; H, 8.6. $C_{20}H_{24}O_2$ requires C, 81.1; H, 8.1%), ν max 1730 (C = O), 1105, 862, 740, 697 cm^{-1} . $\tau(CDCl_3)$, 2.86 (s, 4H), 3.80-3.95 (quartet, 1H, J_1 6.5 c/sec., J_2 2 c/sec.), 5.46 (d, 1H, J 2 c/sec.), 5.63 (d, 1H, J 6.5 c/sec.), 8.50 (s, 1H), 8.53 (s, 1H), 8.80 (s, 3H), 8.86 (s, 3H), 9.30 (s, 9H). $\frac{m}{e}$, 296 (P), 240, 169, 141.

This adduct gave, on photolysis in benzene using a Rayonet reactor fitted with 310nm. lamps:

2-tert-octylnaphthalene (100%), colourless oil, b.p. ~ 100°/1mm. (purified by microdistillation), (Found: C, 90.3; H, 9.8. $C_{18}H_{24}$ requires C, 89.9; H, 10.1%), ν max 1645, 1630, 1610, 1596, 945, 881, 848, 810, 740 cm^{-1} . $\tau(CCl_4)$ 2.2-2.8 (m, 7H), 8.17 (s, 3H), 8.54 (s, 6H), 9.28 (s, 9H). $\frac{m}{e}$, 240 (P), 169, 141.

Oxidation of 1-aminobenzotriazole (2.5mmole.) in the presence of
4-methyl-o-benzoquinone (4.0mmole.) in benzene.

2-methyl-benzobicyclo[2.2.2.]octa-2,5-diene-7,8-dione (14%), canary-yellow prisms, m.p. 104° (from ether-petrol), (Found: C, 78.4; H, 5.3. $C_{13}H_{10}O_2$ requires C, 78.8; H, 5.1%), ν max 1740 (C = O), 1630, 1120, 1100, 840, 755 cm^{-1} . $\tau(CDCl_3)$, 2.65 (s, 4H), 3.6 - 3.8 (m, 1H), 5.55 (d, 1H, J 6 c/sec.), 5.70 (d, 1H, J 2 c/sec.), 7.90 (d, 3H, J 1.2 c/sec.). $\frac{m}{e}$, 198 (P), 142.

Oxidation of 1-aminobenzotriazole (2.3mmole.) in the presence of 3-iso-propyl-6-methyl-o-benzoquinone (4.3mmole.) in benzene.

1-iso-propyl-4-methylbenzobicyclo[2.2.2.]octa-2,5-diene-7,8-dione (25%), orange prisms, m.p. $73-4^{\circ}$ (from petrol), ν max 1745 (C = O), 1260, 855, 800, 770, 705, 695 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.65 (s, 4H), 3.60 (d, 2H, J 3.5 c/sec.), 6.8-7.3 (m, 1H), 8.28 (s, 3H), 8.72 (d, 3H, J 6 c/sec.), 8.80 (d, 3H, J 6 c/sec.). $\frac{m}{e}$, 240 (P), 184.

A satisfactory analysis could not be obtained.

Oxidation of 1-aminobenzotriazole (2.6mmole.) in the presence of o-benzoquinone (5.0mmole.) in benzene.

- i) biphenylene (3%) m.p. 110° .
- ii) yellow oil (30mg.), ν max 1735 (C = O), 1225, 800, 780, 745, 720 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.62 (s, 4H), 3.15-3.30 (m, 2H), 5.35-5.50 (m, 2H). $\frac{m}{e}$, 128 (all other peaks less than 0.1% of this peak).

Oxidation of 1-aminobenzotriazole (2.6mmole.) in the presence of acenaphthenequinone (5.0mmole.) in benzene.

biphenylene (21%), m.p. 110° .

Oxidation of 1-amino-4-nitrobenzotriazole (2.5mmole.) in furan (10ml.)

Silica workup.

1,4-dihydro-5-nitro-1,4-oxidonaphthalene (17%),

large light yellow plates, m.p. $97-8^{\circ}$ (from petrol), (Found: C, 63.2; H, 3.9; N, 7.7. $\text{C}_{10}\text{H}_7\text{NO}_3$ requires C, 63.5; H, 3.7; N, 7.4%), ν max 1600, 1284, 900, 878, 824, 800, 780, 755, 722, 662 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.1-2.9 (m, 5H), 3.5 (s, 1H), 4.7 (s, 1H).

SECTION 4

Oxidations of 1-aminobenzotriazoles in the presence of acyclic dienes.

All oxidations were performed in a 3-necked 250ml. round-bottomed flask fitted with a magnetic stirrer. The 1-aminobenzotriazole was suspended and/or dissolved in a mixture of the olefin and methylene chloride, and lead tetra-acetate (1.5 equivalents) was added. Excess lead tetra-acetate was destroyed with glycerol, and the solvents were stripped off. The residue was extracted with diethyl ether, and the ether extracts chromatographed on the adsorbant stated.

Oxidation of 1-aminobenzotriazole (2.4mmole.) in butadiene (80ml.) and methylene chloride (250ml.) at -80° . Basic alumina.

1,4-dihydronaphthalene (91%), needles, m.p. $21-2^{\circ}$ (from petrol) (lit.¹⁸ m.p. 23-24.5), ν max 3018, 2960, 2932, 2910, 1500, 1458, 1429, 786, 747, 660 cm^{-1} . λ max 266.5, 274nm. (lit.⁶⁹ λ max 267, 274nm.) $\tau(\text{CCl}_4)$, 3.0 (s, 4H), 4.0-4.2 (m, 2H), 6.7 (m, 4H).

This compound was unstable, changing slowly to 1,2-dihydronaphthalene, and naphthalene.

Treatment with 10% palladium on charcoal at $200-250^{\circ}$ for six hours gave naphthalene (30%), m.p. 76° , mixed m.p. 78° (lit. m.p. 80°).

Oxidation of 1-amino-5-methoxybenzotriazole (1.1mmole.) in butadiene (10ml.) and methylene chloride (10ml.) at -80° . Basic alumina.

1,4-dihydro-6-methoxynaphthalene (98%), oil, ν max 1629, 1608, 1500, 1040, 910, 837, 800, 660 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.7-3.4 (m, 3H), 4.0-4.2 (m, 2H), 6.24 (s, 3H), 6.66 (s, 4H). This compound decomposed rapidly to 1,2-dihydro-methoxynaphthalenes and 2-methoxynaphthalene.

Treatment with 10% palladium on charcoal at 250° for one and a half hours gave 2-methoxynaphthalene (85%), needles, m.p. 70° (after sublimation) (lit. m.p. 72°), ν max 1632, 1600, 1502, 1030, 840, 815,

740, 697 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.0-2.8 (m, 7H), 6.06 (s, 3H).

picrate, deep yellow needles, m.p. 111-2° (from ethanol) (lit. m.p. 113°).

Oxidation of 1-amino-4-nitrobenzotriazole (2mmole.) in butadiene (10ml.) and methylene chloride (10ml.) at 0°. Silica.

- i) mixture of adducts (32%), yellow oil with a celery odour, ν max 3040, 3020, 2960, 2930, 2910, 1530, 1350 (NO_2), 910, 849, 800, 764, 730, 658 cm^{-1} . $\tau(\text{CCl}_4)$, 1.8-2.8 (m, 3H), 3.5-7.0 (m, 6H). Treatment with dichlorodicyano-p-benzoquinone (DDQ) (1 equivalent) in boiling benzene for half an hour gave some 1-nitronaphthalene. (Identified by TLC and i.r. comparison with an authentic sample.)
- ii) 3-nitrophenyl acetate (10%), m.p. 53°.

Oxidation of 1-aminobenzotriazole (2.5mmole.) in isoprene (10ml.) and methylene chloride (10ml.) at -20°.

The products were refluxed with maleic anhydride (1mmole.) in benzene (1ml.) for three hours. Basic alumina workup gave:

- i) Mixture of hydrocarbons.
- Treatment with potassium permanganate (100mg.) in "Analar" acetone (3ml.) for 0.75 hours, followed by filtration and evaporation of the acetone, gave a gummy residue. This residue was extracted with petrol to give 2-methylnaphthalene (18%), oil (crude), ν max 1650, 1608, 890, 851, 813, 743, 700 cm^{-1} . $\tau(\text{CCl}_4)$, 2.15-3.00 (m, 7H), 7.53 (s, 3H). picrate, yellow needles, m.p. 113-4° (lit. m.p. 115°).
- ii) 4-benzyl- Δ^4 -tetrahydrophthalic anhydride (4%), microcrystals, m.p. 80-3°, mixed m.p. 84-6°, (after sublimation) (lit.¹⁸ m.p. 85-86.5°), ν max 1845, 1780 (C = O), 1500, 1240, 988, 961, 935, 871, 831, 788, 750, 710 cm^{-1} .

Oxidation of 1-aminobenzotriazole (2.4mmole.) in 2,3-dimethylbutadiene (15ml.) and methylene chloride (20ml.) at -80°. Basic alumina.

- i) 2-benzyl-3-methylbutadiene (50%), sweet smelling oil, ν max 1608, 1500, 899, 752, 736, 720, 700 cm^{-1} .

Treatment with maleic anhydride (1.5mmole.) in boiling toluene (0.5ml.) for two-and-a-half hours gave:

4-benzyl-5-methyl- Δ^4 -tetrahydrophthalic anhydride (97%), prisms, m.p. 76-7° (from ether-petrol) (lit.¹⁸ m.p. 77-8°), ν max 1840, 1775 (C = O), 1700, 1600, 1237, 990, 965, 958, 940, 920, 803, 783, 758, 717 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.5-3.1 (m, 5H), 6.1-7.0 (m, 4H), 7.2-7.9 (m, 4H), 8.11 (s, 3H).

- ii) 1,4-dihydro-2,3-dimethylnaphthalene (15%) plates, m.p. 59.5-60° (after sublimation), (lit.¹⁸ m.p. 61.5-62.5°) ν max 1600, 740 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.86 (s, 4H), 6.58 (s, 4H), 8.20 (s, 6H).

Treatment with 10% palladium on charcoal at 150° for two hours gave 2,3-dimethylnaphthalene (50%), plates, m.p. 102° (from petrol) (lit.¹⁸ m.p. 99-101°), ν max 1650, 943, 865, 736 cm^{-1} .

Oxidation of 1-aminobenzotriazole (2.4mmole.) in 2,5-dimethylhexa-2,4-diene (20ml.) and methylene chloride (10ml.). Basic alumina.

- i) 2,5-dimethyl-3-phenylhexa-1,4-diene (48%), oil, ν max 3040, 3020, 2990, 2965, 1650, 1609, 1500, 895, 840, 753, 740, 702 cm^{-1} . $\tau(\text{CCl}_4)$, 2.88 (s, 5H), 4.4-4.7 (m, 1H), 5.10-5.25 (m, 2H), 5.9 (d, 1H, J 9 c/sec.), 8.27 (s, 3H), 8.30-8.47 (m, 6H).

Treatment with potassium permanganate (1.5g.) in "analar" acetone (30ml.) and pyridine (2ml.) for twenty-four hours gave, after acidification, ether extraction and chromatography on silica gel, benzoic acid (80%), m.p. 120°.

- ii) biphenylene (10%), m.p. 110°.

Oxidation of 1-aminobenzotriazole (2.2mmole.) in trans,trans-hexa-2,4-diene (1g.) and methylene chloride (5ml.). Basic alumina.

- i) cis-1,4-dihydro-1,4-dimethylnaphthalene (60%), oil, ν max 1520, 1500, 1090, 1070, 980, 958, 755 cm^{-1} . $\tau(\text{CCl}_4)$, 2.91 (s, 4H), 4.30 (d, 2H, J 2.5 c/sec.), 6.35-6.93 (m, 2H), 8.70 (d, 6H, J 7 c/sec.)

Treatment with 10% palladium on charcoal at 260° for five hours gave 1,4-dimethylnaphthalene (50%), oil, b.p. 260° (lit. b.p. $262-4^\circ$), ν max 1605, 1030, 827, 800, 780, 760, 700 cm^{-1} .

- ii) biphenylene (6%), m.p. 110° .

Oxidation of 1-aminobenzotriazole (2.2mmole.) in cis,trans-hexa-2,4-diene (1g.) and methylene chloride (5ml.). Basic alumina

- i) intractable mixture of 1:1 adducts (9%).
ii) biphenylene (70%), m.p. 110° .

Oxidation of 1-amino-5-methoxybenzotriazole (3.7mmole.) in trans,trans-hexa-2,4-diene (5ml.) and methylene chloride (15ml.).

Silica.

- i) mixture of cis-1,4-dihydro-1,4-dimethyl-6-methoxynaphthalene (45%) and 1,2 adducts (15%) (n.m.r. analysis), oil, ν max 3005, 2950, 2910, 2850, 2820, 1610, 1500, 815, 782, 750, 710, 670 cm^{-1} . $\tau(\text{CCl}_4)$ (1,4 adduct only), 2.9-3.5 (m, 3H), 4.29 (d, 2H, J 2.5 c/sec.), 6.36 (s, 3H), 8.73 (d, 3H, J 7 c/sec.), 8.78 (d, 3H, J 7 c/sec.).

Treatment with dichlorodicyano-p-benzoquinone (2 equivalents) in boiling benzene for one hour, gave, after chromatography on basic alumina:

1,4-dimethyl-6-methoxynaphthalene (10%), microblades, m.p. 45° (from ethanol-water) (lit.⁷⁰, oil, b.p. $156-8^\circ/12\text{mm.}$), (Found:

C, 83.6; H, 7.6. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%), ν max 1622, 1600, 1272, 1260, 1221, 1210, 910, 838, 820 cm^{-1} . $\frac{m}{e}$, 186 (P), 171, 143, 128. picrate, orange-red microcrystals, m.p. 107°, (from ethanol) (lit. 70 m.p. 107-8°), ν max 1630, 1600, 1530, 1342 (NO_2), 1275, 1260, 1221, 1210, 913, 845, 824, 775, 731, 721, 709, 689 cm^{-1} .

Oxidation of 1-amino-5-methoxybenzotriazole (3.7mmole.) in cis,trans-hexa-2,4-diene (5ml.) and methylene chloride (15ml.).

Silica.

mixture of 1,2 adducts (38%), oil, (purified by microdistillation),

(Found: C, 80.6; H, 8.6. $C_{13}H_{16}O$ requires C, 82.9; H, 8.6%), ν max 2955, 2920, 2830, 1610, 1590, 972, 920, 860, 820, 700 cm^{-1} . $\tau(CCl_4)$ 2.9-3.5 (m, 3H), 4.3-4.6 (m, 2H), 5.8-7.2 (m, 2H), 6.35 (s, 3H), 8.15-8.40 (m, 3H), 8.5-8.95 (m, 3H). $\frac{m}{e}$, 188 (P), 173, 158.

Oxidation of 1-amino-4-nitrobenzotriazole (3.2mmole.) in trans,trans-hexa-2,4-diene (5ml.) and methylene chloride (12ml.).

Silica.

mixture of 1,4-dihydro-1,4-dimethyl-5-nitronaphthalene (21%) and 1,2

adducts (42%) (n.m.r. analysis), oil, ν max 1610, 1590, 1530 (NO_2), 1452, 1352 (NO_2), 965, 924, 905, 809, 789, 762, 738 cm^{-1} . $\tau(CCl_4)$

(visible peaks of 1,4 adduct only) 4.20 (d, J 3 c/sec.), 8.79 (d, J 7 c/sec.).

Treatment with dichlorodicyano-p-benzoquinone (1.5 equivalents) in boiling benzene for two hours gave, after chromatography on basic alumina:

mixture of 1,2 adducts and 1,4-dimethyl-5-nitronaphthalene, oil, b.p.

62°/1mm. (purified by microdistillation), ν max 1608, 1590, 1535 (NO_2) 1450, 1348 (NO_2), 960, 920, 901, 825, 805, 789, 732 cm^{-1} . $\tau(CCl_4)$

(visible peaks of the naphthalene only), 7.35 (s), 7.56 (s).

Oxidation of 1-amino-4-nitrobenzotriazole (1.6mmole.) in cis,trans-hexa-2,4-diene (5ml.) and methylene chloride (12ml.).

Silica.

mixture of 1,2 adducts (60%), oil, b.p. 62°/1mm (purified by micro-distillation), (Found: C, 70.5; H, 6.4; N, 7.2. $C_{12}H_{13}NO_2$ requires C, 70.9; H, 6.5; N, 6.9%), ν max 1608, 1589, 1525 (NO_2), 1450, 1350 (NO_2), 960, 920, 902, 802, 788, 731 cm^{-1} . $\tau(CCl_4)$ 1.8-2.8 (m, 3H), 4.1-4.9 (m, 2H), 5.3-6.8 (m, 2H), 8.1-8.35 (m, 3H), 8.35-8.80 (m, 3H). $\frac{m}{e}$, 148, 146 (P = 203).

Oxidation of 1-aminobenzotriazole (4.1mmole.) in the presence of 1,4-diphenylbutadiene (10mmole.) in methylene chloride (40ml.).

Basic alumina.

biphenylene (33%), m.p. 112°.

Oxidation of 1-amino-7-nitrobenzotriazole (1.2mmole) in the presence of 1,4-diphenylbutadiene (3.1mmole.) in methylene chloride (30ml.). Silica.
3-nitrophenyl acetate (47%) (crude), i.r. identical to that of an authentic sample.

Oxidation of 1-aminobenzotriazole (2.7mmole.) in the presence of cis,cis-mucononitrile (7mmole.) in methylene chloride (20ml.). Silica.

i) biphenylene (41%), m.p. 110°.

ii) 2-acetoxibiphenylene (11%), yellow needles, m.p. 89-90° (after sublimation), ν max 1760 (C = O), 1210 (C-O-C), 750, 740, 691 cm^{-1} .

i.r. identical with that of an authentic sample supplied by

Dr. C.D. Campbell.

TABLE 2

1-AMINO- BENZO- TRIAZOLE	MMOLE TRIAZOLE	TRAP	YIELD OF ADDUCT	OTHER PRODUCTS
UNSUBST	2.3	VINYL ACETATE	6% ^b	biphenylene ^a 65%
5-CH ₃	2.9	DITTO	6% ^c	3- and 4-tolyl acetates ^d 12% 2,6- and 2,7-dimethyl- biphenylenes ^e 67%
5-CH ₃ O	1.8	DITTO	16% ^f	3- and 4-methoxyphenyl acetates ^g trace 2,6- and 2,7-dimethoxy- biphenylenes ^g 29%
5-Cl	2.5	DITTO	24% ^h	3- and 4-chlorophenyl acetates ^h 10% 2,6- and 2,7-dichloro- biphenylenes ^g 20% dichloro-1-phenyl- benzotriazoles ^g 6%
5-CF ₃	1.9	DITTO	39% ^j	2,6- and 2,7-bis(trifluoro- methyl)-biphenylenes ^g 17%
6-NO ₂	1.8	DITTO	32% ^k	—
4-NO ₂	0.84	DITTO	51% ^l	—
6-NO ₂	2.7	t-BUTYL ETHYLENE Z	17% ^m	3- and 4-nitrophenyl acetates ^g 20%
4-NO ₂	1.7	DITTO _Z	3% ⁿ	3-nitrophenyl acetate ^g 31%

TABLE 2 [continued]

1-AMINO-BENZO-TRIAZOLE	MMOLE TRIAZOLE	TRAP	YIELD OF ADDUCT	OTHER PRODUCTS
5-Cl	2.4	<i>t</i> -BUTYL ETHYLENE _z	2% ^p	3- and 4-chlorophenyl acetates ^g 10% 2,6- and 2,7-dichloro-biphenylenes ^g 23%
5-CF ₃	2.2	DITTO _z	0	3- and 4-trifluoromethyl-phenyl acetates ^g 3% 2,6- and 2,7-bis(trifluoro-methyl)-biphenylenes ^g 60%
4-NO ₂	1.7	INDENE	0	3-nitrophenyl acetate ^g 6%
4-NO ₂	1.7	<i>trans</i> -DICHLORO-ETHYLENE	0	3-nitrophenyl acetate ^g 31%
4-NO ₂	1.6	METHYL ACRYLATE	0	3-nitrophenyl acetate ^g 33%
6-NO ₂	2.7	METHYL METH-ACRYLATE	60% ^r	-
5-CH ₃ O	1.3	CYCLO-HEXENE	62% ^s	-
UNSUBST	2.3	<i>trans</i> -DICHLORO-ETHYLENE	0	biphenylene ^a 41%
UNSUBST	6.5	2,4,4-TRI-METHYLPEN-T-2-ENE	0	biphenylene ^a 39%
UNSUBST	2.6	DIPHENYL-CYCLO-PROPEN-ONE _x	0	biphenylene ^a 41% tolan ^{g,t} 6% phenyl acetate ^g 7%

SECTION 5

Oxidations of 1-aminobenzotriazoles in the presence of mono-enes.

All experiments were performed exactly in the way described for the oxidations with no benzyne trap. The olefin was used as the solvent, except where otherwise stated. Silica workup. All experiments are set out in Table 2.

Notes to Table 2.

- a) m.p. 110° .
- b) benzocyclobutenyl acetate, oil (purified by microdistillation), ν max 1740 (C = O), 1600, 1380, 1358, 1220 (C-O-C), 1045, 814, 753, 715, 708 cm^{-1} . This i.r. was identical to that of an authentic sample, supplied by Dr. C.D. Campbell.
- c) 4- and 5-methylbenzocyclobutenyl acetates (impure with tolyl acetates - ratio: estimated by n.m.r.), oil (purified by microdistillation), ν max 1735 (C = O), 1220 (C-O-C) cm^{-1} . $\tau(\text{CCl}_4)$, 2.7-3.4 (m, 3H), 4.19-4.32 (m, 1H), 6.5-7.0 (m, 2H), 7.70 (s, 3H), 8,10 (s, 3H).
these compounds were mixed with:
- d) 3- and 4-tolyl acetates (ratios estimated by n.m.r.), oil (purified by microdistillation), ν max 1760 (C = O), 1220 (C-O-C) cm^{-1} . $\tau(\text{CCl}_4)$, 2.7-3.4 (m, 4H), 7.70 (s, 3H), 7.86 (s, 3H).
- e) light yellow solid, m.p. $80-110^{\circ}$. Slow crystallisation from petrol gave a mixture of thin plates and large granules which could easily be mechanically separated to give:
 - i) 2,6-dimethylbiphenylene, light yellow granules, m.p. 140° (from petrol) (lit.⁷² m.p. $139-141^{\circ}$), ν max 1593, 1260, 1180,

- 1099, 1060, 1030, 980, 930, 899, 852, 820, 788 cm^{-1} .
- ii) crude 2,7-dimethylbiphenylene, very light yellow plates, m.p. 95-100° (from petrol) (lit.⁷² m.p. 110°), ν max 1260, 1103, 1060, 1035, 975, 933, 897, 872, 806, 740, 700 cm^{-1} .
- f) 4- and 5-methoxybenzocyclobutenyl acetates, oil, b.p. 50°/1mm. (purified by microdistillation), (Found: C, 68.8; H, 6.2. $\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C, 68.7; H, 6.3%), ν max 1735 (C = O), 1609, 1590, 1220 (C-O-C), 954, 905, 850, 828, 782, 765, 691 cm^{-1} . $\tau(\text{CCl}_4)$, 2.9-3.5 (m, 3H), 4.16-4.40 (m, 1H), 6.30 (s, 3H), 6.5-7.2 (m, 2H), 8.00 (s, 3H).
- g) identified by i.r. comparison with authentic samples.
- h) inseparable mixture, oil, b.p. 57°/1mm., consisting of
- i) 4- and 5-chlorobenzocyclobutenyl acetates, ν max 1732 (C = O), 1230 (C-O-C) cm^{-1} . $\tau(\text{CCl}_4)$ 2.6-3.2 (m, 3H), 4.15-4.35 (m, 1H), 6.48-7.10 (m, 2H), 7.98 (s, 3H). $\frac{m}{e}$ (^{35}Cl), 196 (P), 154, 153, 136, 128.
- ii) 3- and 4-chlorophenyl acetates, ν max 1768 (C = O), 1230 (C-O-C). $\tau(\text{CCl}_4)$ 2.6-3.2 (m, 4H), 7.80 (s, 3H). The relative amounts of these components in the mixture were estimated by n.m.r.
- j) 4- and 5-trifluoromethylbenzocyclobutenyl acetates, oil, b.p. 50°/1mm. (purified by microdistillation), (Found: C, 57.1; H, 4.1. $\text{C}_{11}\text{H}_9\text{O}_2\text{F}_3$ requires C, 57.5; H, 3.9%), ν max 1745 (C = O), 1615, 1235 (C-O-C), 1200, 1160, 1125 (C-F), 1065, 1050, 914, 895, 840, 815, 712, 680 cm^{-1} . $\tau(\text{CCl}_4)$, 2.3-2.9 (m, 3H), 4.1-4.3 (m, 1H), 6.1-7.0 (m, 2H), 7.98 (s, 3H).
- k) 4- and 5-nitrobenzocyclobutenyl acetates, yellow oil, b.p. 80°/1mm. (purified by microdistillation), (Found: C, 57.0; H, 4.5.

$C_{10}H_9NO_4$ requires C, 58.0; H, 4.4%), ν max 1740 (C = O), 1620, 1600, 1540, 1360 (NO_2), 1240 (C-O-C), 914, 880, 855, 822, 802, 744, 710 cm^{-1} . $\tau(CCl_4)$, 1.7-2.9 (m, 3H), 4.0-4.25 (m, 1H), 5.9-7.0 (m, 2H), 7.89 (s, 3H). $\frac{m}{e}$, 207 (P), 181, 165, 148, 147.

- 1) 3- and 6-nitrobenzocyclobutenyl acetates, gummy light yellow solid, ν max 1730 (C = O), 1525, 1350 (NO_2), 1220 (C-O-C), 974, 941, 928, 900, 860, 810, 791, 739, 691, 665 cm^{-1} . Ratio of components in mixture, 3-nitro: 6-nitro \approx 50 : 22 by n.m.r. analysis.

This mixture was crystallised from petrol, giving:

3-nitrobenzocyclobutenyl acetate, light yellow prisms, m.p. $84-5^\circ$, (Found: N, 6.8. $C_{10}H_9NO_4$ requires N, 6.8%). $\tau(CCl_4)$; from mixture), 1.8-2.6 (m, 3H), 3.5-3.8 (m, 1H), 5.9-7.0 (m, 2H), 7.89 (s, 3H). $\frac{m}{e}$, 207 (P), 165, 147.

6-nitrobenzocyclobutenyl acetate could not be obtained pure, $\tau(CCl_4)$; from mixture) 7.69 (s).

- m) 1-t-butyl-4-nitrobenzocyclobutene and 1-t-butyl-5-nitrobenzocyclobutene, yellow oil, b.p. $75^\circ/1\text{mm}$. (purified by microdistillation), ν max 2940, 1603, 1590, 1535, 1345 (NO_2), 900, 862, 844, 835, 818, 745, 723 cm^{-1} . $\tau(CCl_4)$, 1.7-3.0 (m, 3H), 6.0-7.2 (m, 3H), 9.0 (s, 9H). $\frac{m}{e}$, 205 (P), 190, 188, 149. A satisfactory analysis could not be obtained for this compound.

- n) 1-t-butyl-3-nitrobenzocyclobutene and 1-t-butyl-6-nitrobenzocyclobutene, yellow oil, b.p. $75^\circ/1\text{mm}$. (purified by microdistillation), ν max 2950, 1603, 1599, 1540, 1350 (NO_2), 983, 900, 872, 811, 804, 745, 711 cm^{-1} . $\frac{m}{e}$, 205 (P), 149.

- p) 1:1 adduct, oil, ν max 2965, 2940, 2900, 2875, 1590, 900, 870, 837, 810, 737, 703 cm^{-1} . $\frac{m}{e}$ (^{35}Cl), 194 (P), 179.

- r) 1-carboxymethyl-1-(3-nitrobenzyl)-ethylene and 1-carboxymethyl-1-(4-nitrobenzyl)-ethylene, yellow oil, b.p. $85^{\circ}/1\text{mm.}$ (purified by microdistillation), (Found: C, 59.7; H, 4.9; N, 6.5. $\text{C}_{11}\text{H}_{11}\text{NO}_4$ requires C, 59.7; H, 5.0; N, 6.3%), ν max 2980, 1725 (C = O), 1637, 1605, 1540, 1360 (NO_2), 1210, 1150, 1000, 965, 865, 830, 745, 720, 680 cm^{-1} . $\tau(\text{CCl}_4)$, 1.7-2.8 (m, 4H), 3.73 (s, 1H), 4.39 (s, 1H), 6.30 (s, 5H).
- s) intractable mixture of 1:1 adducts, oil, ν max 3004, 2915, 2840, 2820, 1650, 1612, 1584, 895, 880, 845, 822, 800, 760, 750, 725, 715, 695, 665, 643 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.7-3.3 (m, 4H), 4.0-9.0 (m, ~ 9H). Treatment with 10% palladium on charcoal at 220° for two hours gave a yellow oil which crystallised from petrol to give 4-methoxybiphenyl (10%), m.p. 88° (after sublimation), mixed m.p. 89° (lit. m.p. 90°).
- t) yield based on diphenylcyclopropenone.
- x) diphenylcyclopropenone (15mmole.) was dissolved in methylene chloride (25ml.)
- z) t-butylethylene (5ml.) and methylene chloride (10ml.) used as solvent.

SECTION 6

Oxidation of 1-aminobenzotriazoles in the presence of acetylenes.

The procedure used was identical to that used for mono-enes.

Silica workup.

Oxidation of 1-aminobenzotriazole (2.2mmole.) in methylene chloride (5ml.) and hex-1-yne (8g.).

- i) 1-phenylhexa-1,2-diene (13%), unstable colourless oil, ν max 1970 (C=C=C), 1610, 1510, 1080, 1037, 970, 939, 780, 750, 695 cm^{-1} . $\tau(\text{CCl}_4)$, 2.80 (s, 5H), 3.75-4.05 (quintet, 1H), 4.20-4.65 (quartet, 1H, J 6.5 c/sec.), 7.6-9.2 (m, 7H). The i.r. of this compound was almost identical to that of 1-phenylhepta-1,2-diene, supplied by Prof. H.J. Bestmann.

The above compound was treated with bromine in carbon tetrachloride to yield 1-phenyl-1,2,2,3-tetrabromohexane, oil, ν max 1500, 790, 700 cm^{-1} . $\tau(\text{CCl}_4)$ 2.64 (s, 5H), 8.4-9.5 (m, 9H).

$\frac{m}{e}$ (^{79}Br), 474 (P). A satisfactory analysis could not be obtained for this compound.

- ii) biphenylene (43%), m.p. 110°.

Oxidation of 1-aminobenzotriazole (5.2mmole.) in methylene chloride (10ml.) and hept-1-yne (10ml.)

- i) 1-phenylhepta-1,2-diene (8%), oil, ν max 1940 (C=C=C), 1590, 911, 877, 771, 690 cm^{-1} . $\tau(\text{CCl}_4)$, 2.82 (s, 5H), 3.88-4.1 (quintet, 1H), 4.3-4.7 (quartet, 1H, J 6.5 c/sec.), 7.5-9.5 (m, 9H). The i.r. of this compound was superimposable upon that of an authentic sample supplied by Prof. H.J. Bestmann.

- ii) biphenylene (41%), m.p. 110°.

iii) phenyl acetate (2%).

Oxidation of 1-aminobenzotriazole (3.7mmole.) in methylene chloride (10ml.) and methyl acetylene (8g.) at -80° .

i) biphenylene (61%), m.p. 110° .

ii) phenyl acetate (4%).

Oxidation of 1-aminobenzotriazole (3.0mmole.) in methylene chloride (3ml.) and 1,4-dichlorobut-2-yne (3ml.)

i) biphenylene (47%), m.p. 110° .

ii) phenyl acetate (5%).

Oxidation of 1-amino-6-nitrobenzotriazole (2.8mmole.) in methylene chloride (10ml.) and hex-1-yne (8g.).

1-(3-nitrophenyl)-hexa-1,2-diene and 1-(4-nitrophenyl)-hexa-1,2-diene

(56%), unstable rose oil with an apricot odour, ν max 1960 (C=C=C), 1600, 1540, 1360 (NO_2), 1118, 875, 820, 735, 680 cm^{-1} . $\tau(\text{CCl}_4)$, 1.8-2.8 (m, 4H), 3.7-3.95 (quintet, 1H), 4.1-4.5 (quartet, 1H, J 6.5 c/sec.) 7.5-9.2 (m, 7H).

Treatment of this oil with bromine in carbon tetrachloride gave the dibromo derivative, light yellow oil, b.p. $140^{\circ}/1\text{mm}$. (purified by microdistillation) (Found: N, 3.9. $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{Br}_2$ requires N, 3.9%), ν max 1600, 1540, 1360 (NO_2), 1110, 890, 870, 830, 815, 755, 740, 700 cm^{-1} . $\tau(\text{CCl}_4)$, 1.5-3.0 (m, 4H), 5.0-5.5 (m, 2H), 7.5-9.3 (m, 7H), $\frac{m}{e}$ (^{79}Br), 361 (P), 281, 280, 203, 202.

Oxidation of 1-amino-6-nitrobenzotriazole (2.8mmole.) in methylene chloride (30ml.) and tolan (diphenyl acetylene) (6mmole.)

i) tolan (100% recovery).

ii) 2,6- and 2,7-dinitrobiphenylene (2.5%). Identical by i.r. comparison with the mixture prepared on p. 40.

SECTION 7

Oxidation of 1-aminobenzotriazoles in the presence of ethers and alcohols.

The procedure used was identical to that used for mono-enes. The ether or alcohol was used as the solvent. Silica workup.

Oxidation of 1-aminobenzotriazole (2.4mmole.) in diethyl ether (40ml.)

- i) biphenylene (39%), m.p. 110°.
- ii) phenyl acetate (27%).

Oxidation of 1-amino-5-methoxybenzotriazole (1.8mmole.) in diethyl ether (80ml.).

- i) 2,6- and 2,7-dimethoxybiphenylenes (29%). Identical with other samples by i.r. comparison.
- ii) 3- and 4-ethoxyanisoles (1%), liquid mixture, identified by i.r. comparison with the mixture obtained from the oxidation of the same precursor in ethanol.
- iii) 3- and 4-acetoxyanisoles (5%). Identified by i.r. comparison with previous samples.

Oxidation of 1-amino-5-chlorobenzotriazole (1.8mmole.) in diethyl ether (30ml.).

- i) 2,6- and 2,7-dichlorobiphenylenes (17%), identical, by i.r. comparison, with previous samples.
- ii) 3- and 4-chlorophenyl acetates (1%), identical by i.r. comparison, with previous samples.

Oxidation of 1-amino-5-trifluoromethylbenzotriazole (1.0mmole.) in diethyl ether (30ml.)

- i) 2,6- and 2,7-bis(trifluoromethyl)-biphenylene (23%), identical, by i.r. comparison, with previous samples.
- ii) 3- and 4-trifluoromethylphenyl acetates (5%), identical, by i.r. comparison, with previous samples.
- iii) light yellow oil (5mg.), ν max 1623, 1320, 1160, 1120, 1060, 1010, 895, 848, 795, 740, 699, 685, 650 cm^{-1} .

Oxidation of 1-amino-4-nitrobenzotriazole (1.6mmole.) in diethyl ether (20ml.).

- i) 3-nitrophenetole (45%), needles, m.p. 32° (from petrol) (lit. m.p. 34°), ν max 1618, 1580, 1525, 1350 (NO_2), 1288, 1252, 1112, 1098, 1044, 998, 959, 870, 825, 810, 790, 740, 670 cm^{-1} . $\tau(\text{CCl}_4)$, 2.0-3.0 (m, 4H), 5.89 (quartet, 2H, J 6.5 c/sec.), 8.55 (t, 3H, J 6.5 c/sec.).
- ii) 3-nitrophenyl acetate (16%), m.p. 53° .

Oxidation of 1-amino-4-nitrobenzotriazole (1.3mmole.) in tetrahydrofuran (10ml.).

4-(m-nitrophenoxy)-butyl acetate (64%), light yellow oil, b.p.

$120^{\circ}/1\text{mm.}$ (purified by microdistillation), (Found: C, 57.3; H, 6.0; N, 5.3. $\text{C}_{12}\text{H}_{15}\text{NO}_5$ requires C, 56.9; H, 6.0; N, 5.5%), ν max 1750 (C = O), 1640, 1600, 1545, 1360 (NO_2), 1250, 1200, 1050, 930, 870, 820, 804, 743 cm^{-1} . $\tau(\text{CCl}_4)$, 1.9-2.9 (m, 4H), 5.6-6.7 (m, 4H), 7.97 (s) and 7.80-8.50 (m) (total: 7H), $\frac{m}{e}$, 253 (P), 219, 181, 139, 115.

Oxidation of 1-amino-6-nitrobenzotriazole (1.8mmole.) in ethanol (50ml.).

3-nitrophenetole and 4-nitrophenetole (mixture) (43%) light yellow oil, identical to authentic samples by i.r. comparison, g.l.c., and n.m.r.

Oxidation of 1-amino-5-methoxybenzotriazole (1.2mmole.) in ethanol (30ml.)

3-ethoxyanisole and 4-ethoxyanisole (mixture) (57%), oil, shown by solution i.r. (CHCl_3) and n.m.r. to be a mixture of 3-ethoxy and 4-ethoxy in the ratio $1 : 1.24 \pm 0.06$.

SECTION 8

Generation of arynes in the presence of bromotrichloromethane.

Oxidation of 1-aminobenzotriazole in bromotrichloromethane.

1-Aminobenzotriazole (6mmole.) was suspended in bromotrichloromethane (10ml.) and lead tetra-acetate (9mmole.) added with stirring. After the exothermic reaction had subsided, glycerol (7 drops) was added, and the solution was stirred for 10 minutes. Ether (100ml.) was added, and the lead salts were filtered off. The organic filtrate was evaporated off, and the oily residue chromatographed on silica gel to give:

- i) hexachloroethane (10%), needles, subliming at 180° , ν max 790, 753, 684 cm^{-1} . i.r. identical to that of an authentic sample supplied by Dr. R.C. Storr.
- ii) 2-bromobenzotrichloride (12-13%), oil, b.p. $80^{\circ}/1\text{mm.}$ (purified by microdistillation) (Found: C, 30.7; H, 1.5. $\text{C}_7\text{H}_4\text{Br Cl}_3$ requires C, 30.6; H, 1.5%), ν max 1581, 1567, 1461, 1435, 1423, 1277, 1183, 1168, 1122, 1044, 1032, 868, 823, 783, 738, 696, 671 cm^{-1} . $\tau(\text{CCl}_4)$, 1.5-3.0 (m).
A sample was treated with concentrated sulphuric acid for twelve hours. Hydrogen chloride was evolved, and, after pouring onto ice, a white solid separated and was filtered off. This was 2-bromobenzoic acid, needles, m.p. and mixed m.p. $148-9^{\circ}$ (from ether-petrol) (lit. m.p. 150°).
- iii) 2,2'-dibromobiphenyl (6-13%), needles, m.p. 74° (after sublimation) (lit. m.p. 81°) (Found: C, 46.1; H, 2.6. $\text{C}_{12}\text{H}_8\text{Br}_2$ requires C, 46.2; H, 2.6%), ν max 1050, 1032, 1010, 770, 730, 675, 658 cm^{-1} . $\frac{m}{e}$ (^{79}Br), 310 (P), 266, 231.
- iv) biphenylene (10-18%), m.p. 110° .
- v) phenyl acetate (4%).

- vi) 2-bromobenzoic acid (1%), needles, m.p. and mixed m.p. $148-9^{\circ}$
(from ether-petrol) (lit. m.p. 150°).

Decomposition of benzenediazonium chloride 2-carboxylic acid in
bromotrichloromethane in the presence of propylene oxide.

- a) Anthranilic acid (20mmole.) was suspended in ethanol (30ml.) and hydrochloric acid (36%; 2.0ml.) was added. Amyl nitrite (25mmole.) was added at 0° , and the reaction mixture stirred at 0° for 15 minutes. The solution was diluted with ether, and the brown-pink diazonium salt (80%) was filtered off.
- b) The diazonium salt (15mmole.) was suspended in bromotrichloromethane (30ml.), containing propylene oxide (3.0g.) and trichloroacetic acid (1 crystal). The reaction mixture was rapidly heated to 80° , and stirred at this temperature for 0.75 hour, by which time the gas evolution had ceased. The solvents were evaporated off, and the gummy residue was chromatographed on silica gel to give:
- i) hexachloroethane (5%).
- ii) 2-bromobenzotrichloride (trace) - identified by i.r. comparison with previous sample.
- iii) colourless oil (400mg.), ν max 1589, 1575, 1280, 1250, 1055, 1035, 830, 750, 704 cm^{-1} . $\tau(\text{CCl}_4)$, 2.4-3.5 (m, 4H), 5.0-7.3 (m, 3H), 8.0-9.0 (m, 3H). $\frac{m}{e}$ (^{79}Br , ^{35}Cl), 330 (BrCl_3 pattern), 291, 172.
- iv) 2-chlorobenzoic acid (12%), long needles, m.p. 140° (from petrol (60-80)) (lit. m.p. 142°) ν max 3200 - 2000 (-OH), 1689 (C = O), 1054, 1047, 916, 816, 793, 746, 713, 685, 646 cm^{-1} .

Decomposition of benzenediazonium 2-carboxylate in
benzene-bromotrichloromethane-carbon tetrachloride.

Benzenediazonium 2-carboxylate (c. 2.0mmole.), prepared by the method of Wasserman and Solodar⁷³, was slurried in carbon tetrachloride (5ml.) and poured into a boiling mixture of benzene (10ml.) and bromotrichloromethane (10ml.). After 0.5 hour, the reaction mixture was cooled, and the solvents stripped off, and the residual tar chromatographed on silica gel to give 2-chlorobenzoic acid (2%), long needles, mp.p 141-2° (from petrol (60-80)) (lit. m.p. 142°).

Oxidation of 1-amino-5-methoxybenzotriazole in bromotrichloromethane.

1-Amino-5-methoxybenzotriazole (1.8mmole.) was suspended in bromotrichloromethane (5ml.) and lead tetra-acetate (2.7mmole.) was added with stirring. After the evolution of gas had ceased (c. 15 minutes), glycerol (4 drops) was added, and the reaction mixture was stirred for a further 10 minutes. Ether (100ml.) was added, and the lead salts were filtered off. The organic filtrate was evaporated to dryness and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (10%).
- ii) 4- and 5-methoxy-2-bromobenzotrichlorides (12%), oil, b.p. 80°/1mm., ν max 1600, 1570, 1300, 1250, 1233, 1040, 1030, 950, 880, 865, 845, 810, 775, 693, 645 cm^{-1} . $\tau(\text{CCl}_4)$, 2.1-3.4 (m, 3H), 6.20 (s) and 6.24 (s) (total: 3H), $\frac{m}{e}$ (^{79}Br , ^{35}Cl), 302 (P), 267.

A satisfactory analysis could not be obtained for this mixture.

- iii) 4- and 5-acetoxyanisoles (9%)
- iv) 2-bromo-4-methoxybenzoic acid (2%), needles, m.p. 196°
 (from petrol [60-80]) (lit. m.p. 199°), (Found: C, 41.5;
 H, 2.9. $C_8H_7BrO_3$ requires C, 41.5; H, 3.0%), ν max 1699
 (C = O), 1600, 1568, 1300, 1248, 1041, 1037, 887, 877, 870,
 842, 830, 775 cm^{-1} .

Oxidation of 1-amino-4-nitrobenzotriazole in bromotrichloromethane.

1-Amino-4-nitrobenzotriazole (2.2mmole.) was suspended in bromotrichloromethane (10ml.) and lead tetra-acetate (3.1mmole.) was added with stirring. After gas evolution had ceased (c. 2 hours), glycerol (4 drops) was added and the solution was stirred for a further 20 minutes. Ether (100ml.) was added, and the lead salts were filtered off. The organic filtrate was evaporated to dryness, and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (trace).
- ii) 3-nitrophenyl acetate (34%), m.p. $53-4^{\circ}$.
- iii) 2-bromo-3-nitrophenyl acetate (8%), light yellow tablets, m.p. 70° (from petrol [60-80]), (Found: C, 36.4; H, 2.6; N, 5.2. $C_8H_6NO_4Br$ requires C, 36.9; H, 2.3; N, 5.4%), ν max 1790 (C = O), 1595, 1540, 1365. (NO_2), 1290, 1255, 1190 (C-O-C), 1049, 1020, 959, 920, 872, 830, 799, 742, 719, 709 cm^{-1} . $\tau(CCl_4)$, 2.2-2.9 (m, 3H), 7.69 (s, 3H). $\frac{m}{e}$ (^{79}Br), 259 (P), 217.

Oxidation of 1-amino-4-nitrobenzotriazole in bromotrichloromethane and methylene chloride, using nickel peroxide as oxidant.

1-Amino-4-nitrobenzotriazole (2.2mmole.) was suspended in a mixture of bromotrichloromethane (10ml.) and methylene chloride (10ml.). Nickel peroxide (2.0g.; finely ground) and anhydrous

sodium sulphate (1.0g.) were added, and the mixture was stirred until the gas evolution had ceased (c. 20 minutes). Ether (100ml.) was added, and the inorganic material was filtered off. The organic filtrate was evaporated, and the residual oil was chromatographed on silica gel to give:

- i) 3-nitrochlorobenzene (18%), light yellow needles, m.p. and mixed m.p. 40° (lit. m.p. 46°).
- ii) 2,3-dibromonitrobenzene (1%), m.p. and mixed m.p. 76° (lit. m.p. 85°), i.r. identical with previous sample.

Oxidation of 1-aminobenzotriazole in bromotrichloromethanebenzene.

1-Aminobenzotriazole (4.5mmole.) was suspended in a mixture of bromotrichloromethane (10ml.) and benzene (10ml.) and lead tetraacetate (6.8mmole.) was added with stirring. After the exothermic reaction had subsided, glycerol (4 drops) was added and the solution stirred for a further 10 minutes. Ether (100ml.) was added, and the lead salts were filtered off. The organic filtrate was evaporated, and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (2%).
- ii) 2-bromobenzotrichloride (16%)
- iii) biphenylene (15%). m.p. 110° .
- iv) 2,2'-dibromobiphenyl (15%), m.p. 74° .
- v) phenyl acetate (10%).

Oxidation of 1-aminobenzotriazole in bromotrichloromethane in the presence of tetracyclone.

1-Aminobenzotriazole (3.0mmole.) was suspended in bromotrichloromethane (10ml.) and tetracyclone (5mmole.) was added. Lead tetraacetate (4.5mmole.) was added with stirring. When the exothermic

reaction had subsided, glycerol (5 drops) was added, and the reaction mixture was stirred for a further 10 minutes. Ether (100ml.) was added and the lead salts were filtered off. The organic filtrate was evaporated, and the purple residue was chromatographed on silica gel to give:

- i) 2-bromobenzotrichloride (1%).
- ii) biphenylene (1%). m.p. 110° .
- iii) 1,2,3,4-tetraphenylnaphthalene (64%), m.p. $201-2^{\circ}$.
- iv) tetracyclone (10% recovery)

Oxidation of 1-aminobenzotriazole in bromotrichloromethane-ether.

1-Aminobenzotriazole (3.7mmole.) was dissolved in a mixture of diethyl ether (20ml.) and bromotrichloromethane (10ml.). Lead tetra-acetate (5.2mmole.) was added with stirring. After the vigorous reaction had ceased, glycerol (6 drops) was added, and the reaction mixture was stirred for a further 10 minutes. Ether (50ml.) was added, and the lead salts were filtered off. The organic filtrate was evaporated, and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (trace).
- ii) 2-bromobenzotrichloride (5%).
- iii) biphenylene (5%), m.p. 110° .
- iv) 2,2'-dibromobiphenyl (5%), m.p. 74° .
- v) 2-bromophenetole (16%), oil, ν max 1590, 1570, 1290, 1275, 1246, 1054, 1039, 925, 799, 748, 710, 660cm^{-1} . $\tau(\text{CCl}_4)$, 2.4-3.5 (m, 4H), 6.00 (quartet, 2H, J 6.5 c/sec.), 8.59 (t, 3H, J 6.5 c/sec.). Identical with an authentic sample by i.r. comparison.

Decomposition of 1,2,3-benzothiadiazole-1,1-dioxide in bromotrichloromethane-ether.

1,2,3-Benzothiadiazole-1,1-dioxide (4.7mmole.; supplied by Mr. F. Graveling) was added in diethyl ether (10ml.) to bromotrichloromethane (10ml.) at 40°. After the evolution of gas had ceased (c. 5 minutes), the reaction mixture was evaporated, and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (trace).
- ii) 2-bromobenzotrichloride (trace).
- iii) 2-bromophenetole (90%).

Oxidation of 1-aminobenzotriazole in bromotrichloromethane with N-bromosuccinimide (NBS).

1-Aminobenzotriazole (3mmole.) was suspended in bromotrichloromethane (10ml.) and NBS (6mmole.) was added with stirring. After the evolution of gas had ceased (c. one hour), the reaction mixture was filtered to remove most of the succinimide, and the organic filtrate was evaporated. The residual oil was chromatographed on silica gel to give o-dibromobenzene (51%), oil, identical with an authentic sample by i.r. comparison.

Oxidation of 1-aminobenzotriazole in bromotrichloromethane-ethyl iodide.

1-Aminobenzotriazole (3mmole.) was dissolved in a mixture of ethyl iodide (50ml.) and bromotrichloromethane (8.5ml.), and lead tetraacetate (4.5mmole.) was added with stirring. When the gas evolution had ceased (c. 5 minutes), glycerol (4 drops) was added, and the reaction mixture was stirred for a further ten minutes, and then filtered. The organic filtrate was evaporated to dryness, and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (~ 10%)
- ii) iodine (trace)
- iii) 2-bromobenzotrichloride (19%)
- iv) biphenylene (32%), m.p. 110°
- v) 2,2'-dibromobiphenyl (18%), m.p. 75°
- vi) phenyl acetate (4%)
- vii) 2-bromobenzoic acid (2%), m.p. 148-9°.

Oxidation of 1-aminobenzotriazole in bromotrichloromethane-t-butylethylene-benzene.

1-Aminobenzotriazole (3mmole.) was suspended in a mixture of t-butylethylene (8ml.), bromotrichloromethane (8ml.) and benzene (15ml.). Lead tetra-acetate (4.5mmole.) was added with stirring. When gas evolution had ceased (c. 15 minutes), glycerol (5 drops) was added, and the reaction mixture stirred for a further 30 minutes. Ether (100ml.) was added, and the lead salts were filtered off. The organic filtrate was evaporated, and the residual oil was chromatographed on silica gel to give:

- i) hexachloroethane (trace)
- ii) (100mg.), oil, b.p. 100°/1mm.
(purified by microdistillation) (Found: C, 30.1; H, 4.5.
 $C_6H_{12}Br_2$ requires C, 29.6; H, 4.9%), ν max 1473, 1462, 1368,
1149, 961, 893, 800, 779, 735, 700, 648 cm^{-1} .
- iii) 2-bromobenzotrichloride (7%)
- iv) biphenylene (26%), m.p. 110°
- v) 2,2'-dibromobiphenyl (16%), m.p. 74°
- vi) 2-bromobenzoic acid (5%), m.p. 148-9°

SECTION 9

Reactions of 1-aminobenzotriazoles in the presence of silver perchlorate or mercuric acetate.

a) With silver perchlorate.

Preparation of the 1:1 complex of 1-aminobenzotriazole and silver perchlorate.

1-Aminobenzotriazole (0.38mmole.) was dissolved in warm benzene (12ml.) and silver perchlorate (0.38mmole.) was added in benzene (5ml.).

The resulting white precipitate was filtered off to yield the amorphous 1:1 complex of 1-aminobenzotriazole and silver perchlorate (100%), m.p. (slow heating) 210° (dec.), detonation point (fast heating) $\sim 300^{\circ}$. (Found: C, 20.8; H, 2.0; N, 15.9. $C_6H_6N_4O_4AgCl$ requires C, 21.1; H, 1.8; N, 16.4%), ν max 3500, 3370, 3300, 3170, (NH_2) , 789, 768, 760.

Pyrolysis of the 1:1 complex of 1-aminobenzotriazole and silver perchlorate in the presence of tetracyclone.

The complex (1.5mmole.) was dissolved in dimethyl formamide (25ml.) and tetracyclone (4.0mmole.) was added. The solution was refluxed at 156° for three hours, and then poured into water (500ml.). The aqueous solution was extracted with ether (300ml.). The organic layer was dried, and evaporated. The residual purple solid was chromatographed on basic alumina to give:

- i) 1,2,3,4-tetraphenylnaphthalene (2%), m.p. $199-200^{\circ}$
- ii) tetracyclone (80% recovery)
- iii) yellow solid (160mg.), m.p. $77-80^{\circ}$, ν max 1703 (C = O), 1636, 1125, 1067, 1020, 740, 688 cm^{-1} .

Preparation of the 1:1 complex of 1-amino-6-nitrobenzotriazole and silver perchlorate.

1-Amino-6-nitrobenzotriazole (0.56mmole.) was dissolved in a mixture of chloroform (1ml.) and benzene (10ml.), and silver perchlorate (0.56mmole.) in benzene (5ml.) was added. The buff precipitate was filtered off to give the 1:1 complex of 1-amino-6-nitrobenzotriazole and silver perchlorate (95%), buff amorphous solid, m.p. (slow heating) 80-190° (dec.), detonation point (fast heating) ~ 280°. (Found: C, 25.7; H, 2.3; N, 16.7. $C_6H_5O_5AgCl \cdot \frac{1}{2}C_6H_6$ requires C, 25.4; H, 1.9; N, 16.3%), ν max 3450, 3300, 3200 (NH₂), 1640, 1540, 1350 (NO₂), 821, 802, 783, 740, 691 cm⁻¹.

Oxidation of 1-aminobenzotriazole in the presence of silver perchlorate.

1-Aminobenzotriazole (2.3mmole.) and silver perchlorate (0.5mmole.) were stirred in benzene (50ml.) and heated to 45°. Lead tetra-acetate (2.8mmole.) was then added. After gas evolution had ceased, the solution was filtered, and, after evaporation, the residue was chromatographed on basic alumina to give biphenylene (9%), m.p. 110°, as the only identifiable product.

b) With mercuric acetate.

Oxidation of 1-aminobenzotriazole in methylene chloride in the presence of mercuric acetate.

1-Aminobenzotriazole (3.7mmole.) was dissolved in methylene chloride (100ml.) and mercuric acetate (17mmole.) added. The suspension was stirred for one hour to effect solution of most of the mercuric acetate. Lead tetra-acetate (5.2mmole.) was then added. When the evolution of gas had ceased (c. 2 minutes), glycerol (4 drops) was added, and the mixture was stirred for a further 10 minutes. Ether

(150ml.) was added, and the inorganic residue was filtered off. The filtrate was evaporated, and the gummy residue was chromatographed on silica gel to give:

- i) colourless needles with a green fluorescence (120mg.), m.p. $144-5^{\circ}$ (from ether-petrol), (Found: C, 21.1; H, 1.4%; M.W. 429 (osmometer)), ν_{\max} 1416, 1267, 1250, 1110, 1100, 1029, 1020, 1010, 943, 742, 712 cm^{-1} . $\frac{m}{e}$ (^{35}Cl , ^{202}Hg), 440, 424, 392, 313, 202, 111 (base peak). Beilstein test positive.
- ii) intractable mixture of organo-mercury compounds (c. 200 mg.).

Oxidation of 1-aminobenzotriazole in acetic acid in the presence of mercuric acetate.

1-Aminobenzotriazole (2.6mmole.) was dissolved in glacial acetic acid (50ml.) and mercuric acetate (12mmole.) added. Lead tetra-acetate (4.0mmole.) was then added. When the evolution of gas had ceased (c. 2 minutes), ether (100ml.) was added, and the reaction mixture was filtered. The filtrate was evaporated to dryness, and the grey gummy residue was extracted with boiling benzene. The benzene extract was evaporated to dryness to yield a colourless gum, which was chromatographed on silica gel to give colourless blades (25mg.), m.p. 167° (from ether-petrol), (Found: C, 24.4; H, 1.7; N, 0.0%), ν_{\max} 1750 (C = O), 1246, 1204, 1066, 1045, 1020, 952, 925, 866, 830, 755, 716 cm^{-1} . $\frac{m}{e}$ (^{202}Hg), 464, 422, 295, 202, 135 (base peak).

Oxidation of 1-aminobenzotriazole in acetic acid-benzene in the presence of mercuric acetate.

1-Aminobenzotriazole (3.7mmole.) was dissolved in a mixture of benzene (30ml.) and glacial acetic acid (3ml.), and mercuric acid (10mmole.) was added. The solution was refluxed for 10 minutes to

effect solution of some of the mercuric acetate. Lead tetra-acetate (5.0mmole.) was then added to the hot solution. When gas evolution had ceased (c. 2 minutes), the reaction mixture was filtered, and the filtrate evaporated to yield a colourless gum, which was chromatographed on silica gel to give long feathery needles (80mg.), m.p. 161-2° (from petrol (60-80)), (Found: C, 37.0; H, 2.4%), ν max 1572, 1422, 1071, 1028, 1000, 939, 904, 765, 717, 693 cm^{-1} . $\tau(\text{CDCl}_3)$, 2.52 (s). $\frac{m}{e}$ (^{202}Hg), 482, 436, 355, 280, 202, 153 (base peak).

SECTION 10

Miscellaneous preparations

1. 4-Benzyl- Δ^4 -tetrahydrophthalic anhydride and triphenylene¹⁸.

Dry magnesium turnings (125mg.-atoms) were placed in a 3-necked 500ml. flask fitted with a magnetic stirrer, a condensor and a dropping funnel. Dry tetrahydrofuran (60ml.) was added, together with one drop of 2-fluorobromobenzene. The reaction mixture was stirred, and isoprene (200mmole.; stabilised with hydroquinone) was added. A mixture of 2-fluorobromobenzene (120mmole.) and isoprene (400mmole.) was added dropwise over about one hour. The mixture was then refluxed for a further 45 minutes on a water bath, cooled, and decanted into a slurry of ice (300g.) and concentrated hydrochloric acid (100ml.). The resulting solution was thoroughly extracted with ether (5 \times 100ml.), and the combined ether extracts were dried. The ether was then evaporated on a water bath to leave a yellow oily mass, which was transferred to a distillation apparatus and distilled at 25m.m pressure. The fraction, which distilled at 80-120^o, was collected as a colourless oil (8g.).

The oil (8g.) was then diluted with benzene (1ml.), and maleic anhydride (20mmole.) added, together with one crystal of hydroquinone. The mixture was then refluxed for four hours, and then allowed to cool, when a white solid crystallised out. The reaction mixture was filtered and the white solid (743mg.) was discarded. The filtrate was evaporated, and the residual oil was chromatographed on silica gel. Elution with petrol afforded a hydrocarbon fraction. Elution with ether gave 4-benzyl- Δ^4 -tetrahydrophthalic anhydride

(5.0g.; 17%), m.p. 86-7° (lit.¹⁸ 85-86.5°). The residue from the distillation was chromatographed on basic alumina. Elution with petrol gave a hydrocarbon fraction (3g.), followed by triphenylene (124mg.; 1.4%), m.p. and mixed m.p. 192-6°.

2. trans,trans-1,4-Diphenylbutadiene.

- a) Triphenyl phosphine (25mmole.) was dissolved in benzene (50ml.) and benzyl bromide (30mmole) was added. The solution was refluxed on a water bath for two hours under nitrogen. The solution was then cooled, and filtered to give benzyltriphenylphosphonium bromide (92%).
- b) Sodium metal (180mg.-atoms) was dissolved in methanol (dry; 100ml.) and benzyltriphenylphosphonium bromide (20mmole.) was added with stirring. Cinnamaldehyde (30mmole.) in methanol (dry; 30ml.) was added over a period of 3 minutes, and the reaction mixture was left to stand for three hours. The white precipitate was filtered off, and recrystallised from glacial acetic acid to give trans,trans-1,4-diphenylbutadiene (40%).

3. 2,3-Dimethylbutadiene⁷⁴.

Anhydrous pinacol (200mmole.) was heated in a Claisen flask with aqueous hydrogen bromide (50/50 w/w; 0.2ml.). All fractions boiling below 95° were collected, and, upon standing, the combined fractions separated into two layers. The lower (aqueous) layer was discarded, and the upper layer was redistilled from a Claisen flask to give:

- i) 2,3-dimethylbutadiene (69%), b.p. 69-70°.
- ii) pinacolone (10%), b.p. 105-6°.

4. o-Chloranil⁷⁵.

- a) Catechol (455mmole.) was dissolved in glacial acetic acid (380ml.) and chlorine was passed into the solution with stirring. The temperature was kept below 40° by cooling in an ice bath. After about one hour, a dense white precipitate had formed, and the solution was beginning to turn orange. At this point, the chlorination was complete, and the reaction mixture was filtered. The white residue was washed with petrol (1 litre) and air-dried to give tetrachlorocatechol (94%), m.p. 180-3°.
- b) Tetrachlorocatechol (100mmole.) was dissolved in ethanol (40ml.), and a mixture of nitric acid (d, 1.4; 20ml.) and glacial acetic acid (100ml.) was added with rapid agitation. The resulting deep red solution was poured onto ice (450g.) and left to stand for one hour. The solution was filtered, and the red residue was washed with water and dried in an oven at 65°, to give o-chloranil(tetrachloro-o-benzoquinone) (90%), m.p. 121-3°.

5a. 4-tert-Octyl-o-benzoquinone⁷⁶.

4-tert-Octylcatechol (50mmole.) was dissolved in ether (25ml.) and a solution of o-chloranil (50mmole.) in ether (150ml.) was added. The mixture was allowed to stand at -35° for 14 hours, filtered, and the residue was washed with ether, and sucked dry at the pump to give 4-tert-octyl-o-benzoquinone (79-100%), red plates with a purple reflex, m.p. 115-6° (dec.) (lit.⁷⁶ 118-20°). This compound was unchanged after six months in the dark.

Prepared in a similar manner from their corresponding catechols were:

- 5b. o-Benzoquinone (25%), brown solid, polymerising on heating. This compound decomposed rapidly at room temperature, and had completely changed to a brown tar within one hour of preparation.

- 5c. 4-Methyl-o-benzoquinone (60%), deep red plates, m.p. 66° (lit.⁷⁷ m.p. 88°). This compound decomposed to a yellow powder with a week of preparation.
- 5d. 3-Isopropyl-6-methyl-o-benzoquinone (30%), deep red needles, polymerising on heating. This compound decomposed rapidly to a black tar within four hours at room temperature.
6. 4-Nitro-o-phenylenediamine⁷⁸.
2,4-Dinitroaniline (12mmole.) was suspended in ethanol (24ml.), and ammonia (d = 0.88; 12ml.) was added. Hydrogen sulphide was passed into the reaction mixture with stirring for 25 minutes, at which point TLC showed that there was no starting material left. The reaction mixture was heated on a water bath for 10 minutes to expel excess hydrogen sulphide, and then cooled. Filtration afforded a red solid, which was washed with ethanol (50ml.) and petrol (50ml.), and air dried to give 4-nitro-o-phenylenediamine (45%), red needles. A small portion was sublimed at $160^{\circ}/1\text{mm.}$ to give deep red plates with a mauve reflex, m.p. 199° (lit. m.p. 198°).
- 7a. 4-Methoxybiphenyl
Sodium hydroxide pellets (40mmole.), were dissolved in water (20ml.) and 4-hydroxybiphenyl (Hopkin and Williams; 21mmole.) was added. Dimethyl sulphate (50mmole.) was added dropwise to this mixture at 0° , and then the reaction mixture was heated at 100° for two hours, and allowed to cool. Filtration afforded a white solid, which was dissolved in chloroform (100ml.), and extracted with sodium hydroxide solution (2N; $2 \times 200\text{ml.}$), and then with water ($2 \times 100\text{ml.}$). The chloroform layer was dried, and evaporated to dryness. The residual

white solid was recrystallised from ethanol to give 4-methoxybiphenyl, needles, m.p. 89° (lit. m.p. 90°).

Prepared in a similar manner from their corresponding phenols and diethyl sulphate were:

7b. 4-nitrophenetole (7%), needles, m.p. $57-8^{\circ}$ (lit. m.p. $57-8^{\circ}$).

7c. 3-nitrophenetole (50%), oil (lit. m.p. 34°).

7d. 3-methoxyphenetole (10%), oil.

7e. 4-methoxyphenetole (40%), oil.

8. cis,cis-Mucononitrile⁶⁰.

o-Phenylene diamine (94mmole.) was suspended in ether (100ml.) and nickel peroxide (40g.) was added with stirring. After 1.5 hours, the reaction mixture was filtered, and the filtrate was extracted with aqueous sodium hydroxide (2N; $2 \times 500\text{ml.}$). The ether layer was dried, and evaporated to small bulk (c. 5ml.). Warm petrol was added, and cis,cis-mucononitrile (10-15%) slowly crystallised as needles, m.p. $122-3^{\circ}$ (lit.⁷⁹ m.p. 124°).

9. 3,4-Dibromonitrobenzene.

o-Dibromobenzene (Koch-Light; 3mmole.) was added to a mixture of concentrated nitric acid (2ml.) and fuming nitric acid (2ml.) and heated on a water bath for 30 minutes. Ice (10g.) was added, and the light yellow precipitate was filtered off, washed thoroughly with water, and air dried. Recrystallisation from ethanol gave 3,4-dibromonitrobenzene (70%), m.p. $53-4^{\circ}$ (lit.⁸⁰ m.p. $58-9^{\circ}$).

SECTION 11

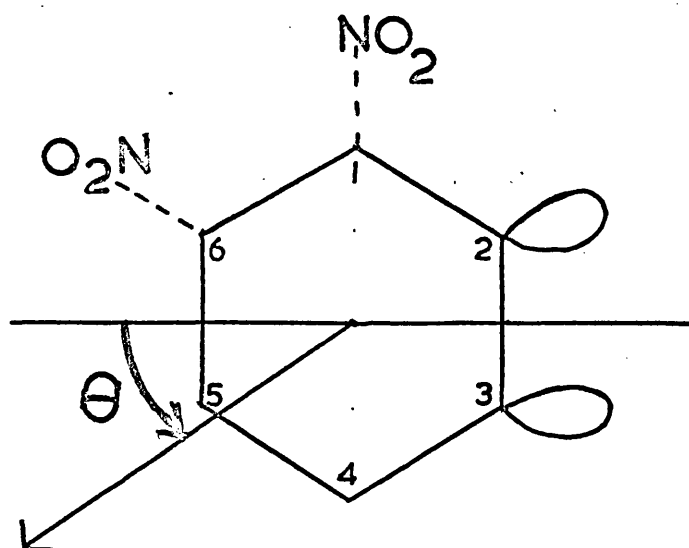
Semi-empirical calculations regarding the electronic structure of arynes.

General procedure and co-ordinates

Extended Hückel⁹⁸ and SCF-MO CNDO2^{99,100} calculations were computed on an I.C.L. Elliott 4130 machine. The following atomic co-ordinates were used:

Atomic Number	3-nitrobenzyne ^a 4-nitrobenzyne ^b			benzyne ^c		
	x	y	z	x	y	z
8 ^c	1.130	-3.450	0			
8 ^c	-1.130	-3.450	0			
7 ^c	0.000	-2.880	0			
6	-1.200	-0.695	0	0.660	1.264	0
6	-1.200	0.695	0	-0.660	1.264	0
6	0.000	-1.390	0	-0.660	-1.264	0
6	0.000	1.390	0	0.660	-1.264	0
6	1.200	0.695	0	1.450	0.000	0
6	1.200	-0.695	0	-1.450	0.000	0
1	-2.170	-1.255	0	-1.184	-2.209	0
1	-2.170	1.255	0	1.184	-2.209	0
1 ^b	0.000	2.510	0	2.450	0.000	0
1 ^a	2.170	-1.255	0	-2.450	0.000	0

The superscripts a,b,c refer to the atomic number to be ignored, corresponding to whatever aryne has the relevant superscript.



The numbering system used for the arynes. The arrow and the angle θ refer to the dipole moment vector, measured in a direction from negative to positive charge.

RESULTS

i) Extended Hückel calculations.

Total energies of singlet and triplet states (in eV.)

	BENZYNE	4-NITROBENZYNE	3-NITROBENZYNE
E[SINGLET]	-492.959	-833.761	-833.917
E[TRIPLET]	-491.105	-833.208	-833.250
° DIFFERENCE	1.854	0.553	0.667

Atomic charges for singlet states.

CENTRE	BENZYNE	4-NITROBENZYNE	3-NITROBENZYNE
C* <div> <div>1</div> <div>2</div> <div>3</div> <div>4</div> <div>5</div> <div>6</div> </div>	-0.010 -0.128 -0.128 -0.010 +0.013 +0.013	+0.163 -0.152 -0.078 +0.084 +0.085 +0.247	+0.321 -0.143 -0.097 +0.170 +0.020 +0.089
<div> <div>N</div> <div>O</div> <div>O</div> </div>		+1.406 -0.937 -0.935	+1.387 -0.938 -0.939
2 - 3	0.000	-0.074	-0.046

* The numbering is defined in the diagram on p. 86.

ii) SCF-MO CNDO2 calculations.

Total energies of singlet and triplet states (in a.u.)

	BENZYNE	4-NITROBENZYNE	3-NITROBENZYNE
E SINGLET	-45.064	-92.989	-92.993
E TRIPLET	-44.979	-92.940	-92.936
DIFFERENCE	0.085	0.049	0.057
EHT [*]	0.068	0.020	0.025

Dipole moment vectors for singlet states.

	BENZYNE	4-NITROBENZYNE	3-NITROBENZYNE
μ	1.21	3.81	6.44
θ	0°	148° 4'	78° 44'

μ is measured in Debyes; θ is defined in the diagram on p. 86.

Atomic charges for singlet states.

CENTRE	BENZYNE	4-NITROBENZYNE	3-NITROBENZYNE
1	+0.030	+0.085	+0.060
2	-0.051	-0.002	-0.112
C + 3	-0.051	-0.048	+0.076
4	+0.030	+0.052	+0.112
5	+0.010	+0.011	+0.015
6	+0.010	+0.049	+0.007
N		+0.442	+0.402
O		-0.322	-0.310
O		-0.312	-0.308
2 - 3	0.000	+0.046	-0.188

* Difference between singlet and triplet energies from extended Hückel calculation.

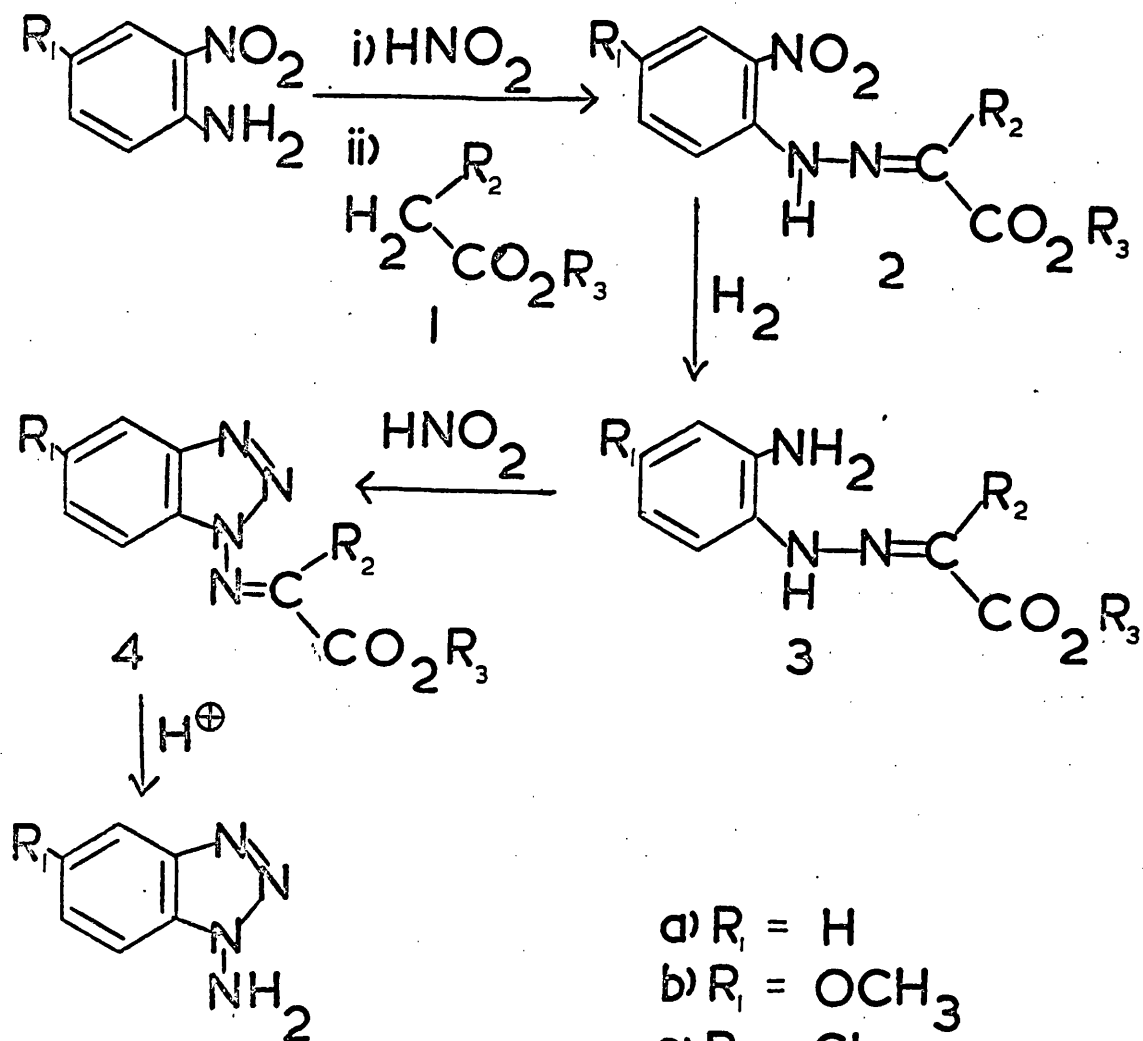
+ The numbering system is defined in the diagram on p. 86.

D I S C U S S I O N

This Discussion is divided into Sections
which correspond roughly with those in the
Experimental part of this Thesis

SECTION 1

Preparation of 1-aminobenzotriazoles.



- a) $R_1 = \text{H}$
- b) $R_1 = \text{OCH}_3$
- c) $R_1 = \text{Cl}$
- d) $R_1 = \text{CF}_3$
- e) $R_1 = \text{NO}_2$
- f) $R_1 = \text{CH}_3$

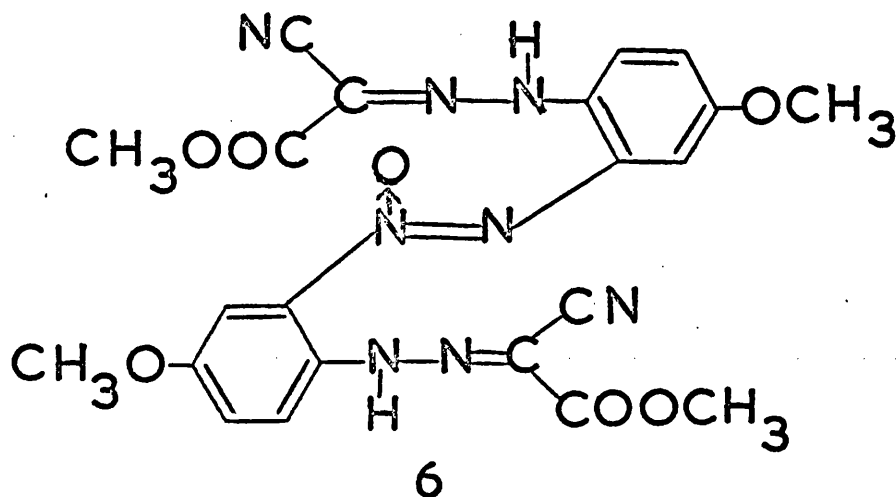
The route of Trave and Bianchetti⁶² was used to prepare a series of substituted 1-aminobenzotriazoles.

The unsubstituted compound (5a) was best prepared by using methyl cyanoacetate [(1); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$] as the protecting group. The nitro-compound [(2a); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$] was obtained in high yield, and was hydrogenated to give the amine [(3a); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$] in quantitative yield. Diazotisation of this amine gave a compound which had the literature⁶² melting point, but only exhibited a very weak cyanide absorption in the i.r. spectrum. This compound, however, gave a good yield of the amine (5a) after heating with a large excess of concentrated hydrochloric acid for five hours. The compound [(4a); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$], when treated with a mixture of nitric and acetic acid, gave no nitrated products, but instead gave a compound with the same elemental analysis as the starting material. This compound differed from the starting material in having a much higher melting point and a significantly different i.r. spectrum. This compound was probably a geometrical isomer of the starting material, and gave the amine (5a) upon hydrolysis with concentrated hydrochloric acid.

If diethyl malonate [(1); $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$] was used as the protecting group, then the overall yield was lower. Campbell^{27b}, however, obtained a 55% overall yield of the amine by this route.

1-Amino-5-methoxybenzotriazole (5b) was prepared using methyl cyanoacetate as the protecting group. The nitro-compound [(2b); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$] was obtained in very high yield, and gave a good elemental analysis. Hydrogenation of this compound by

the method of Trave⁶² proved impossible, the rate of uptake of hydrogen being very slow when 10% palladium on charcoal was used as the catalyst. To rectify this anomaly, Adams' catalyst was used, and the hydrogenation proceeded rapidly in ethanol or ethyl acetate. Unfortunately, the major product of this reduction was not the amine [(3b); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$], but the corresponding azoxy-compound (6), which was identified by elemental analysis and mass spectral data; the first loss from the parent ion was an oxygen atom.



The use of glacial acetic acid as the solvent for hydrogenation afforded a quantitative yield of the amine [(3b); $R_2 = \text{CN}$, $R_3 = \text{CH}_3$], which exhibited a weak cyanide absorption in the i.r. spectrum. This compound had a much higher melting point than that reported by Trave⁶², and gave an almost quantitative yield of the amine (5b) upon treatment with concentrated hydrochloric acid at 100° for ten minutes. The m.p. of this amine was also higher than reported by Trave⁶², but was identical with a sample prepared by amination of 5-methoxybenzotriazole, and also showed all the properties of a 1-aminobenzotriazole.

An attempted preparation of 1-amino-5-chlorobenzotriazole (5c), using methyl cyanoacetate as the protecting group, failed because the

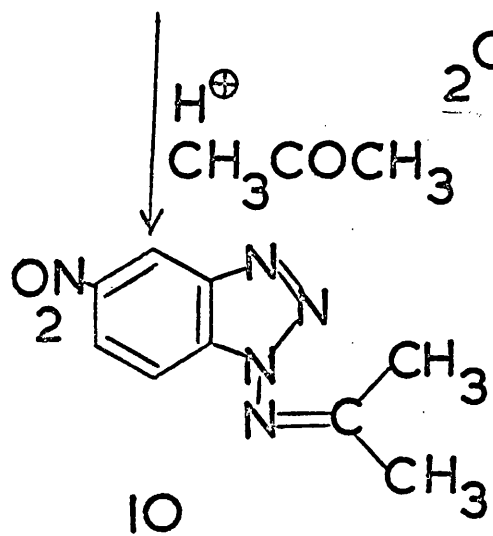
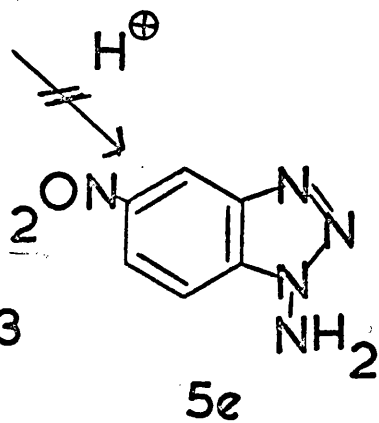
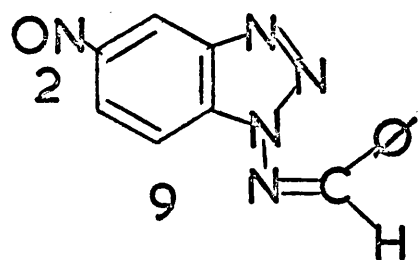
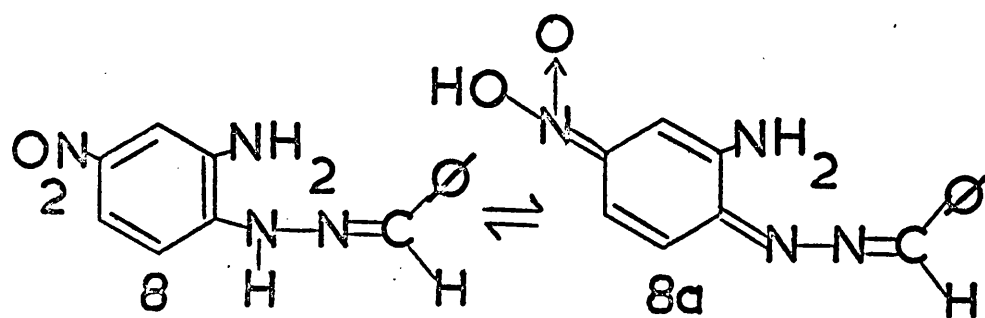
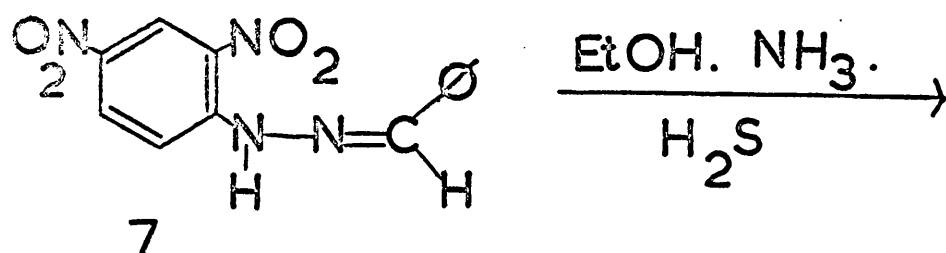
protecting group could not be removed in the final step. When diethyl malonate was used as the protecting group, the nitro-compound [(2c); $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$] was obtained in good yield and gave a satisfactory elemental analysis. Hydrogenation afforded the amine [(3c), $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$] which also gave a satisfactory elemental analysis. Diazotisation of this amine gave an uncrystallisable viscous brown oil, which only showed one spot on TLC, and was presumably compound [(4c), $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$]. Hydrolysis of this oil with concentrated hydrochloric acid gave 1-amino-5-chlorobenzotriazole (5c), which gave a good elemental analysis.

Diethyl malonate was also used as the protecting group in the preparation of 1-amino-5-trifluoromethylbenzotriazole (5d). The nitro-compound [(2d), $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$] was obtained in quantitative yield, and gave a good elemental analysis, as did the derived amine [(3d), $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$]. This amine was extremely sensitive to strong acid, and diazotisation gave a yellow-brown oil with a strong fruity odour. The i.r. spectrum of this oil showed the presence of an azide, and the odour could be attributable to mesoxalic ester. The strong acid, therefore, must have hydrolysed off the protecting group (as mesoxalic ester) to give an aryl hydrazine, which, upon diazotisation, would give an azide. Some of compound [(4d), $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$] must have been present since, upon treatment with concentrated hydrochloric acid, the amine (5d) was obtained. This amine was also unstable in strong acid solution, and deaminated rapidly to give 5-trifluoromethylbenzotriazole. Both the amine (5d) and the triazole were extracted from the strongly acid solution with ether, and the triazole was then removed by extracting

the organic layer with aqueous sodium hydroxide. Because of these side reactions, the overall yield of 1-amino-5-trifluoromethylbenzotriazole (5d) was low. The elemental analysis of this compound was satisfactory, and the i.r. spectrum showed the characteristic C-F bands.

An attempted synthesis of 1-amino-5-nitrobenzotriazole (5e), using methyl cyanoacetate as the protecting group, failed. The nitro-compound [(2e), $R_2 = \text{CN}$, $R_3 = \text{CH}_3$] was obtained in good yield, but gave a low nitrogen figure in the elemental analysis. This compound did not give the amine [(3e), $R_2 = \text{CN}$, $R_3 = \text{CH}_3$] upon attempted monoreduction with ethanolic ammonia and hydrogen sulphide. If diethyl malonate was used as the protecting group, then the nitro-compound [(2e), $R_2 = \text{CO}_2\text{C}_2\text{H}_5$, $R_3 = \text{C}_2\text{H}_5$] was not obtained at all.

The failure of these two routes to the amine (5e) led to a further route being attempted. Benzaldehyde 2,4-dinitrophenylhydrazone (7) was reduced with ethanolic ammonia and hydrogen sulphide to give the amine (8) in high yield. This amine gave a satisfactory elemental analysis, but did not show the presence of a nitro-group in the i.r. spectrum, and was very soluble in base. A possible explanation of this phenomenon is that this compound exists predominantly as the aci-nitro-compound (8a), which has a more extended conjugation of double bonds. Diazotisation of this amine gave 1-benzylideneamino-5-nitrobenzotriazole (9), which gave a good elemental analysis. This compound was resistant to hydrolysis, even with constant boiling hydrobromic acid at 100° for several days. Only small amounts of unidentifiable yellow solids were isolated. If acetone was present in the acid solution, then the isopropylidene derivative (10) was



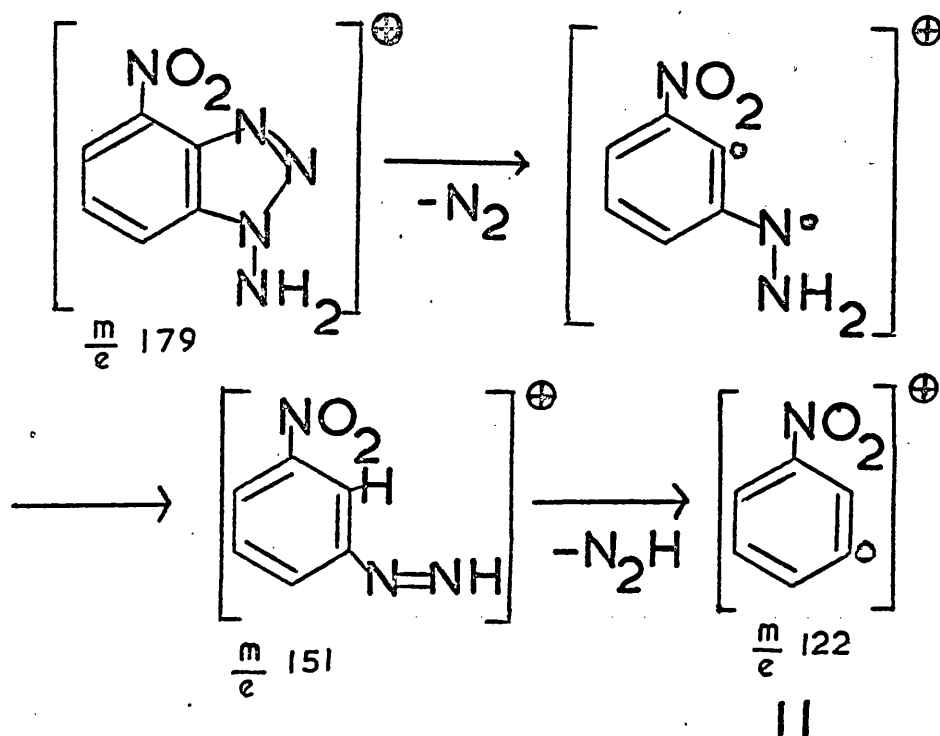
obtained, presumably by an acid-catalysed hydrazone exchange reaction. This isopropylidene derivative was identified by its mass spectrum and elemental analysis. 4-Nitro-o-phenylenediamine (20%) was also obtained by degradation of the triazole ring in the strongly acidic solution.

Amination of benzotriazoles with hydroxylamine-O-sulphonic acid (HOS) is an alternative route to N-aminobenzotriazoles.

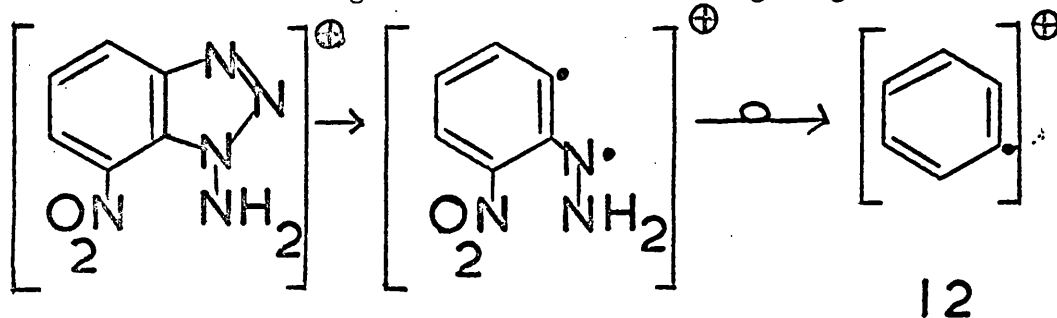
Amination of benzotriazole by the method of Campbell and Rees^{27b} gave 2-aminobenzotriazole (10%) and 1-aminobenzotriazole (25%). These yields could be improved by using sodium carbonate, instead of sodium hydroxide, as the base in the amination reaction. Using this modified method, 2-aminobenzotriazole (27%) and 1-aminobenzotriazole (63%) were obtained from benzotriazole. This method was also beneficial in the separation of the two isomers, since in some instances, nearly all of the 2-substituted compound separated out from the reaction mixture; this made subsequent chromatographic separation of the isomers much easier.

4-Nitrobenzotriazole was prepared by diazotisation of the corresponding diamine or by low-temperature nitration of the benzotriazole, and was aminated by an identical procedure to benzotriazole. Two isomeric 1-aminobenzotriazoles were obtained by chromatography on silica gel. These two isomers had similar i.r. and n.m.r. spectra, but T.L.C. showed that they were quite different in polarity. The mass spectrum of the more polar compound showed a parent ion at $\frac{m}{e}$, 179, and another ion at $\frac{m}{e}$, 122 corresponding to a loss of N_4H from the parent ion. The less polar compound showed a parent ion, and an ion corresponding to loss of a molecule of nitrogen,

but the ion at $\frac{m}{e}$, 122 was totally absent, the next intense ion being at $\frac{m}{e}$, 77. If the more polar compound was 1-amino-4-nitrobenzotriazole and the less polar compound was 1-amino-7-nitrobenzotriazole, then these mass spectra could be interpreted. The breakdown of the 4-nitro-compound involves loss of a molecule of nitrogen from the triazole ring,



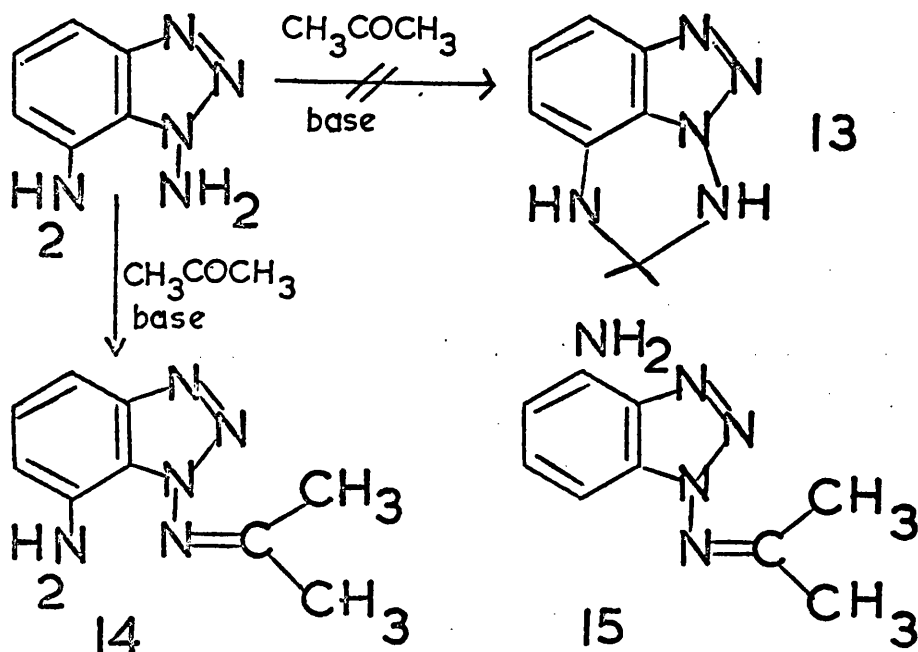
to give a diradical ion. This ion then rearranges to the imino-ion, which then loses N_2H to give the ion (11). The 7-nitro-compound loses a molecule of nitrogen from the triazole ring to give the diradical ion,



which does not rearrange to the imino-ion, but, due to the proximity of the nitro-group undergoes some reaction involving this nitro-group to give the ion (12). Consideration of the dipole moments of the 4-

and 7-nitro-isomers also predicts that the more polar isomer would be the 4-nitro-isomer. The dipole vectors in the 4-nitro-isomer would reinforce each other, but those in the 7-nitro-isomer would oppose each other.

Reduction of 1-amino-7-nitrobenzotriazole gave 1,7-diaminobenzotriazole, which was treated with acetone and basic alumina in an attempt to synthesise the interesting new heterocyclic system (13).



However, the product was 7-amino-1-isopropylideneaminobenzotriazole (14).

This structure was confirmed by i.r., n.m.r, and analytical data.

The 4-amino-derivative (15) was prepared from 1-amino-4-nitrobenzotriazole in the same way. Neither of the amines [(14) and (15)] gave any evolution of gas when treated with lead tetra-acetate in dry methylene chloride, thus confirming that the isopropylidene derivative was on the triazole amino-group.

5-Nitrobenzotriazole was prepared by nitration of benzo-triazole at 100° with a 1:1 mixture of nitric and sulphuric acids. The product was a mixture of 4- and 5-nitrobenzotriazole, from which the pure 5-nitro-isomer could be obtained by recrystallation from ethanol. On some occasions, more of the 4-nitro-compound than the 5-nitro-compound was formed in this reaction, and then separation was difficult. Amination of this triazole with HOS, using sodium hydroxide as the base, gave a mixture of 1-aminobenzotriazoles in very low yield, together with a small amount of 4-nitro-o-phenylenediamine. Up to a 30% yield of aminated material could be obtained if sodium carbonate was used as the base. This aminated material was shown to be predominantly 1-amino-6-nitrobenzotriazole by comparison of the benzylidene derivative of this mixture with the benzylidene derivative of 1-amino-5-nitrobenzotriazole, prepared by an unambiguous route. 1-Amino-6-nitrobenzotriazole gave a satisfactory elemental analysis and was, as expected, intermediate in polarity between the 4- and 7-nitro-isomers, as shown by TLC.

5-Methoxybenzotriazole was prepared by diazotisation of the corresponding diamine⁶⁵. The yield was low because of competing reactions, and large amounts of red tars were obtained, presumably from diazo-coupling reactions.

Amination of this triazole, using HOS and sodium hydroxide, gave a mixture of 5- and 6-aminobenzotriazoles. This mixture could be separated by recrystallisation from diethyl ether, in which the 6-methoxy-isomer was very much more insoluble. The 5-methoxy-compound was then recovered from the mother liquor, and was shown to be identical with a sample prepared by the unambiguous route (see p. 91), and the structure was confirmed by i.r., n.m.r., and analytical data.

1-Amino-6-methoxybenzotriazole was a new compound, and was characterised by i.r. and analytical data. This isomer gave the same products, upon oxidation, as the 5-methoxy-compound.

No substituted 2-aminobenzotriazoles were isolated in these syntheses, although Barton⁸¹, using a different amination technique, has isolated these compounds in certain cases.

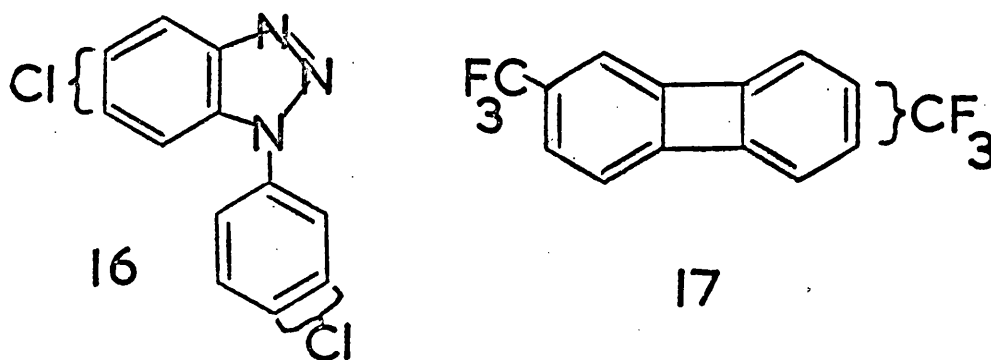
SECTION 2

Oxidation of 1-aminobenzotriazoles with no benzyne "trap".

Campbell and Rees^{27b} oxidised 1-aminobenzotriazole with lead tetra-acetate and obtained an abnormally high yield of the benzyne dimer, biphenylene (83%). Similarly, 1-amino-5-methylbenzotriazole gave a mixture of 2,6- and 2,7-dimethylbiphenylenes (67%), and 1-amino-⁷⁻methylbenzotriazole gave a mixture of 1,5- and 1,8-dimethylbiphenylenes (51%).

In view of these results, other 1-aminobenzotriazoles were oxidised to try to obtain other substituted biphenylenes. Oxidation of 1-amino-5-methoxybenzotriazole with lead tetra-acetate in methylene chloride gave only a 5% yield of a mixture of 2,6- and 2,7-dimethoxybiphenylenes. This mixture of biphenylenes, which were both known compounds^{66,82}, gave good analytical figures, and had an ultraviolet spectrum commensurate with those of other biphenylenes. Comer⁸³ has found that the ratio of biphenylenes obtained from this reaction is approximately 1:1. In addition to these dimers of 4-methoxybenzyne, a mixture of 3- and 4-acetoxyanisoles (10%) was obtained. These acetoxy-compounds presumably arose from attack of 4-methoxybenzyne on acetic acid or lead tetra-acetate. Higher yields of the dimer were obtained in different solvents (see later). Both 1-amino-5-methoxybenzotriazole and 1-amino-6-methoxybenzotriazole gave mixtures of 2,6- and 2,7-dimethoxybiphenylenes (20-41%) and biphenylene (32-63%) upon attempted "cross-dimerisation" in the presence of one equivalent of benzyne, produced by simultaneous oxidation of 1-aminobenzotriazole. No 2-methoxybiphenylene could be detected by u.v. analysis.

Oxidation of 1-amino-5-chlorobenzotriazole in ethyl acetate with lead tetra-acetate gave a mixture of 2,6- and 2,7-dichlorobiphenylenes (18%), which gave a satisfactory elemental analysis. In addition to these compounds, a light yellow solid, which melted between 122° and 138°, was obtained. Mass spectral data, supported by an elemental analysis, showed that this product was a mixture of isomeric dichloro-1-phenylbenzotriazoles (16). The characteristic loss of a



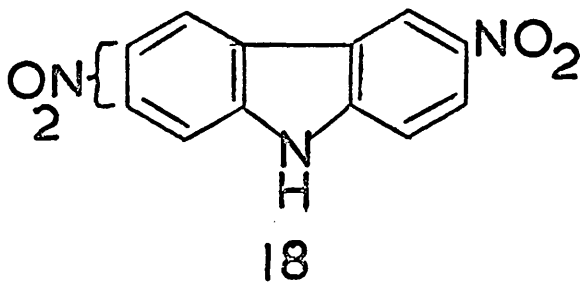
nitrogen molecule from the parent ion in the mass spectrum showed that this was the 1-substituted benzotriazole. A small amount of a mixture of 3- and 4-chlorophenylacetates was also obtained.

Cross-dimerisation of 4-chlorobenzene with an equivalent amount of benzyne gave 2-chlorobiphenylene (19%), which is a known compound⁶⁶, and was further characterised by its mass spectrum. Biphenylene (26%) and the mixture of dichlorobiphenylenes (16%) were also obtained, as was a small amount of a mixture of 3- and 4-chlorophenylacetates.

Oxidation of 1-amino-5-trifluoromethylbenzotriazole in benzene with lead tetra-acetate gave a mixture of 2,6- and 2,7-bis(trifluoromethyl)-biphenylenes (17) (53%). This product gave a good elemental analysis, but neither of the unknown bis(trifluoromethyl)-biphenylenes could be obtained free of the other isomer, either by

recrystallisation or by sublimation. Cross-dimerisation of the 4-trifluoromethylbenzynes with one equivalent of benzyne gave a mixture of mono- and bis(trifluoromethyl)-biphenylenes; biphenylene (21%) was also isolated. A small amount of 2-trifluoromethylbiphenylene was separated from the mixture by careful fractional sublimation; the sample gave poor analytical data, but the mass spectrum fitted this compound.

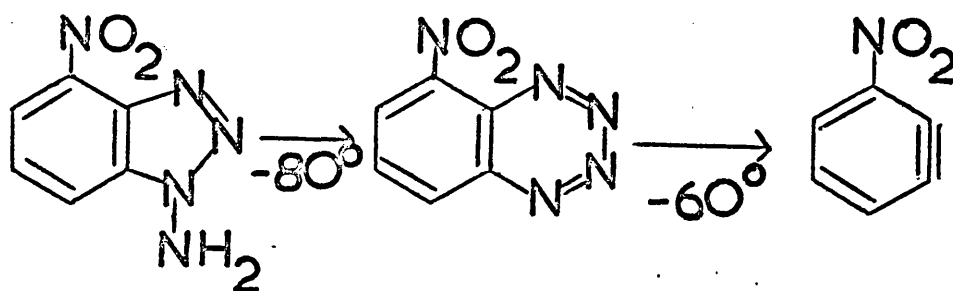
Oxidation of 1-amino-6-nitrobenzotriazole in methylene chloride with lead tetra-acetate gave only a 1% yield of a mixture of 2,6- and 2,7-dinitrobiphenylenes. This mixture was identified by its characteristic u.v. spectrum, and the mass spectral data. A further product was isolated, which analysed for $C_{12}H_7N_3O_4$; it showed a complex set of peaks in the i.r. spectrum around 3200 cm^{-1} , and could be a mixture of dinitrocarbazoles (18). However, this product was not examined further.



A corresponding oxidation in acetonitrile gave a mixture of 3- and 4-nitrophenyl acetates (16%) as the only recognisable product. Cross-dimerisation of 4-nitrobenzyne with one equivalent of benzyne gave biphenylene (18%) and 2-nitrobiphenylene (9%). This compound was identified by comparison with the physical data provided by Baker⁶⁶.

Oxidation of 1-amino-7-nitrobenzotriazole in benzene with

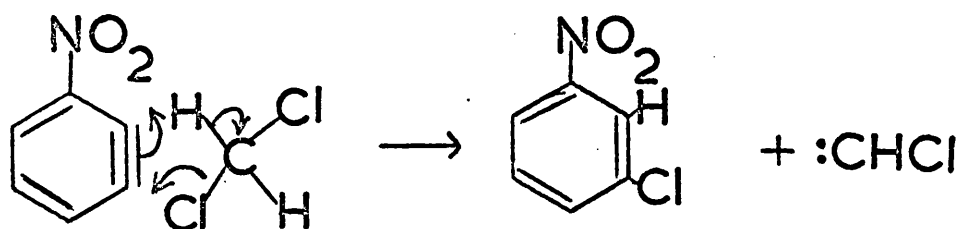
lead tetra-acetate gave no benzyne dimer, but gave a moderate yield of 3-nitrophenyl acetate (17%), presumably arising from attack of 3-nitrobenzyne on acetic acid or lead tetra-acetate. When 3-nitrobenzyne was generated from the other precursor, 1-amino-4-nitrobenzotriazole, in methylene chloride at -60° , 3-nitrophenylacetate (23%) was still the only recognisable product. Interestingly, if this reaction was performed at -80° , no gas evolution was observed, but a precipitate of lead diacetate was noted. On heating to -60° , gas evolution commenced. Formation of the relatively stable ^{tetrazine may be involved;} tetrazines formed



from other 1-aminobenzotriazoles are presumably less stable. Oxidation of 1-amino-4-nitrobenzotriazole with lead tetra-acetate in the presence of potassium carbonate still gave 3-nitrophenyl acetate in comparable yield (27%).

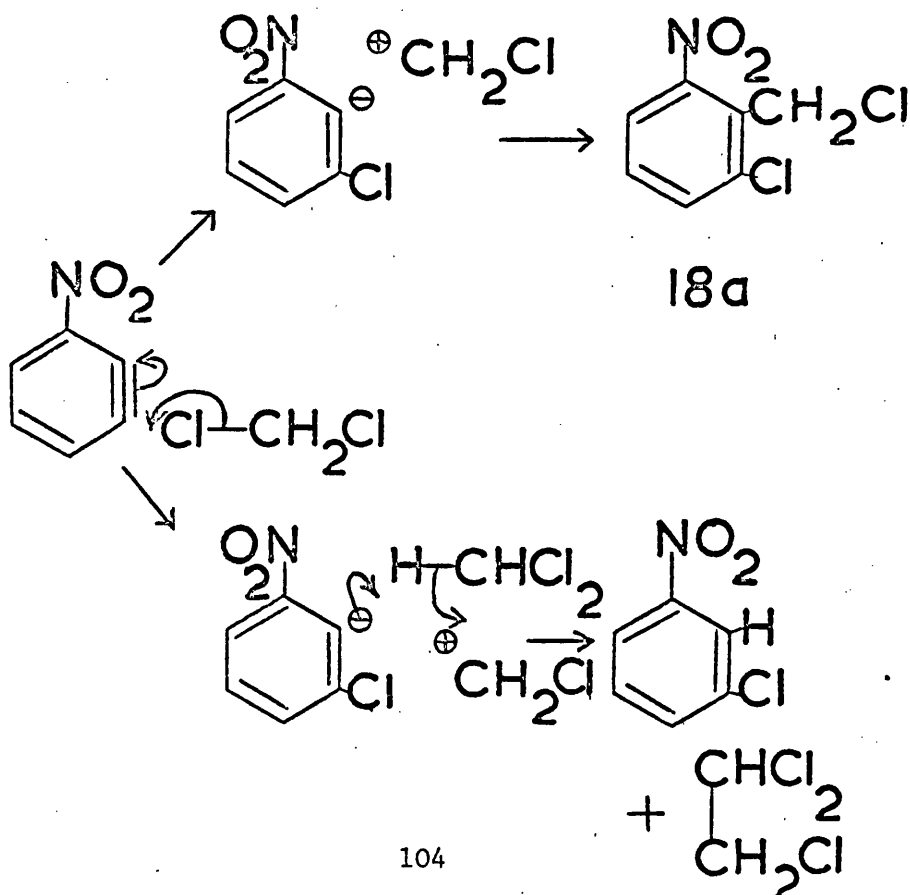
Attempted cross dimerisations of 3-nitrobenzyne (from both precursors) with one equivalent of benzyne produced only biphenylene (13-21%) and 3-nitrophenylacetate (26-30%). An attempted cross dimerisation of 3-nitrobenzyne with one equivalent of 4-methoxybenzyne produced only 3-nitrophenylacetate (54%). Remarkably, no dimethoxybiphenylenes could be detected, even by TLC, which is very sensitive to these compounds. An attempted cross dimerisation with 1,8-dehydronaphthalene, from 1-aminonaphtho[1,8-de]-triazine in methylene chloride also failed, as expected, giving only naphthalene

(contaminated with 1-chloronaphthalene) (7.5%) and 3-nitrophenylacetate (14%). Oxidation of 1-amino-7-nitrobenzotriazole in methylene chloride with nickel peroxide produced 3-nitrochlorobenzene (1%), which was the only recognisable product. The chlorine atom must have come from the solvent, possibly as shown.



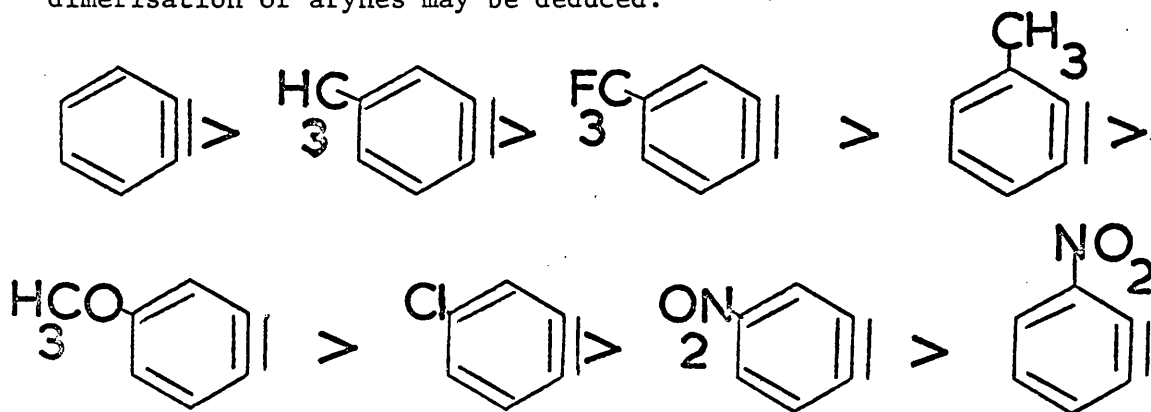
This reaction is a thermally allowed concerted process, and would be a consequence of the very high electrophilicity of 3-nitrobenzyne.

A stepwise process cannot be ruled out, however.

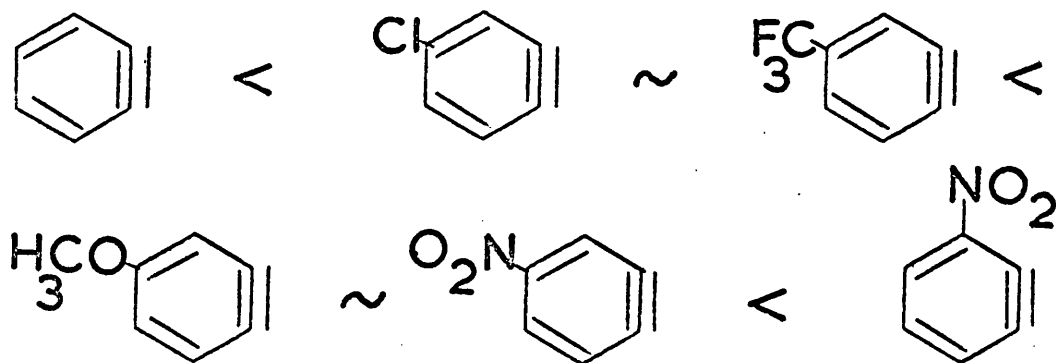


It was not possible to say whether any of compound (18a) had been formed, since the reaction gave such a low overall yield of material.

From the above results, the following order of degree of dimerisation of arynes may be deduced:

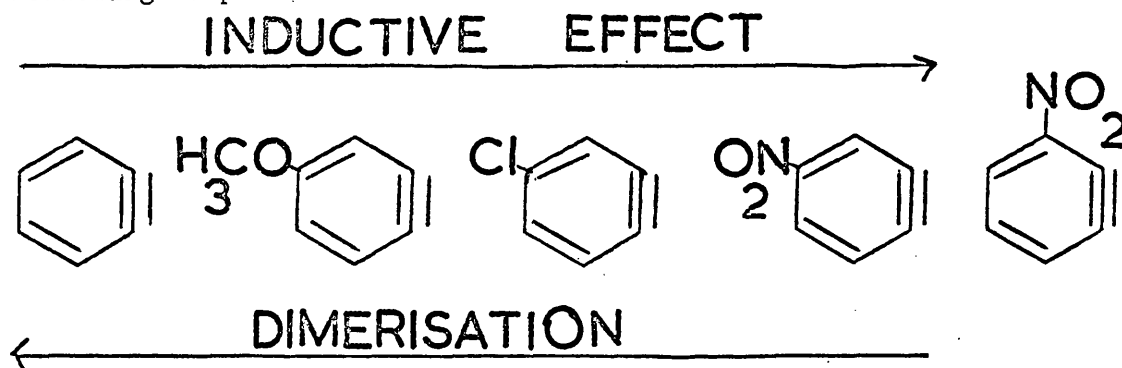


If it is assumed that competing reactions can remove the aryne from the reaction medium before it has the chance to dimerise, then the statistical probability of the collision of two arynes to form the dimer must be a function of the lifetime of the aryne. The nature of these competing reactions is to some extent unknown, but reactions with the starting amine, or with the partially decomposed amine seem feasible, as do reactions with nucleophiles, such as acetic acid, which may be present in the reaction medium. If one considers the amounts of phenyl acetates which are produced from oxidations with lead tetra-acetate, then the order of formation of these compounds is:

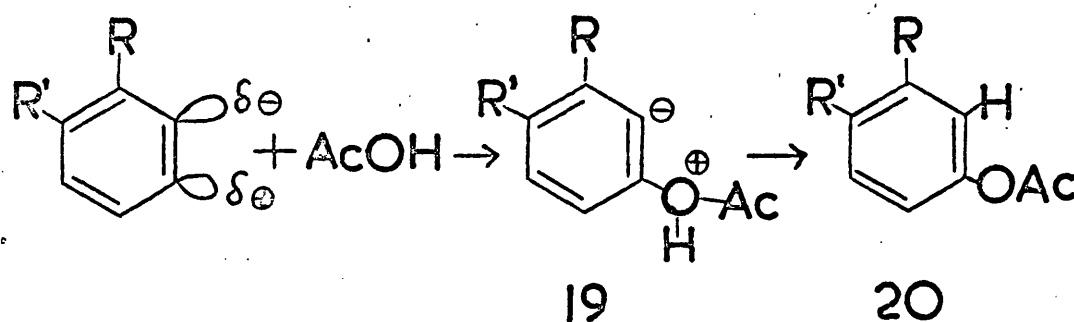


By comparing this order of phenyl acetate formation with that of dimerisation, it is evident that phenyl acetate formation

is highest with those arynes which dimerise the least and vice-versa. Hence, phenyl acetate formation is competing with dimerisation. If the tendency to dimerise is compared with the order of expected inductive effects on the non-bonded σ -orbitals of the arynes, then the following comparison is obtained:



Hence the higher the dipole across the two non-bonded σ -orbitals, the lower the degree of dimerisation, and the higher the yield of phenyl acetates. The increase in yield of phenyl acetates as the dipolarity across the non-bonded σ -orbitals increases is due to the stabilisation of the ionic intermediate (19), which then can rearrange to the phenyl acetate (20).



Comparing the two extreme cases, benzyne and 3-nitrobenzyne, it can be seen that the carbanion in the intermediate (19) has little or no stabilisation in benzyne ($R = R^1 = H$), but in 3-nitrobenzyne ($R = NO_2$, $R^1 = H$), this carbanion is now ortho to a nitro-group and thus has a large inductive stabilisation. Hence, in the case of benzyne, the

the equilibrium for the formation of the intermediate $[(19); R=R^1=H]$ would lie to the left, and a high concentration of benzyne would be present for dimerisation. In 3-nitrobenzyne, this equilibrium would lie to the right, to give a high concentration of the intermediate $[(19); R = NO_2, R^1 = H]$, which effectively removes free 3-nitrobenzyne from the reaction medium, and so no dimer is obtained. The reaction between 3-nitrobenzyne and acetic acid must be very rapid, since added potassium carbonate cannot compete for the acetic acid; the yield of aryl acetate is similar to that of a reaction without added potassium carbonate. When the oxidation of 1-amino-4-nitrobenzotriazole was performed with nickel peroxide in methylene chloride in the presence of acetic acid (4.7 equiv.), only a 3% yield of 3-nitrophenylacetate was obtained. This is a very much lower yield than with lead tetra-acetate, which only provides two equivalents of acetic acid, and hence it may be necessary for the acetic acid to be generated very near to the aryne, as it must be in lead tetra-acetate oxidations, and some sort of solvent-cage reaction may be involved. The arguments used for the interception of arynes by acetic acid can, of course, be extended to reactions with other nucleophiles.

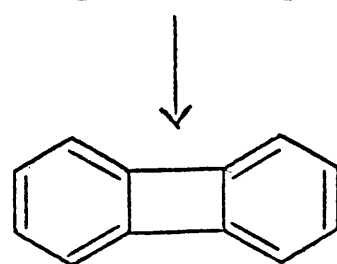
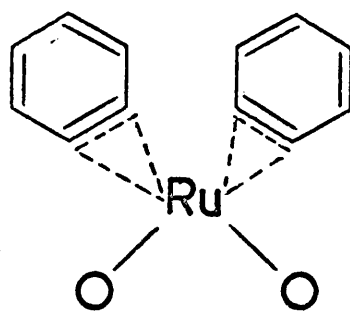
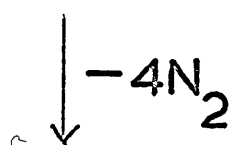
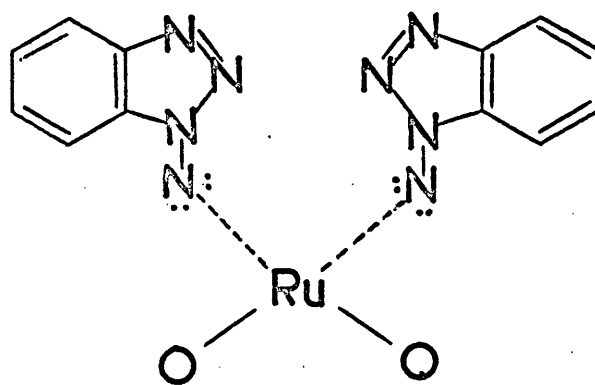
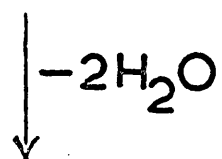
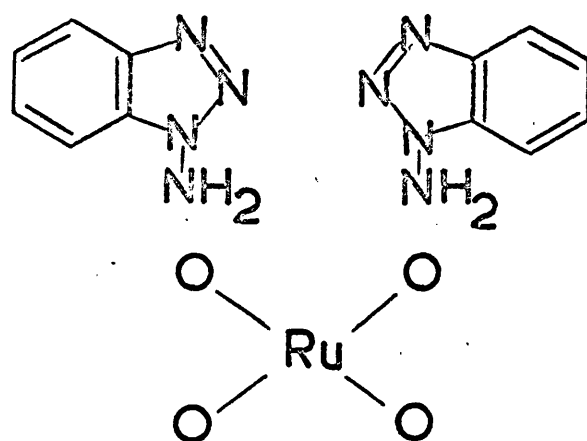
4-Trifluoromethylbenzyne appears to be an exception to the above arguments. Based on inductive effects alone, the dipolarity of the two non-bonded σ -orbitals should be much more than that of the respective orbitals of 4-methoxybenzyne, but 4-trifluoromethylbenzyne dimerises more and acetoxylates less than 4-methoxybenzyne. However, it has been shown that 4-trifluoromethylbenzyne possesses a negligible dipole across the orbitals in question^{11f}.

4-Chlorobenzyne, 4-trifluoromethylbenzyne and 4-nitrobenzyne all cross-dimerised with benzyne, but 4-methoxybenzyne and 3-nitrobenzyne did not. It seems probable that 3-nitrobenzyne has a very much shorter

free lifetime than benzyne, and so not much cross-dimerisation would be expected. No reasonable explanation can be put forward for the failure of 4-methoxybenzyne to cross-dimerise.

Oxidation of 1-aminobenzotriazole with ruthenium tetroxide in carbon tetrachloride in the presence of aqueous sodium metaperiodate gave biphenylene (20%). No phenol could be detected. An analogous experiment, using an excess of tetracyclone* as the benzyne "trap", gave no 1,2,3,4-tetraphenylnaphthalene, but instead gave biphenylene (10%) as the only identifiable product. These results indicate that benzyne was formed, since 1-aminobenzotriazole must form biphenylene via benzyne, but the benzyne must never have been free to react with any external reagent. The only simple explanation for this phenomenon is that two molecules of benzyne were formed intimately bound in an unknown ruthenium complex, and that dimerisation then took place within this complex. Since one molecule of ruthenium tetroxide oxidises two molecules of 1-aminobenzotriazole, the following scheme seems feasible.

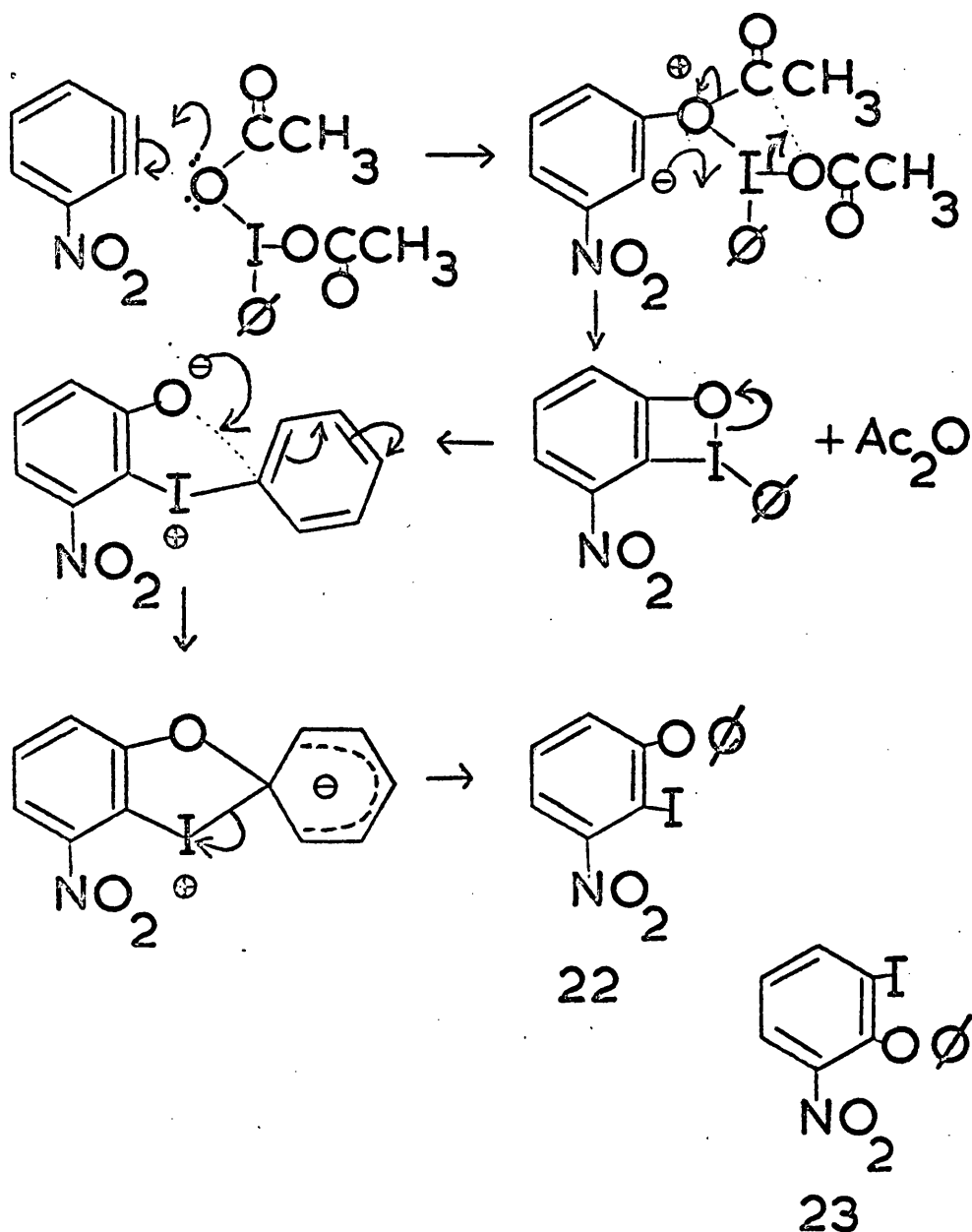
* These tetracyclone experiments are included in this Section as they are more relevant here.



When 1-amino-5-methoxybenzotriazole was oxidised with ruthenium tetroxide in carbon tetrachloride, in the presence of aqueous sodium metaperiodate and an excess of tetracyclone, no dimers were formed, the products being 6-methoxy-1,2,3,4-tetraphenylnaphthalene (5%), 3-methoxyphenol (22%) and 4-methoxyphenol (4%). Thus, free 4-methoxybenzyne must have formed. A possible explanation is that in this case the interaction between the ruthenium atom and the nitrenes is not sufficiently strong to overcome the reduced tendency of 4-methoxybenzyne to dimerise.

Oxidation of 1-amino-4-nitrobenzotriazole with iodobenzenediacetate (21) gave no tetra-azapentalenes analogous to those found by Campbell and Rees⁸⁴ from the reaction of this oxidant with 1-aminobenzotriazole. Instead, 3-nitrophenyl acetate (11%) was formed, presumably in the same way as from lead tetra-acetate, and also a light yellow solid which was homogeneous on TLC. The mass spectrum of this compound had a parent peak corresponding to the analytical data, which fitted the formula $C_{12}H_8INO_3$. The i.r. spectrum showed a nitro-group, but no carbonyl, hydroxyl, or epoxy-groups. Therefore the remaining oxygen atom is probably present as an ether. It seems reasonable to suppose that this compound was the result of attack of 3-nitrobenzyne on iodobenzenediacetate. Nucleophilic attack of the oxygen atom on the meta-position of the aryne, followed by elimination of acetic anhydride, would give the primary adduct, which could then ring-open to give a betaine involving an iodonium ion and a phenolic anion, as shown. Attack of the phenolic anion upon the phenyl ring could then give 2-iodo-3-nitrodiphenyl ether (22) via the spiro-intermediate shown. Some 2-iodo-6-nitrodiphenyl ether (23) could be formed by attack of aryne on the oxidant in the

other orientation.



Either of compounds (22) or (23) would fit the physical data very well. This rather unusual type of mechanism has been used before by Zbiral⁹⁵ to explain the formation of certain products from the reaction of arynes with phosphoranes.

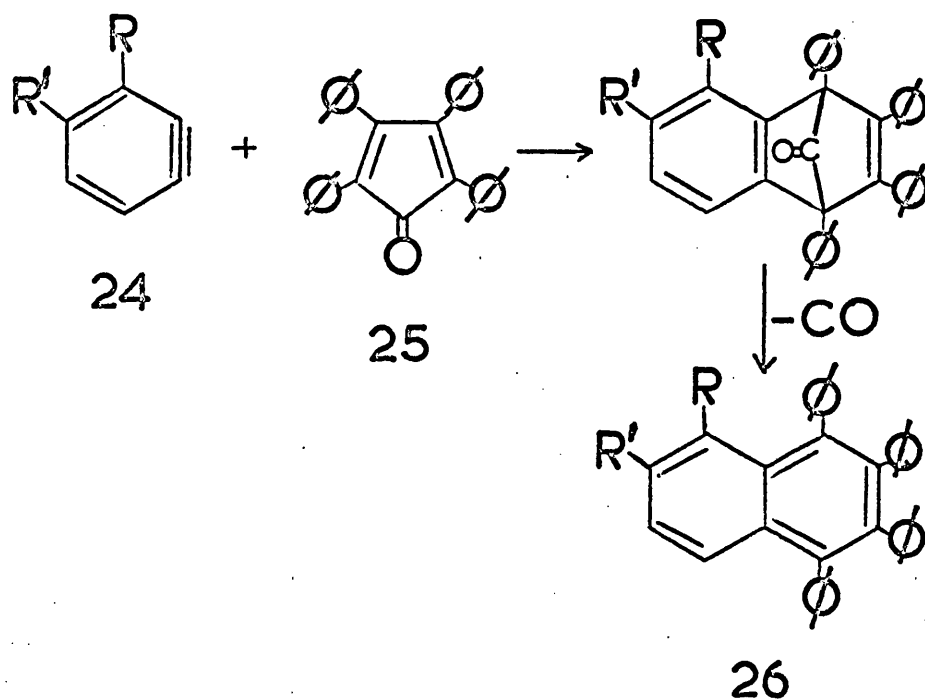
Campbell and Rees⁸⁴ oxidised 1-aminobenzotriazole with N-bromosuccinimide and obtained o-dibromobenzene (52%) by a mechanism involving the scavenging of benzyne with free bromine.

A similar oxidation of 1-amino-6-nitrobenzotriazole gave 3,4-dibromonitrobenzene (27%) together with an unidentifiable oil which showed a strong absorption at 2114 and 2108 cm^{-1} in the i.r. spectrum, and was probably an azide. Oxidation of 1-amino-4-nitrobenzotriazole with the same oxidant gave 2,3-dibromonitrobenzene (10%) as the only recognisable product. The yield of the dibromo-compound was possibly affected by competing reactions in this case.

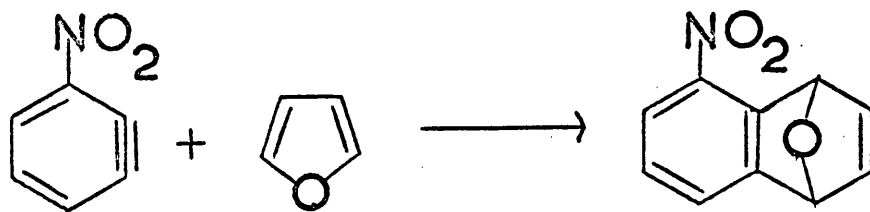
SECTION 3

Oxidations of 1-aminobenzotriazoles in the presence of cyclic dienes.

Tetraphenylcyclopentadienone [tetracyclone] (25) is a very good benzyne "trap", as has been shown by Campbell and Rees^{27c}, who oxidised 1-aminobenzotriazole in benzene with lead tetra-acetate in the presence of tetracyclone, obtained 1,2,3,4-tetraphenylnaphthalene [(26); $R = R^1 = H$] (88%), the product of spontaneous decarbonylation of the initial Diels-Alder adduct. Similarly 1-amino-5-methylbenzotriazole gave 6-methyl-1,2,3,4-tetraphenylnaphthalene [(26); $R = H$, $R^1 = CH_3$] (99%), formed via 4-methylbenzyne [(24); $R = H$, $R^1 = CH_3$], and 1-amino-7-methylbenzotriazole gave 5-methyl-1,2,3,4-tetraphenylnaphthalene [(26); $R = CH_3$, $R^1 = H$] (83%) via 3-methylbenzyne [(24); $R = CH_3$, $R^1 = H$].

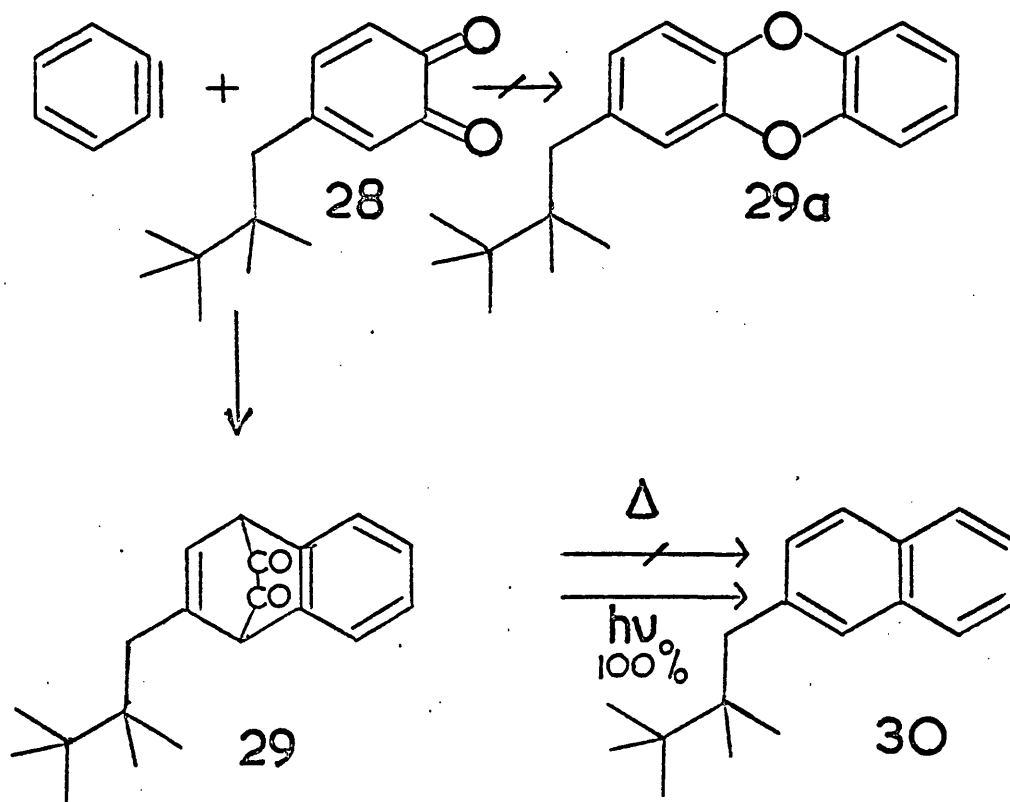


When 1-amino-5-methoxybenzotriazole or 1-amino-6-methoxybenzotriazole was oxidised with lead tetra-acetate in the presence of tetracyclone (0.9-1.0 equiv.), 6-methoxy-1,2,3,4-tetraphenylnaphthalene [(26); $R = H$, $R^1 = OCH_3$] (83-93%) was produced. An excess of tetracyclone could not be used as the adduct could not be readily separated from residual tetracyclone. When 1-amino-5-chlorobenzotriazole, 1-amino-5-trifluoromethylbenzotriazole and 1-amino-6-nitrobenzotriazole were oxidised under the same conditions, the products were 6-chloro-1,2,3,4-tetraphenylnaphthalene [(26); $R = H$, $R^1 = Cl$] (75%), 6-trifluoromethyl-1,2,3,4-tetraphenylnaphthalene [(26); $R = H$, $R^1 = CF_3$] (92%) and 6-nitro-1,2,3,4-tetraphenylnaphthalene [(26); $R = H$, $R^1 = NO_2$] (76%) respectively. These experiments confirmed that all the above triazoles produced a high yield of the aryne upon oxidation with lead tetra-acetate. Only a 24% yield of 5-nitro-1,2,3,4-tetraphenylnaphthalene [(26); $R = NO_2$, $R^1 = H$] was obtained from 1-amino-7-nitrobenzotriazole; but this yield was much lower than with certain other "traps" and 3-nitrobenzyne (see later), and so this aryne is presumably formed efficiently from the triazole. This leads to the conclusion that 3-nitrobenzyne does not have the same affinity for tetracyclone that all the other arynes have. One possibility is that the product, 5-nitro-1,2,3,4-tetraphenylnaphthalene, is a sterically crowded molecule, and a model showed that the nitro-group must be twisted out of the plane of the naphthalene ring; this argument can be negated, to some extent, by consideration of an analogous oxidation in the presence of furan, when the 2 + 4 cycloadduct, 1,4-dihydro-5-nitro-1,4-oxidonaphthalene (27) was only produced in comparable yield (17%).

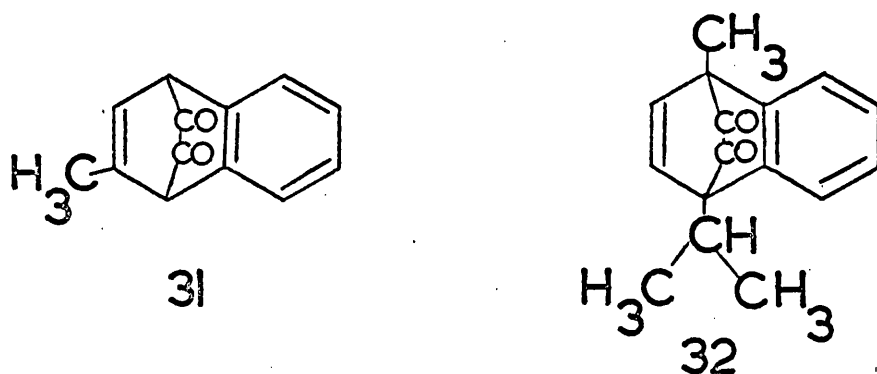


In consequence of this, a steric factor cannot be crucial in the 2 + 4 cycloaddition of this aryne with tetracyclone, since only a similar yield of adduct is obtained with furan, where the adduct is not sterically hindered at all. This problem is discussed further on p.138. All of the aforementioned cycloadducts gave satisfactory analytical data, and their spectroscopic properties were in agreement with the proposed structures.

o-Quinones were found to be benzyne "traps", even though they contain a formally electron-poor diene system. The stable o-quinone, 4-t-octyl-o-benzoquinone (28) gave a 53% yield of the 2 + 4 cycloadduct (29) and no biphenylene could be detected, showing the efficiency of this diene in trapping benzyne. No trace of the alternative adduct (29a) was found. The compound (29) was identified

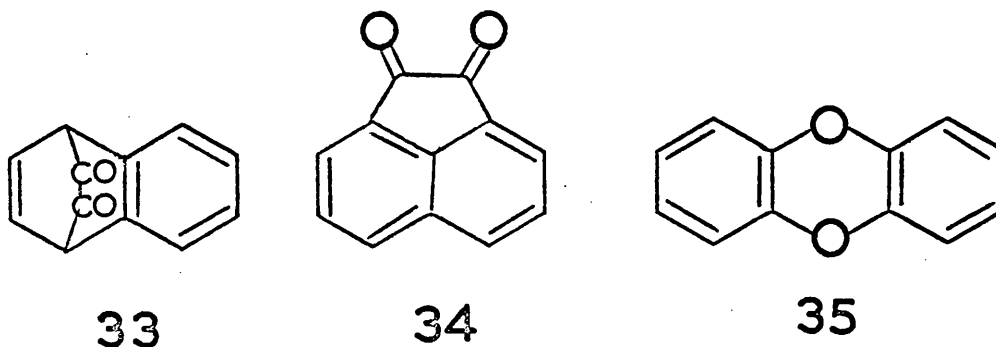


by i.r., n.m.r., and analytical data. The mass spectrum showed a parent ion at $\frac{m}{e}$, 296 which was much less intense than an ion at $\frac{m}{e}$, 240 corresponding to the loss of the bisendocarbonyl bridge. This latter ion was identified as the parent ion of 2-t-octylnaphthalene (30), as the subsequent mass spectral breakdown was identical with that of the decarbonylated product. Pyrolysis of the yellow adduct (29) at $> 360^{\circ}$ gave only unchanged starting material, even after distillation at atmospheric pressure. Photolysis, in benzene solution gave a rapid evolution of a gas, presumably carbon monoxide, and a quantitative yield of 2-t-octylnaphthalene. This unknown compound is an oil, which does not form a picrate; the elemental analysis, n.m.r., and i.r. data fitted the proposed structure. It is difficult to see why thermolysis does not expel the bisendocarbonyl bridge, since, on molecular orbital considerations, this appears to be a thermally allowed reaction. The removal of this bridge by mild photolytic conditions seems to point to the fact that this reaction is only photolytically allowed. 4-Methyl-o-benzoquinone also gave a similar 2 + 4 cycloadduct (31) (14%) with benzyne, which gave a satisfactory elemental analysis and had the



characteristic mass spectrum of this type of compound, and the i.r. and n.m.r. spectral data agreed with the proposed structure. A satisfactory analysis could not be obtained for the adduct (32), which was formed by reaction of benzyne with 3-iso-propyl-6-methyl-o-benzoquinone in 25% yield. The mass spectrum, however, agreed with this

structure, as did the i.r. and n.m.r. spectral data. o-Benzoquinone produced, in a similar experiment, a small amount of yellow oil, which showed an ion at $\frac{m}{e}$, 128 in the mass spectrum which had at least one thousand times the intensity of any other peak. The i.r. spectrum was similar to that of the other adducts (30-32), and this mass peak could have been due to the ready loss of the bisendocarbonyl bridge from the 2 + 4 cycloadduct (33). The quantity of this oil was insufficient for further examination. Biphenylene (3%) was also produced in this reaction. No adduct could be detected when

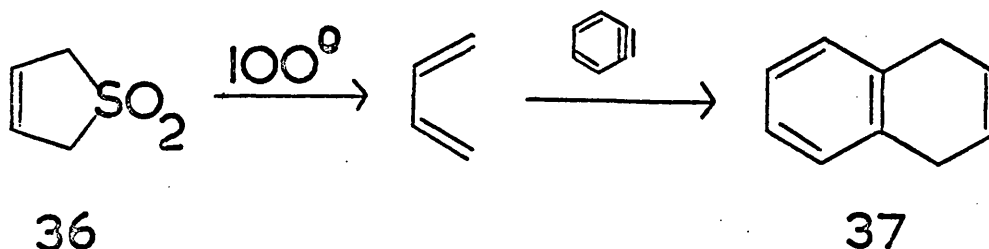


acenaphthenequinone (34) was used as the "trap". No adduct containing the diether linkage as in compound (35) could be detected in any of the above reactions. Thus, the 1,4-cycloaddition of benzyne to the carbon, rather than the oxygen, termini of the conjugated diene systems is clearly preferred.

SECTION 4

Oxidation of 1-aminobenzotriazoles in the presence of acyclic dienes.

In 1964, Wittig and Dürr¹⁸ generated benzyne from 2-fluorobromobenzene and magnesium, in diethyl ether or tetrahydrofuran in the presence of butadiene, isoprene and 2,3-dimethylbutadiene; 2 + 4 cycloaddition occurred in all cases (6-13%), as did the "ene" reaction in the latter two cases. A small amount of 2 + 2 cycloaddition was noted in the reaction between benzyne and 2,3-dimethylbutadiene. In 1968, Hatch and Peter⁸⁵ generated benzyne from benzenediazonium 2-carboxylate at 100° in the presence of butadiene, generated in situ from the cyclic sulphone (36); 1,4-dihydronaphthalene (37) (9%) was obtained.

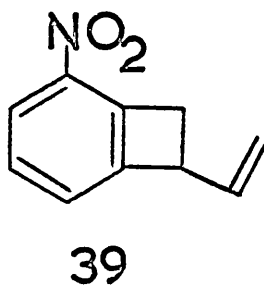
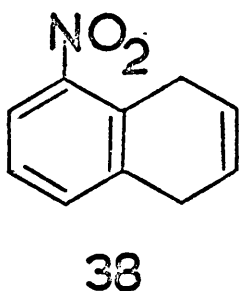


Oxidation of 1-aminobenzotriazole in a mixture of butadiene and methylene chloride with lead tetra-acetate at -80° gave 1,4-dihydronaphthalene (37) but in much higher yield (90%), as the only identifiable product. The adduct was characterised by m.p. and n.m.r. data. This compound was unstable, slowly rearranging to 1,2-dihydronaphthalene and then dehydrogenating to naphthalene; these processes could clearly be seen by examination of the n.m.r. spectrum of an old sample.

Dehydrogenation of the adduct (37) with 10% palladium on charcoal gave naphthalene. In view of this high yield of 2 + 4 cycloadduct, the reaction was extended to other arynes and other dienes.

A similar experiment with 1-amino-5-methoxybenzotriazole gave 1,4-dihydro-6-methoxynaphthalene (98%) which rapidly rearranged to the 1,2-dihydro-isomer and dehydrogenated to 2-methoxynaphthalene.

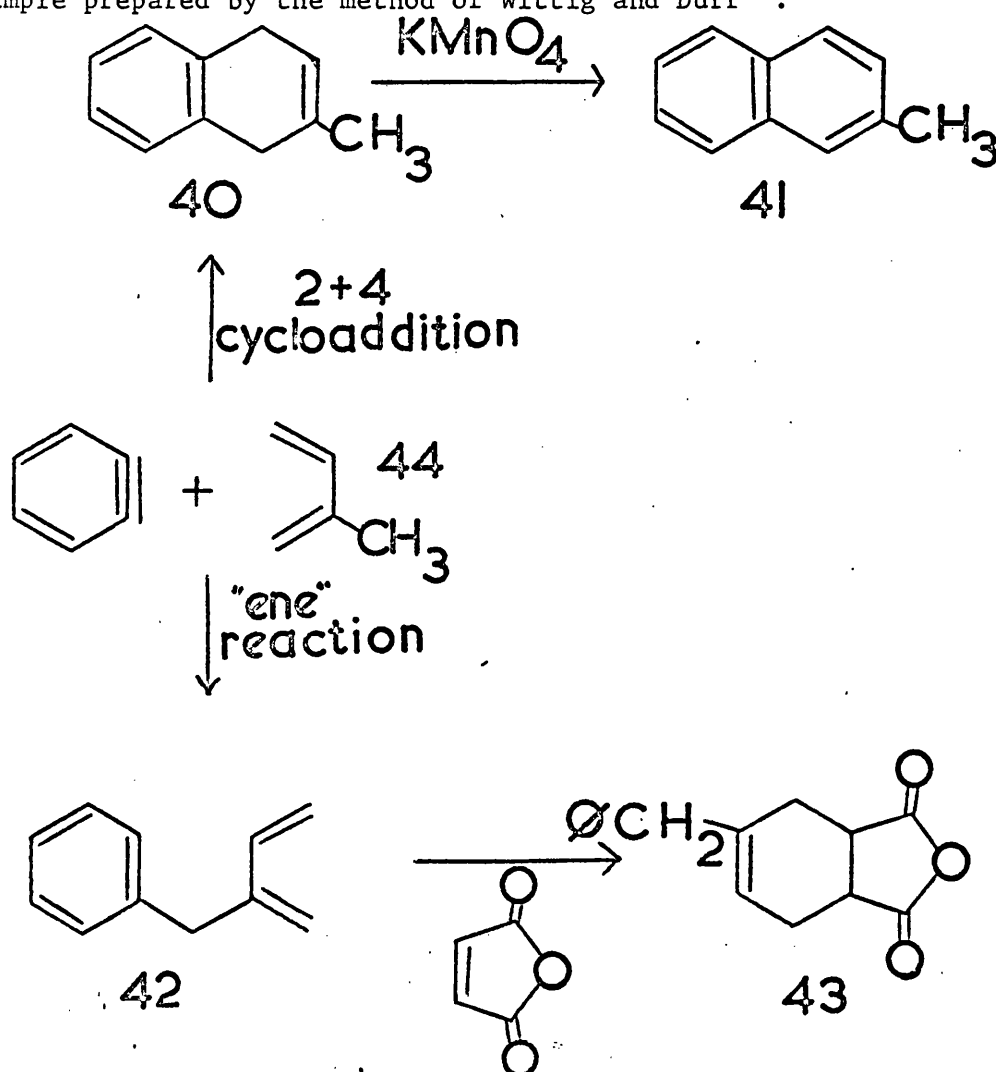
Dehydrogenation of this adduct with 10% palladium on charcoal gave 2-methoxynaphthalene, which was characterised by m.p. and n.m.r. data, and by the m.p. of its picrate. 1-Amino-4-nitrobenzotriazole was oxidised in a mixture of butadiene and methylene chloride with lead tetra-acetate at 0° (there was very little reaction at lower temperatures because of the insolubility of the reactants). The major product was a mixture of 1:1 adducts (32%), proved to be so by examination of the n.m.r. spectrum. When these adducts were treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, a small amount of 1-nitronaphthalene was obtained. Therefore, some of the 2 + 4 cycloadduct (38) must have been present in the mixture; it was not possible to ascertain whether any



2 + 2 cycloadducts e.g. compound (39) were also present. 3-Nitrophenyl acetate (10%) was also produced in this reaction.

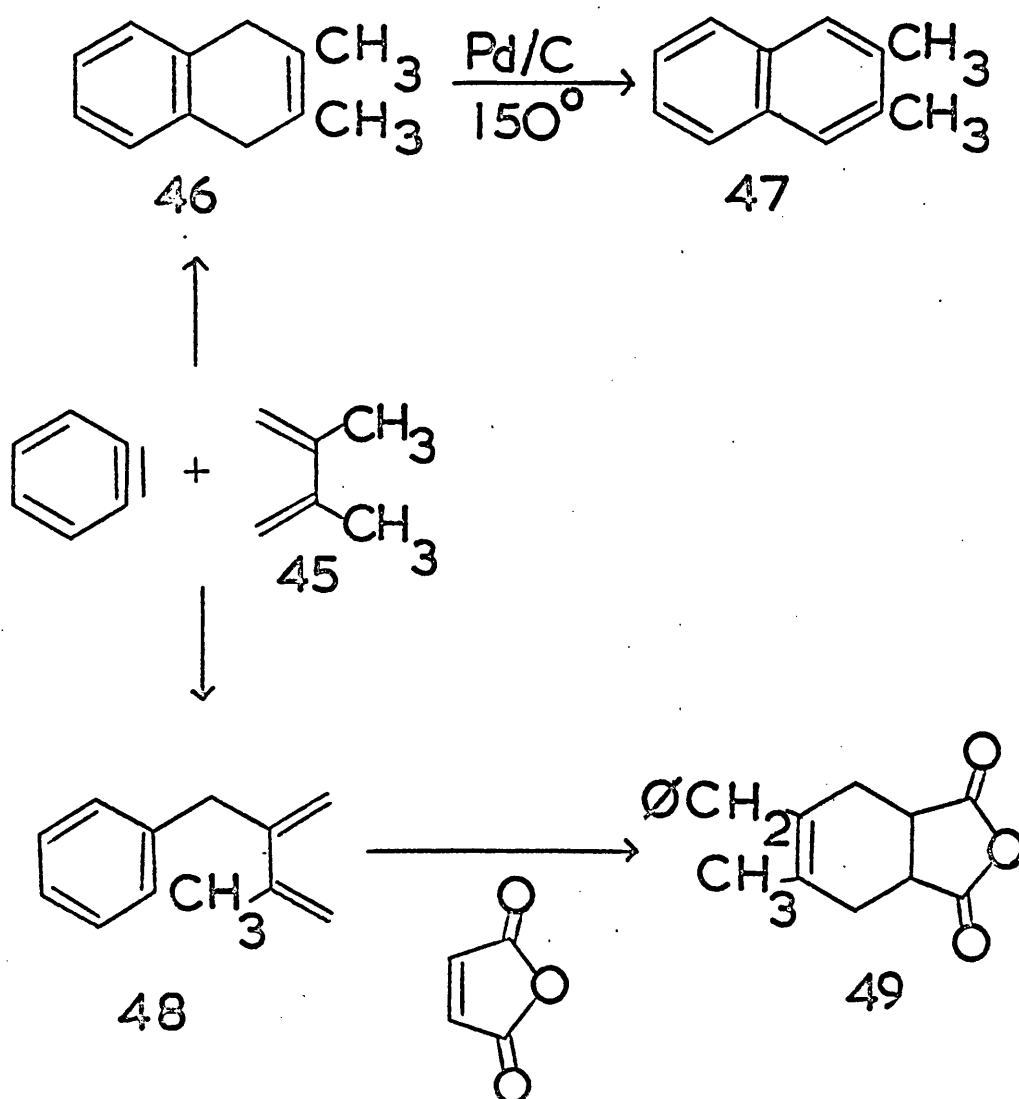
A reaction between benzyne and isoprene (44) in methylene chloride at -80° gave a complex mixture of products. This mixture

was boiled under reflux in benzene solution with maleic anhydride, and then chromatographed on basic alumina. Elution with petrol gave a hydrocarbon fraction, and further elution with ether gave the maleic anhydride adduct (43) (4% overall), which was identical with an authentic sample prepared by the method of Wittig and Dürr¹⁸.

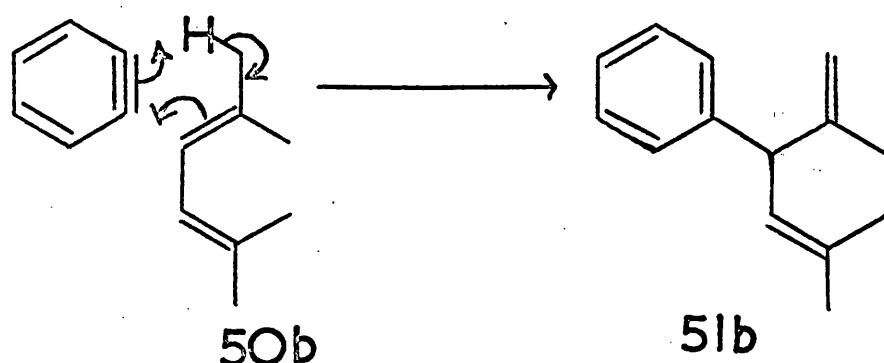


This compound is produced via the "ene" reaction of benzyne and isoprene, which gives 2-benzylbutadiene (42) which is then trapped by maleic anhydride to produce the adduct (43). The hydrocarbon fraction from the chromatography was treated with potassium permanganate in acetone when 2-methylnaphthalene (18%) was isolated. This product arises from 2 + 4 cycloaddition of benzyne and isoprene, followed by dehydrogenation by the potassium permanganate. No trace was found of any compound that could have been a 2 + 2 cycloadduct.

A similar experiment, using 2,3-dimethylbutadiene (45), gave a hydrocarbon mixture which could be separated by chromatography. 2-Benzyl-3-methylbutadiene (48) (50%) was eluted first with petrol. Treatment of this compound with maleic anhydride in boiling toluene gave the adduct (49) which was identified by its m.p. and n.m.r. spectrum. This diene (48) is formed by the "ene" reaction between benzyne and 2,3-dimethylbutadiene. Further elution of the column with petrol gave 2,3-dimethyl-1,4-dihydronaphthalene (46) (15%), which was characterised by its m.p. and n.m.r. spectrum. This is the expected 2 + 4 cycloadduct of benzyne and 2,3-dimethylbutadiene. Treatment of this adduct with 10% palladium on charcoal gave 2,3-dimethylnaphthalene (47).



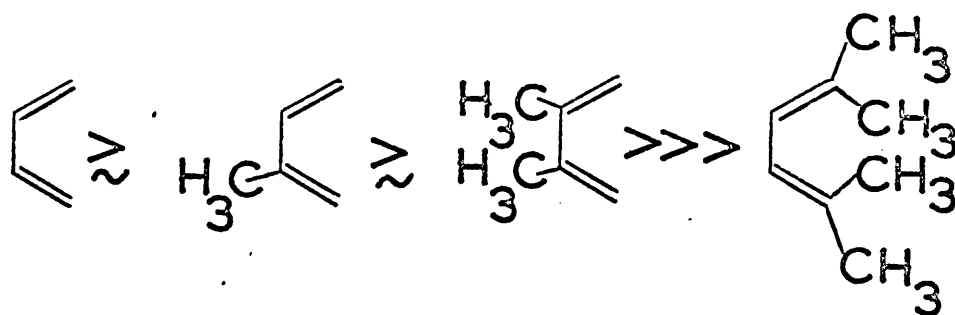
Oxidation of 1-aminobenzotriazole in 2,5-dimethylhexa-2,4-diene (50b) and methylene chloride with lead tetra-acetate gave 2,5-dimethyl-3-phenylhexa-1,4-diene (51b) (48%) as the only detectable adduct. This compound, which has previously been reported by Arnett³², had a n.m.r. spectrum in accord with the expected structure. This compound is formed via the "ene" reaction of benzyne and 2,5-dimethylhexa-2,3-diene.



Biphenylene (10%) was also isolated.

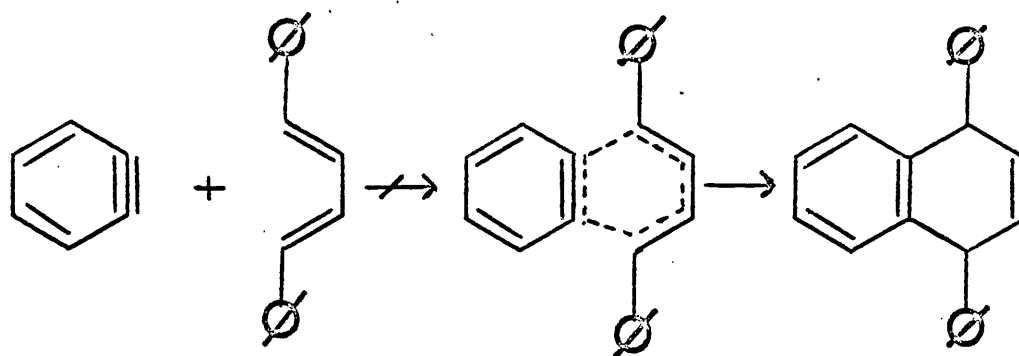
From these few experiments it can be seen that the extent of 2 + 4 cycloaddition falls and that of the "ene" reaction rises with increasing substitution in the diene skeleton. If it is assumed that 2 + 4 cycloaddition is a concerted process, similar to the Diels-Alder reaction, then a planar cisoid-conformation of the diene is a necessary requirement for this reaction to take place.* By examination of spacially-accurate molecular models, the expected stability of the cisoid-conformation as compared with the transoid-conformation, is expected to be

* This assumption is verified later (see p. 127)



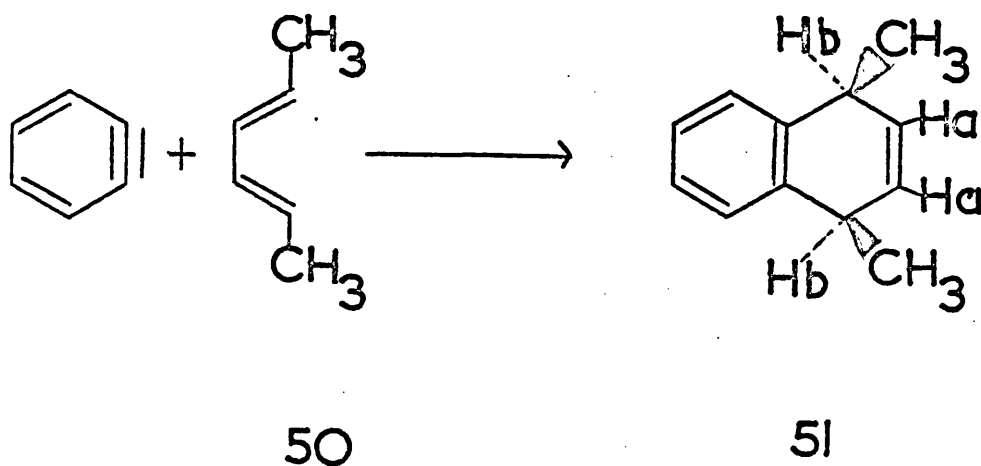
In fact, the dimethylhexadiene cannot exist in the planar cisoid-conformation at all. So, 2 + 4 cycloaddition would be expected to be highest with butadiene and zero with dimethylhexadiene. Conversely, the "ene" reaction would be expected to be lowest with isoprene and highest with dimethylhexadiene. This postulate agrees with the experimental findings, and so the "ene" reaction and 2 + 4 cycloaddition must be competing reactions with this series of compounds, the ratio of the products being governed by the relative stabilities of the cisoid and transoid-conformations.

Benzyne did not react with 1,4-diphenylbutadiene, probably because of the loss of conjugation energy between the phenyl rings of the diene, in the transition state involving 2 + 4 cycloaddition of benzyne and this diene.

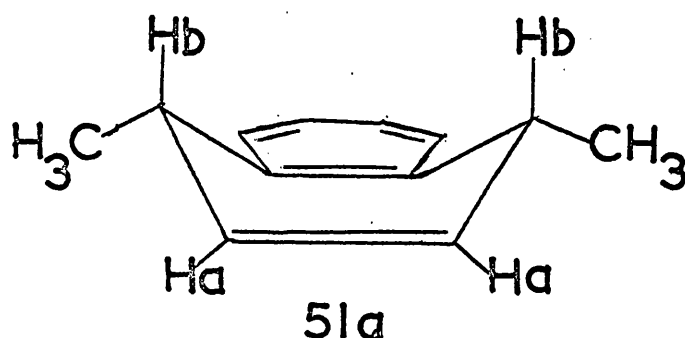


Even the extremely electrophilic aryne, 3-nitrobenzyne did not give any kind of adduct with this diene, and so the energy barrier between that of reactants and the transition state must be very high. Benzyne also gave no apparent reaction with cis,cis-mucononitrile, either because the cisoid-conformation of this diene is unfavourable, or because the diene is too electron-poor to render 2 + 4 cycloaddition a likely process. However, 2-acetoxybiphenylene (11%) was obtained, in addition to biphenylene (41%).

In order to ascertain whether 2 + 4 cycloaddition is a concerted process or not, benzyne was generated in the presence of trans,trans-hexa-2,4-diene, and cis,trans-hexa-2,4-diene⁹². Reaction of benzyne with trans,trans-hexa-2,4-diene (50) gave biphenylene (6%) and cis-1,4-dihydro-1,4-dimethylnaphthalene (51) (60%). The structure of the latter product was determined by examination of the n.m.r. spectrum. This spectrum showed a doublet at τ , 4.30 attributable to Ha.



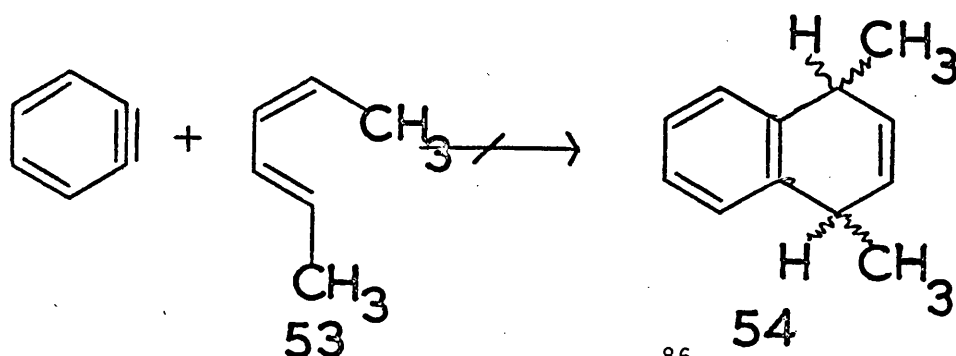
The dihedral angle between Ha and Hb in the most stable conformation (51a), in which the two methyl-groups are both ψ -equatorial, is nearly 90° , and so only a small coupling constant, J_{ab} , would be expected; this is, in fact, observed to be 2.5 c/sec., and hence this compound is the cis-isomer.



Maitland Jones⁸⁷ has synthesised the cis-adduct (51) by an alternative route, and has shown that it is identical to the product obtained from reaction of benzyne with the diene (50). He also showed, by g.l.c. analysis, that no trans-adduct had been formed, and so the reaction is stereospecific. This result was in accord with the n.m.r. analysis of the reaction product of benzyne and the diene (50); no peaks corresponding to the trans-adduct were found.

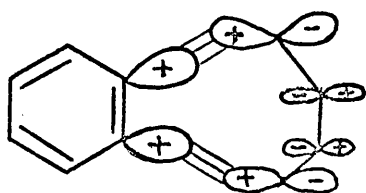
cis,trans-Hexa-2,4-diene (53), in a similar reaction, gave only a 9% yield of benzyne adducts, together with biphenylene (70%). This mixture of adducts gave an uninterpretable n.m.r. spectrum, which showed that not more than 8% (i.e. less than 1% overall) of this mixture could have been the 2 + 4 cycloadduct (54). The major constituent of this mixture could not be identified, but Maitland Jones⁸⁷ has stated that this reaction gives mainly the product of an "ene" synthesis. It was shown, by examination of models, that cis,-trans-hexa-2,4-diene cannot exist in a planar cisoid-conformation, which is necessary for a concerted 2 + 4 cycloaddition of benzyne,

and so no 2 + 4 cycloadduct is expected if 2 + 4 cycloaddition of benzyne is a thermally allowed concerted reaction. If the reaction were not concerted, however, stepwise formation of the 2 + 4 cycloadduct would be possible. Hence both the stereospecificity of the 2 + 4 cycloaddition of benzyne and the diene (50), and the failure of 2 + 4 cycloaddition of benzyne and the diene (53), support the

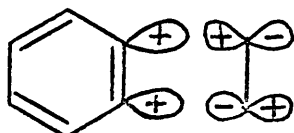


concerted nature of this reaction. Bartlett⁸⁶ obtained an analogous set of results when ethylene was allowed to react with the dienes (50) and (53), and came to the conclusion that the 2 + 4 cycloaddition of ethylene and the dienes was also a concerted reaction.

Orbital symmetry considerations dictate that the highest occupied molecular orbital of benzyne must be symmetric if 2 + 4 cycloaddition is a concerted suprafacial process, and, of course, two electrons must be paired in this orbital i.e. benzyne reacts as a symmetric singlet. It can be seen then, that the highest occupied orbital of benzyne, the symmetric, is of the right symmetry to overlap with the lowest unoccupied orbital of the diene in a suprafacial process.



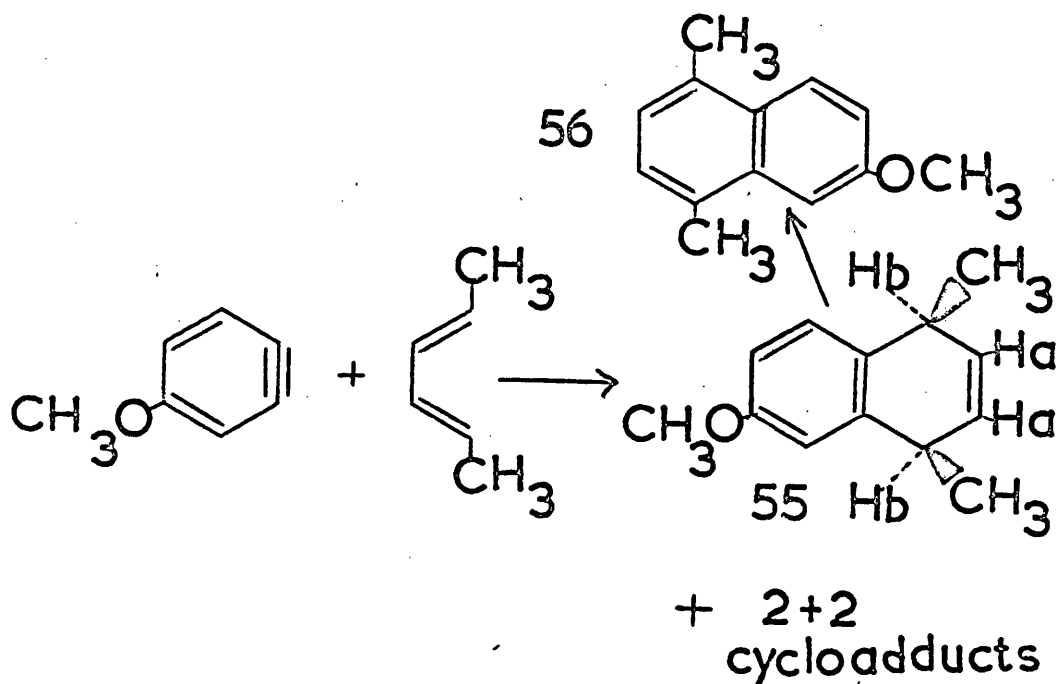
Conversely, the highest occupied orbital of benzyne cannot be of the right symmetry to overlap with the lowest unoccupied orbital of a mono-ene in a suprafacial reaction, and so the $2 + 2$ cycloaddition cannot be concerted. This latter consequence has been verified by



several workers,^{36,37,38,39} who found that benzyne adds to mono-enes stereoselectively, but not stereospecifically. Antarafacial attack of the aryne on the olefin, would, of course, be a concerted reaction, but this reaction is not feasible upon geometrical grounds. These findings are a direct verification of the predictions of Hoffmann⁵⁶, who found, by means of semi-empirical calculations, that the highest occupied orbital of benzyne should, indeed, be symmetric if the molecule is a singlet. These experimental results also are in full agreement with semi-empirical calculations using the CNDO2 approximation, which are described on p173.

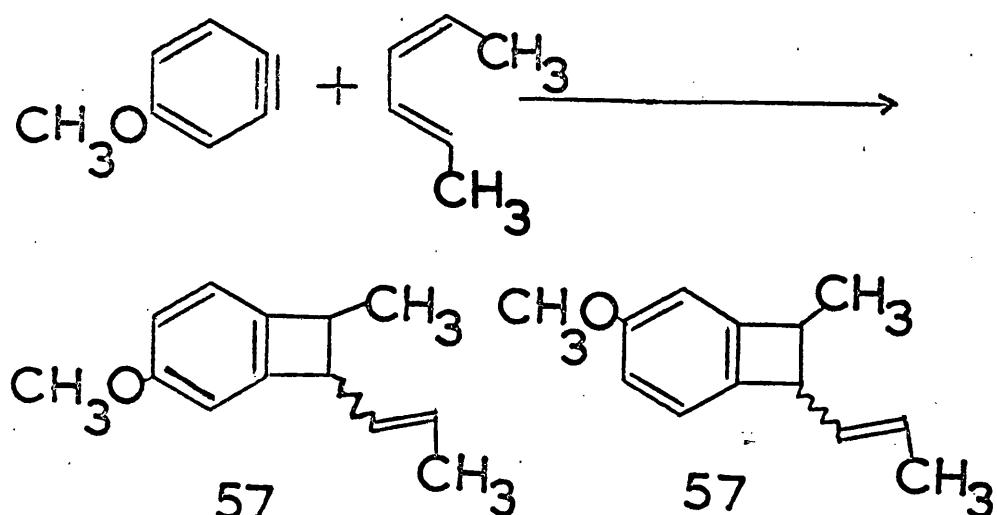
Oxidation of 1-amino-5-methoxybenzotriazole in the presence of trans,trans-hexa-2,4-diene gave an analogous $2 + 4$ cycloadduct (45%) of the diene and 4-methoxybenzyne. This adduct (55) was dehydrogenated to give 1,4-dimethyl-6-methoxynaphthalene (56) which was identified by elemental analysis and mass spectral data. The melting point of the picrate of this compound agreed with the literature value. The adduct (55) was contaminated with $2 + 2$ cycloadducts (15%) which were identified by comparison of the n.m.r. of the mixture with the n.m.r. of the $2 + 2$

cycloadducts produced in the reaction between 4-methoxybenzyne and cis,trans-hexa-2,4-diene. The n.m.r. spectrum of the 2 + 4 cycloadduct (55), which was not masked by the 2 + 2 cycloadducts, showed two doublets with slightly different chemical shifts, attributable to the two methyl groups. The coupling constant, J_{ab} , was only 2.5 c/sec.,

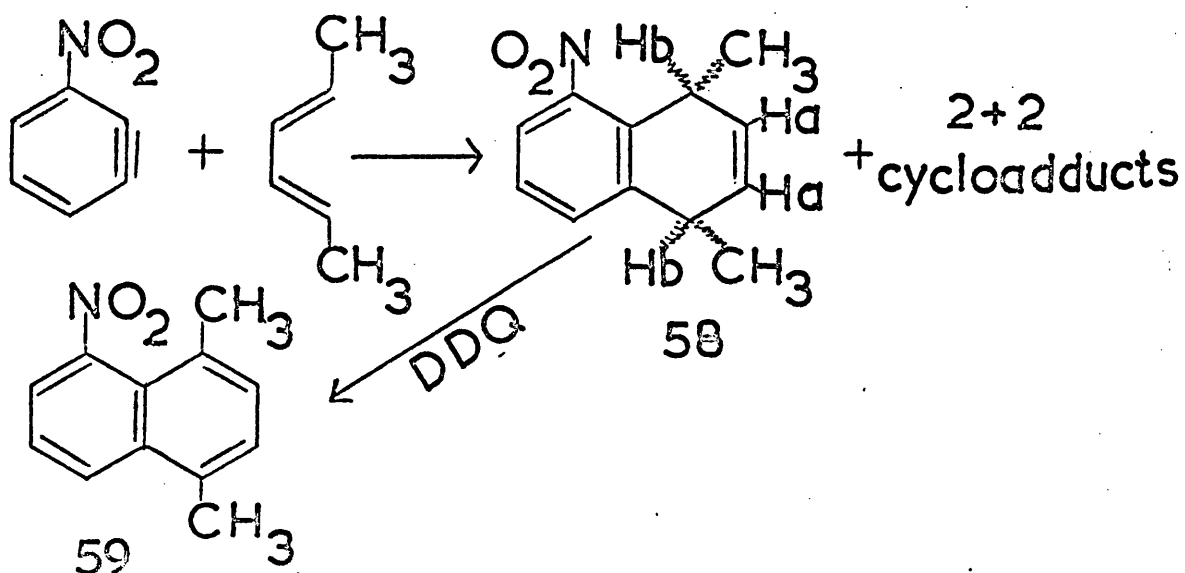


identical to that of adduct (51), and therefore this compound must be cis-1,4-dihydro-1,4-dimethyl-6-methoxynaphthalene. Consequently, 2 + 4 cycloaddition must be a concerted process, since the reaction is stereospecific. An analogous reaction with cis,trans-hexa-2,4-diene produced no detectable 2 + 4 cycloadduct, as expected, but instead afforded a mixture of 2 + 2 cycloadducts (57) (38%). This mixture of adducts [there are eight possible isomers] was identified by n.m.r. and mass spectral data, but gave poor analytical figures.

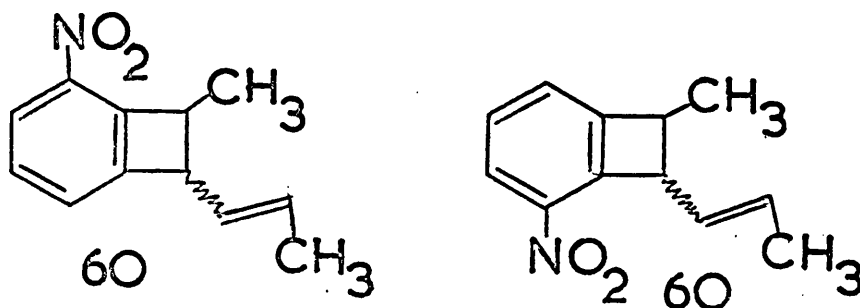
Hence, the highest occupied orbital of 4-methoxybenzyne is also symmetric and 4-methoxybenzyne reacts as a symmetric singlet.



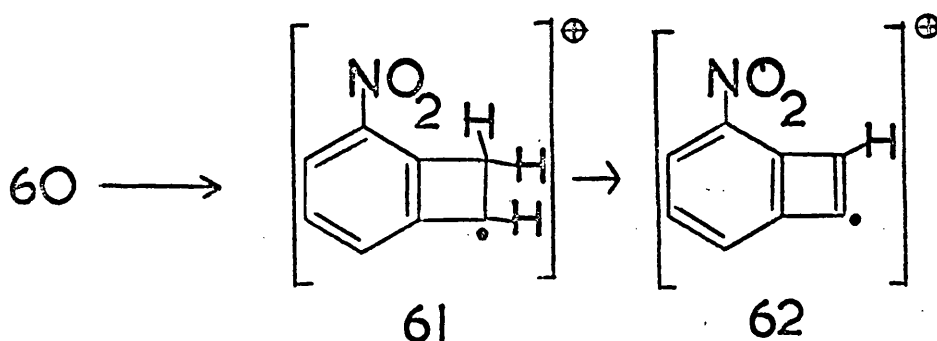
Reaction of 3-nitrobenzyne, produced by oxidation of 1-amino-4-nitrobenzotriazole, with trans,trans-hexa-2,4-diene gave a mixture of adducts (63%), which, upon dehydrogenation with dichloro-dicyano-*p*-benzoquinone, gave a yellow oil. This oil had a n.m.r. spectrum which showed, inter alia, two singlets at τ , 7.35 and τ , 7.56 which were not present in the original mixture of adducts, and which were assigned to the methyl groups in 1,4-dimethyl-5-nitronaphthalene (59). Hence some of the 2 + 4 cycloadduct (58) must have been present in the original mixture. The n.m.r. spectrum of this mixture showed a doublet at 4.20 τ (Jab 3 c/sec.) and a doublet at 8.79 τ (J 7 c/sec.), both of which nearly vanished upon dehydrogenation, and so these peaks can be attributed to adduct (58); no conclusion may be drawn from the low value of Jab, since the effect



of the peri-nitro-group upon the conformation of the adduct is not predictable, and it could not be stated with certainty that the product was the stereospecific cis-adduct. The portion of the original adducts that was unchanged by dehydrogenation was identified as 2 + 2 cycloadducts by n.m.r. comparison with the products of reaction of 3-nitrobenzyne with cis,trans-hexa-2,4-diene. The relative amounts of 2 + 4 and 2 + 2 cycloadducts were calculated from the n.m.r. integrals, and it was found that there was twice as much of the 2 + 2 cycloadducts compared with 2 + 4 cycloadduct. When 3-nitrobenzyne was allowed to react with cis,trans-hexa-2,4-diene, only 2 + 2 cycloadducts (60) (60%) could be detected, and these compounds were characterised by their n.m.r. spectrum, which was complex, owing to the possibility of all eight isomers being present, and by a satisfactory elemental analysis.

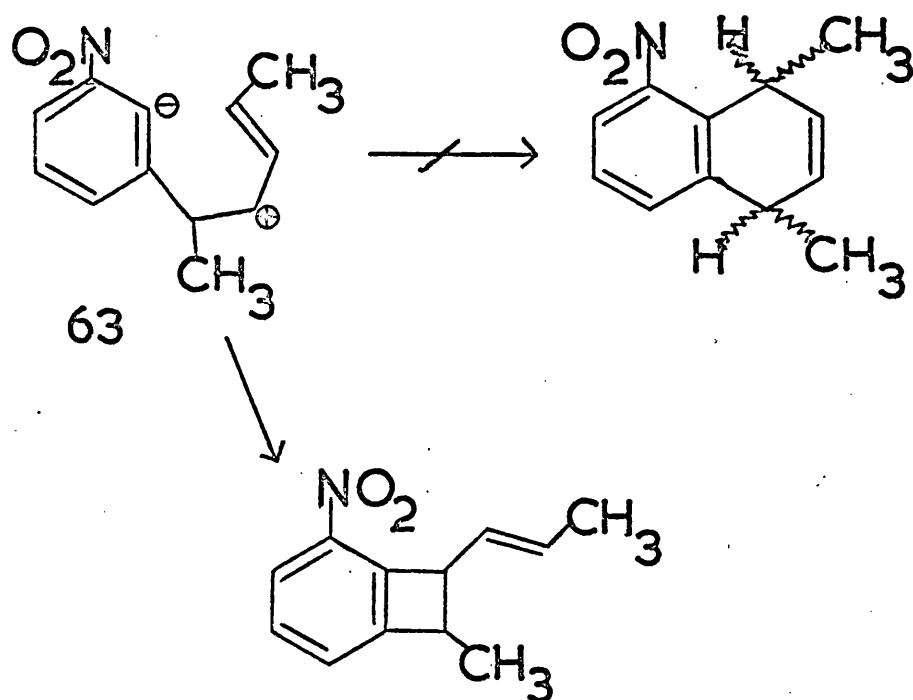
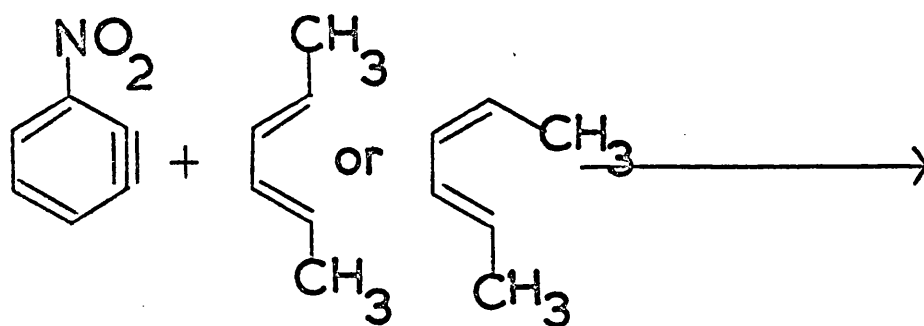
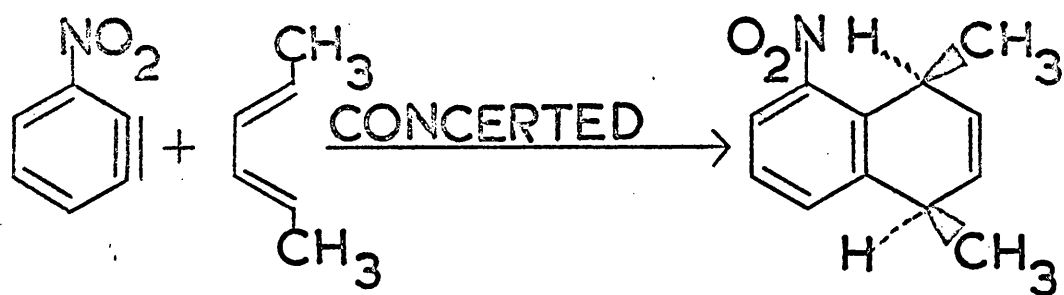


The mass spectrum, however, did not show a parent ion, but showed strong signals at $\frac{m}{e}$, 148 and $\frac{m}{e}$, 146 which were assigned to fragments (61) and (62). No 2 + 4 cycloadducts could be detected, and so, by consideration of the arguments used for the behaviour of benzyne in



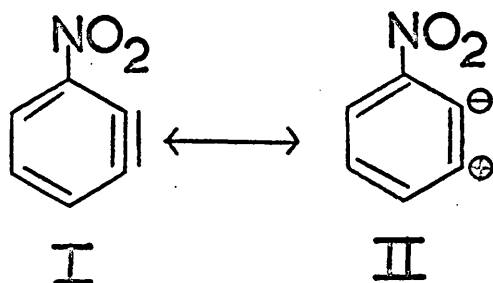
these circumstances, $2 + 4$ cycloaddition must be a concerted process, since a stepwise route would be expected to lead to some $2 + 4$ cycloadduct in this case. Consequently 3-nitrobenzyne must have a symmetric molecular orbital as its highest occupied electronic level, and so 3-nitrobenzyne must show the reactions of a symmetric singlet. This conclusion is in agreement with that reached from semi-empirical calculations using the CNDO2 approximation (see p173).

The reaction of 3-nitrobenzyne with trans,trans-hexa-2,4-diene had produced twice as much $2 + 2$ cycloadduct as $2 + 4$ cycloadduct, and so an explanation has to be found for this phenomenon in the light of the above findings. It is a requirement of a concerted $2 + 4$ cycloaddition reaction that the aryne must approach the diene in a certain sense, and the diene must be in the planar cisoid-conformation; this process is less favourable on entropy grounds than a relatively random attack of 3-nitrobenzyne on the diene to produce the betaine (63) which has a stabilised o-nitrophenyl carbanion and an allylic carbonium ion as its reactive sites. This long-lived betaine may then ring-close to form the benzocyclobutene via the required stepwise process, dictated by the symmetry of the highest occupied aryne orbital. Ring closure to form the dihydronaphthalene does not occur, possibly upon entropy grounds. Hence the $2 + 4$ cycloadducts are formed by a concerted reaction, and the $2 + 2$ cycloadducts are formed, in this case, by the more facile ionic stepwise mechanism. The strongly dipolar nature of 3-nitrobenzyne may be a factor that is favourable for the formation of the betaine (63), rather than undergoing the "ene" reaction as benzyne does in cases where $2 + 4$ cycloaddition is less favourable; this may explain the observation that benzyne forms "ene" reaction products, and 3-nitrobenzyne produces $2 + 2$ cycloadducts when generated in the



+ other 2 + 2
cycloadducts

presence of cis,trans-hexa-2,4-diene. The dipole moment of benzyne is calculated to be 1.21D., whereas the dipole moment of 3-nitrobenzyne is 6.44D. Since the observed dipole moment of nitrobenzene is 4.27D.⁸⁹, the exceptionally large value of the calculated dipole moment of 3-nitrobenzyne is not just a superposition of the nitrobenzene dipole upon the benzyne dipole, and some rearrangement of electron density between the two non-bonded σ -orbitals must have occurred. The most likely source of this increment in the dipole moment is the existence, to a large extent, of 3-nitrobenzyne in the polar form (II).



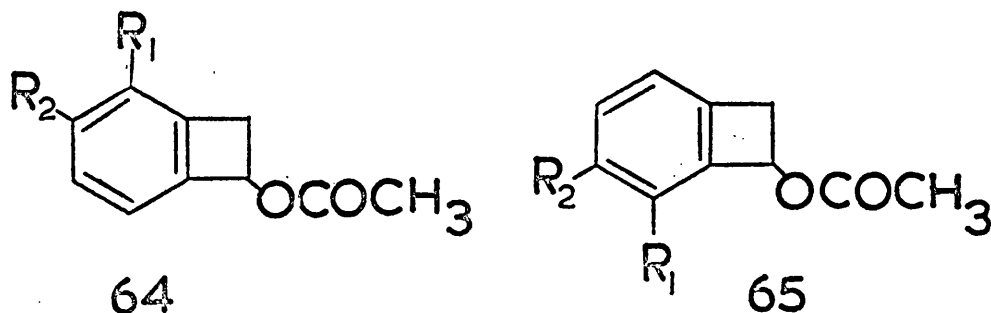
This 1,2-dipole should readily be attacked by an electron-rich centre at the position meta to the nitro-group, and so attack of a diene would readily form the betaine (63). Benzyne itself has been claimed by Simmons⁵⁴ to have only a small tendency to exist in the dipolar form, and so formation of betaine intermediates in the reaction between benzene and the hexadienes would be suppressed. A diradical intermediate would be more likely, but this may require much more energy than that needed to effect the "ene" reaction, and so the latter reaction is favoured with benzyne.

SECTION 5

Oxidation of 1-aminobenzotriazoles in the presence of mono-enes.

Campbell⁸⁸ discovered that benzyne, when generated by oxidation of 1-aminobenzotriazole with lead tetra-acetate, gave little or no 2 + 2 cycloadducts with mono-enes. Of the five olefins that were tried, only one, vinyl acetate, produced any cycloadduct at all and then only a trace quantity. As Campbell had carried out this reaction at -80° , it seemed reasonable to repeat this reaction at room temperature to try to increase the yield of the adduct. Indeed, when this reaction was performed, biphenylene (65%) was produced, and also benzocyclobutenyl acetate [(64); $R_1 = R_2 = H$] (6%) was obtained, and was shown to be identical with an authentic sample. The success of this reaction, albeit in modest yield, spurred the study of this and related reactions. It was hoped to synthesise the relatively inaccessible benzocyclobutenes and also to test the electrophilicity of the aryne, since the more electrophilic the aryne, the more likely reaction is with the relatively inert mono-ene.

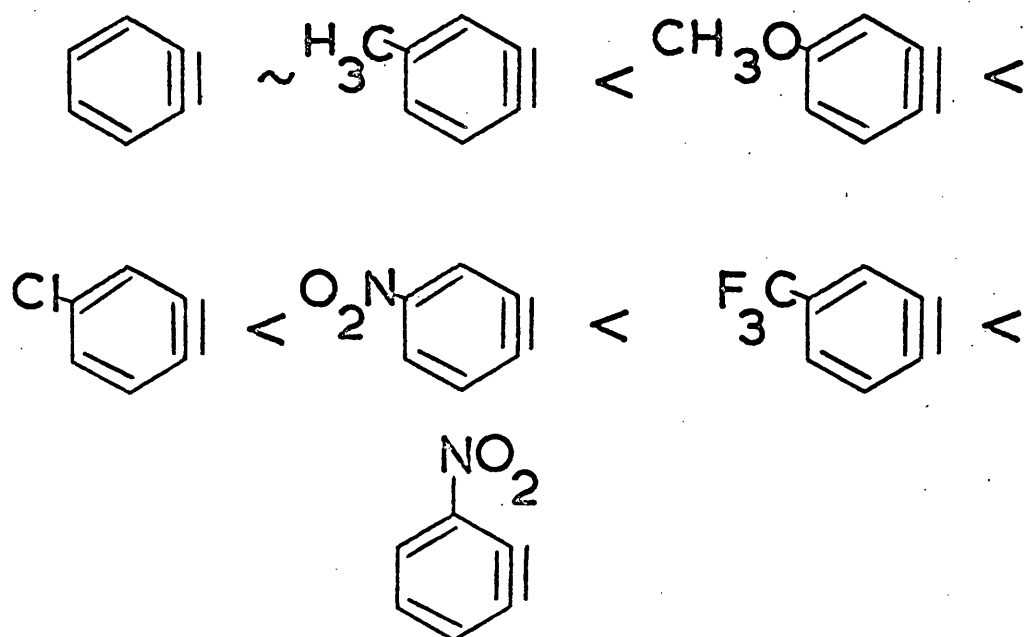
Oxidation of 1-amino-5-methylbenzotriazole in vinyl acetate gave a mixture of methylbenzocyclobutenyl acetates [(64) and (65); $R_1 = H$, $R_2 = CH_3$] (6%), mixed with 3- and 4-tolyl acetates (12%).



The relative yields of these two compounds were estimated by their n.m.r. integrals, and the n.m.r. and i.r. data confirmed that these were the structures of the compounds present. A mixture of 2,6- and 2,7-dimethylbiphenylenes (67%) was also obtained. 4-Methoxybenzyne, generated from 1-amino-5-methoxybenzotriazole, gave a 16% yield of 2 + 2 cycloadducts [(64) and (65); $R_1 = H$, $R_2 = OCH_3$] when generated in vinyl acetate. These adducts were characterised by n.m.r., i.r., and analytical data. A trace of 3- and 4-acetoxyanisoles, and also a moderate yield of the dimers, 2,6- and 2,7-dimethoxybiphenylene (29%), was obtained. 4-Chlorobenzyne, generated in a similar environment, gave the adducts [(64) and (65); $R_1 = H$, $R_2 = Cl$] (24%), mixed with 3- and 4-chlorophenyl acetates (10%). The mixture, which was inseparable, was characterised by n.m.r. and i.r. data, and the relative yields of each compound were estimated from the n.m.r. integrals. The mass spectrum of the mixture showed signals at $\frac{m}{e}$, 198 and $\frac{m}{e}$, 196 corresponding to the parent ions of the 2 + 2 cycloadducts. There were no signals at higher $\frac{m}{e}$. Dichlorobiphenylenes (20%) and dichloro-1-phenylbenzotriazoles (6%) were also produced. 4-Trifluoromethylbenzyne gave a 39% yield of the vinyl acetate adduct [(64) and (65); $R_1 = H$, $R_2 = CF_3$]. This compound gave a satisfactory elemental analysis, and the assigned structure was confirmed by i.r. and n.m.r. data. Bis(trifluoromethyl)biphenylenes (17%) were also produced in this reaction. Oxidation of 1-amino-6-nitrobenzotriazole in vinyl acetate solution gave a mixture of 4- and 5-nitrobenzocyclobutenyl acetates [(64) and (65); $R_1 = H$, $R_2 = NO_2$] (32%). This mixture did not give a satisfactory elemental analysis, but the n.m.r., i.r., and mass spectral data fitted the assigned structures. 3-Nitrobenzyne, generated by oxidation of 1-amino-4-nitrobenzotriazole gave a 51% yield of a mixture of vinyl acetate adducts [(64) and (65); $R_1 = NO_2$, $R_2 = H$], which could be

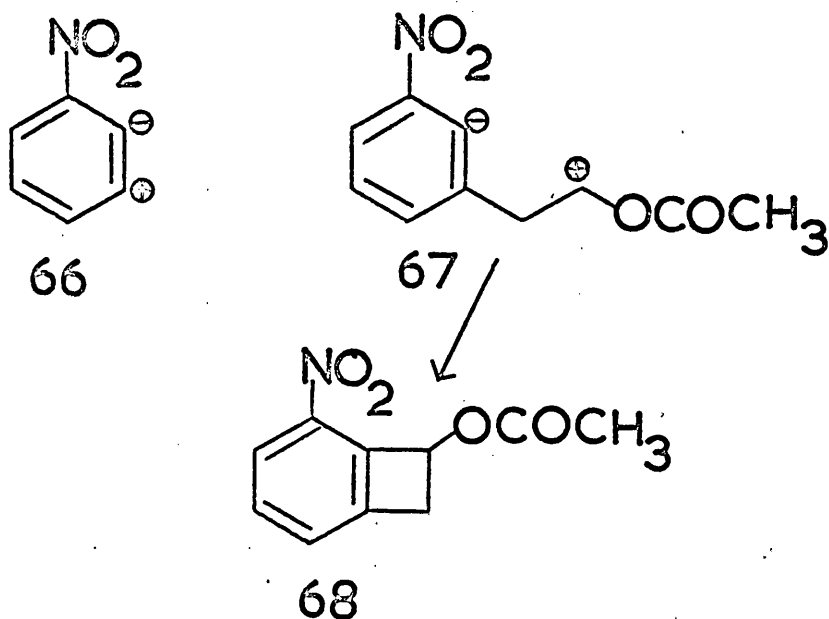
recrystallised from petrol to give pure 3-nitrobenzocyclobutenyl acetate [(64); $R_1 = \text{NO}_2$, $R_2 = \text{H}$], which was the dominant isomer in the mixture. The n.m.r. spectrum of the above mixture of compounds was typical of that class of compound.

Hence, the degree of 2 + 2 cycloaddition of the various arynes to vinyl acetate is



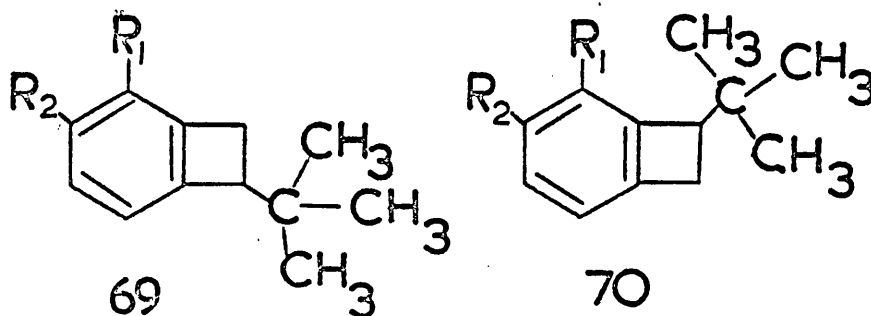
This order of reactivity towards vinyl acetate is in agreement with the expected electrophilicity of the arynes as predicted by consideration of the inductive effect of the substituent upon the non-bonded σ -orbitals of the molecule. The yield of the 2 + 2 cycloadduct of 3-nitrobenzyne with vinyl acetate is, in fact, much higher than the yield of 2 + 4 cycloadduct of the same aryne and tetracyclone or furan. This supports the theories advanced in Section 4 of this Discussion. The high entropy factor in the attack of 3-nitrobenzyne upon tetracyclone or furan would necessitate this reaction being

slower than the favourable attack by nucleophiles, and so the yield of 2 + 4 adduct is depressed by virtue of competing reactions. In the case of vinyl acetate, the olefin attacks the aryne, which is predominantly in the dipolar form (66), to form the betaine (67) which then ring-closes to form the 2 + 2 cycloadduct (68). This reaction is favourable enough to compete with attack by nucleophiles



upon this aryne, and so a good yield of adduct is obtained.

t-Butylethylene was also used as an aryne "trap". 4-Nitrobenzyne, generated in a mixture of the olefin and methylene chloride by oxidation of 1-amino-6-nitrobenzotriazole, gave the adducts [(69) and (70), R₁ = H, R₂ = NO₂] (17%), and also 3- and 4-nitrophenyl acetates (20%). The 2 + 2 cycloadducts gave a satisfactory elemental analysis

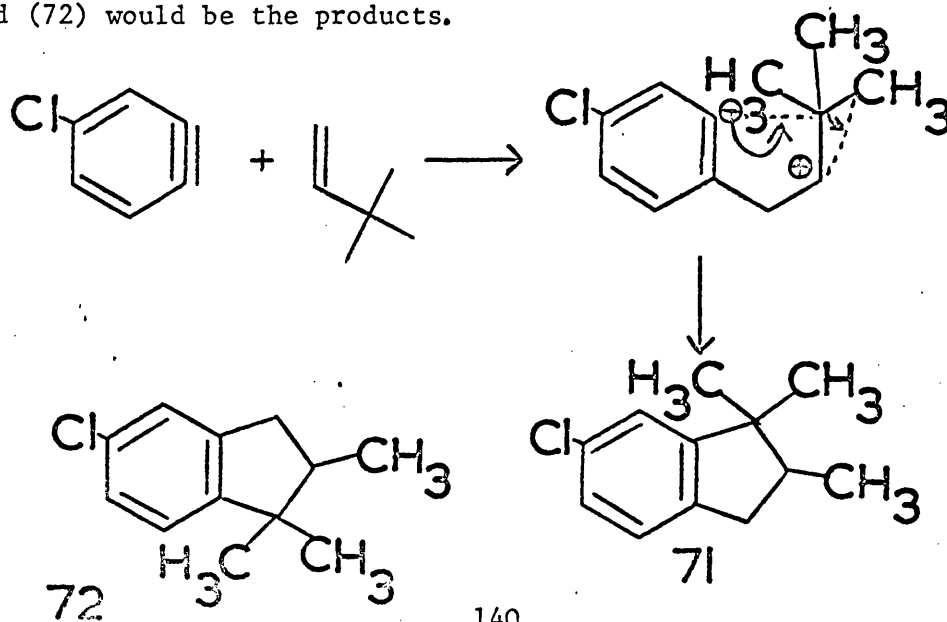


for nitrogen, and the n.m.r. and i.r. spectral data were in agreement with the required structure. The mass spectrum showed an ion at

$\frac{m}{e}$, 149, corresponding to a loss of isobutylene from the parent ion.

3-Nitrobenzyne, when generated from 1-amino-4-nitrobenzotriazole, in a similar experiment, gave only a 3% yield of a mixture of 1:1 adducts. The mass spectrum showed similar characteristics to the adducts obtained from 4-nitrobenzyne, and so these adducts were probably compounds [(69) and (70); $R_1 = \text{NO}_2$, $R_2 = \text{H}$]. The infrared spectrum was also similar to that of the adducts [(69) and (70); $R_1 = \text{H}$, $R_2 = \text{NO}_2$]; 3-nitrophenyl acetate (31%) was also produced in this reaction.

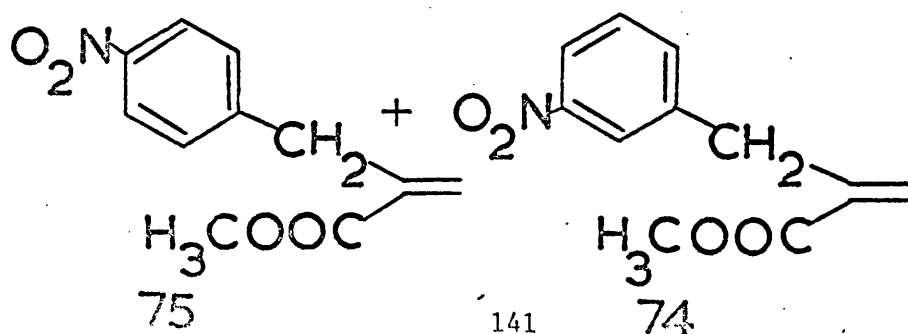
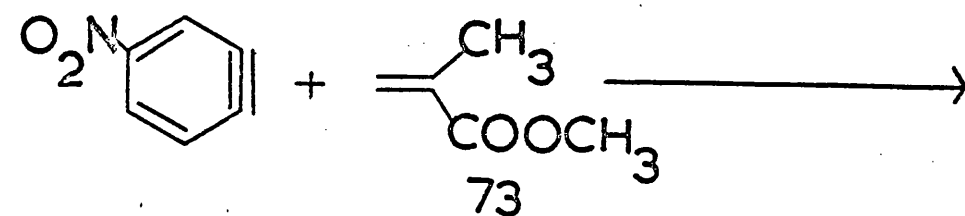
4-Chlorobenzyne, generated by oxidation of 1-amino-5-chlorobenzotriazole in similar environment, gave a mixture of 2,6- and 2,7-dichlorobiphenylenes (23%) and a mixture of 3- and 4-chlorophenyl acetates (10%). In addition, a small amount of an oil was obtained, which was apparently a mixture of 1:1 adducts (2%). The mass spectrum showed parent ions at $\frac{m}{e}$, 196 and $\frac{m}{e}$, 194, but the base peaks were at $\frac{m}{e}$, 181 and $\frac{m}{e}$, 179, corresponding to the loss of a methyl group from the parent ions. Thus the adducts cannot be the t-butylbenzocyclobutenes, since these compounds are expected to lose isobutylene in the mass spectrum to give the base peak. If a methyl group were to migrate during the ionic stepwise cycloaddition reaction, then the adducts (71) and (72) would be the products.



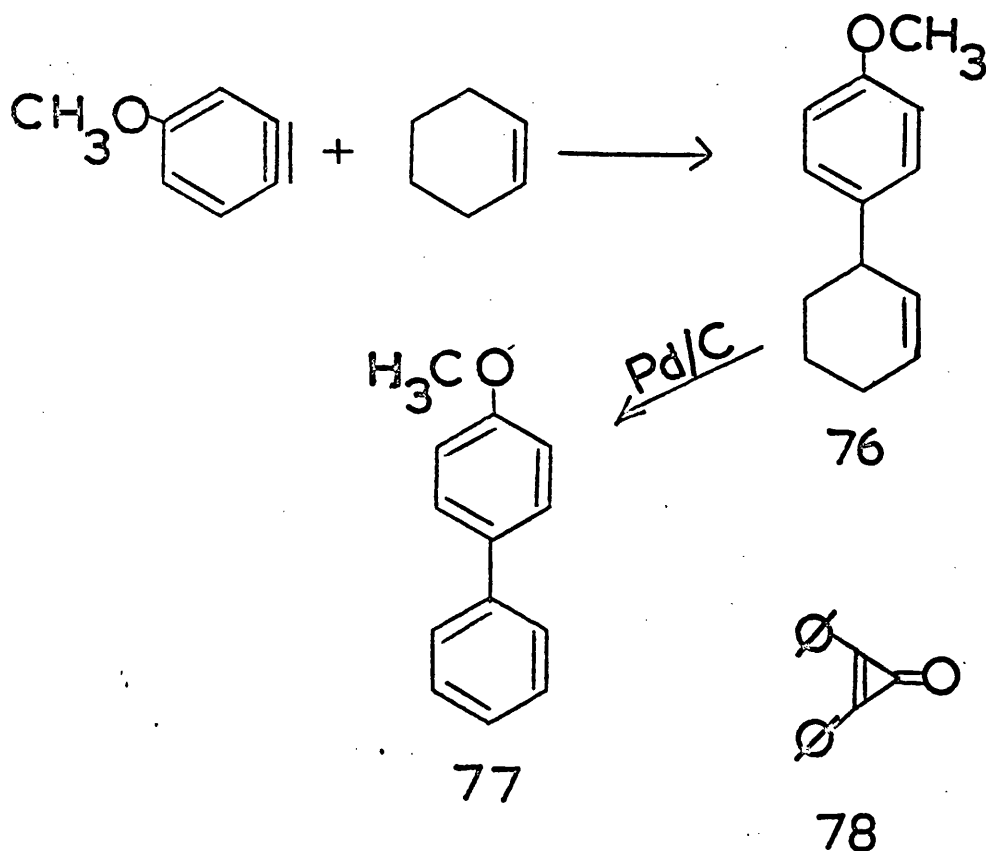
These compounds would be expected to lose a methyl group rather easily in the mass spectrum.

Oxidation of 1-amino-5-trifluoromethylbenzotriazole in t-butylethylene and methylene chloride produced, surprisingly, no detectable quantity of adducts; a mixture of 2,6- and 2,7-bis(trifluoromethyl)-biphenylenes (60%), and also a mixture of 3- and 4-trifluoromethylphenyl acetates (3%) were isolated.

Oxidation of 1-amino-4-nitrobenzotriazole in indene gave 3-nitrophenyl acetate (6%) as the only recognisable product. Large quantities of compounds were found which seemed, from their n.m.r. and i.r. spectral data, to consist of 1:1:1 adducts of 3-nitrobenzyne, indene and acetic acid. 3-Nitrobenzyne did not form an adduct with trans-dichloroethylene or methyl acrylate, 3-nitrophenyl acetate (31-33%) being isolated instead. 4-Nitrobenzyne, generated by oxidation of 1-amino-6-nitrobenzotriazole, reacted with methyl methacrylate (73) to give 1-methoxycarbonyl-1-(m-nitrobenzyl)-ethylene (74) and 1-methoxycarbonyl-1-(p-nitrobenzyl)-ethylene (75) as an inseparable mixture (60%). These products arose from the "ene" reaction between the aryne and the olefin.



Oxidation of 1-amino-5-methoxybenzotriazole in cyclohexene gave an intractable mixture of 1:1 adducts which, upon dehydrogenation with palladium on charcoal at 220°, gave 4-methoxybiphenyl (77). This compound obviously arose via the "ene" reaction between 4-methoxybenzyne and cyclohexene to give, inter alia, the adduct (76), which is then dehydrogenated to the biphenyl (77).



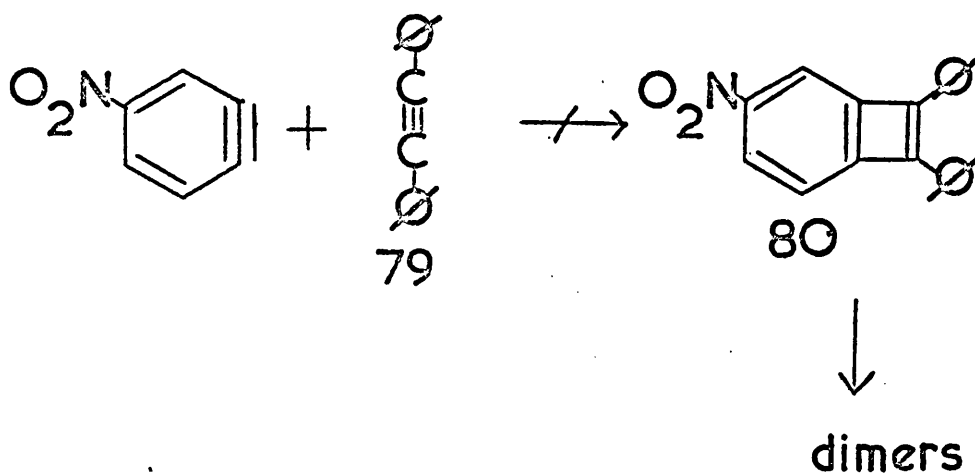
Oxidation of 1-aminobenzotriazole in trans-dichloroethylene or 2,4,4-trimethylpent-2-ene, produced no trace of adduct, forming biphenylene (39-41%) instead. Oxidation of the same triazole in the presence of diphenylcyclopropenone (78) produced no adduct; biphenylene (41%) was formed, as was phenyl acetate (7%) and diphenyl acetylene (tolan) (6%). This latter product was formed by decarbonylation of the diphenylcyclopropenone upon workup.

SECTION 6

Oxidation of 1-aminobenzotriazoles in the presence of acetylenes.

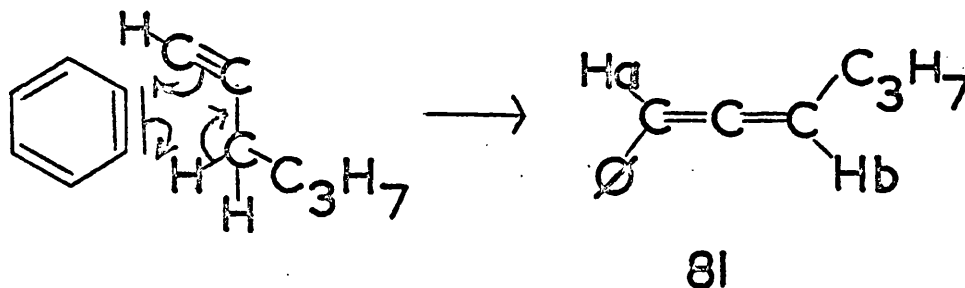
Campbell⁹⁰ attempted to add benzyne, produced by oxidation of 1-aminobenzotriazole with lead tetra-acetate, to phenyl acetylene. A complex hydrocarbon mixture was obtained, from which a trace quantity of phenanthrene was separated. No other component of the mixture could be identified.

Oxidation of 1-amino-6-nitrobenzotriazole in the presence of tolan (79) gave no trace of the dimers of the 2 + 2 cycloadduct, 1,2-diphenyl-4-nitrobenzocyclobutadiene (80), and the tolan was recovered quantitatively.

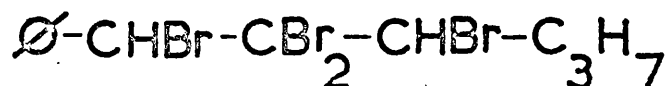


The only recognisable product from this oxidation was a mixture of 2,6- and 2,7-dinitrobiphenylenes (2.5%). The failure of the arynes, generated from their respective 1-aminobenzotriazoles, to form benzocyclobutadienes with acetylenes is in contrast to the success of Stiles⁴⁰, who generated benzyne by decomposition of benzenediazonium 2-carboxylate.

The feasibility of an "ene" reaction between benzyne and acetylenes containing suitable hydrogen atoms has been shown by Stiles and Haag⁹³, who decomposed benzenediazonium 2-carboxylate in the presence of hex-1-yne to give the "ene" reaction product, 1-phenylhexa-1,2-diene (81), in less than 4% yield.



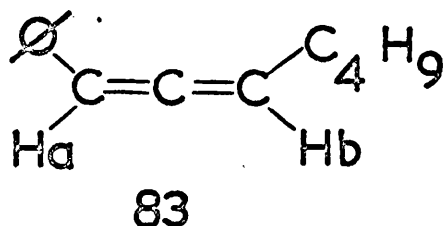
Oxidation of 1-aminobenzotriazole with lead tetra-acetate in the presence of hex-1-yne gave the allene (81) in rather better yield (13%). This compound showed a peak at 1970 cm^{-1} in the infra-red spectrum, characteristic of an allene. The n.m.r. spectrum showed H_a as a quintet and H_b as a quartet. These peculiar splittings arose by long range coupling through the allenic system. This compound polymerised slowly upon standing, and reacted with bromine in carbon tetrachloride to give the tetrabromo-compound (82), the mass spectrum of which showed a set of parent ions corresponding to four bromine



82

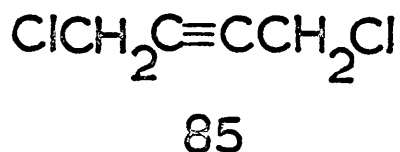
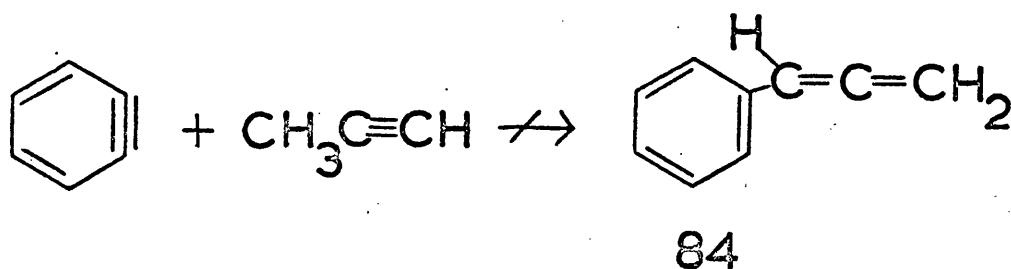
atoms, and of the correct molecular weight. Biphenylene (43%) was also produced in the above oxidation.

An analogous reaction using hept-1-yne as the benzyne "trap", gave 1-phenylhepta-1,2-diene (83) (8%), which had an i.r. spectrum

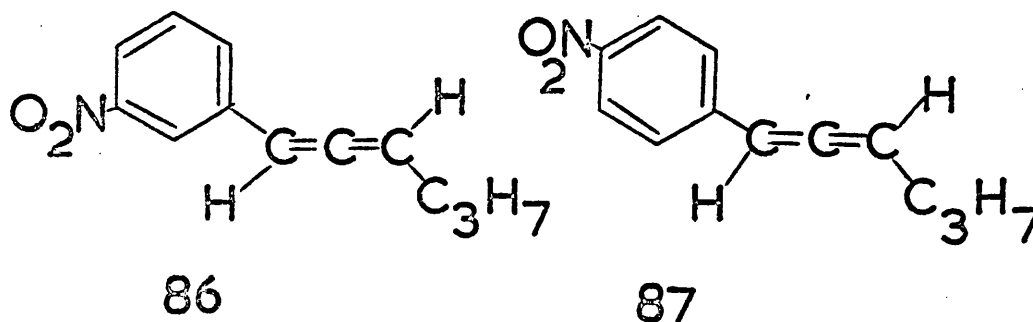


identical with that of an authentic sample. This spectrum showed a strong peak at 1940 cm^{-1} , indicative of an allene. The n.m.r. spectrum showed the same peculiar splittings of H_a and H_b as for compound (81). Biphenylene (41%) and phenyl acetate (29%) were also isolated from this reaction.

Oxidation of 1-aminobenzotriazole in the presence of methyl acetylene at -80° gave only biphenylene (61%) and phenyl acetate (4%). No trace could be found of the "ene" reaction product, phenyl allene (84).



Oxidation of 1-amino-6-nitrobenzotriazole in the presence of hex-1-yne gave a mixture (56%) of 1-(m-nitrophenyl)-hexa-1,2-diene (86) and 1-(p-nitrophenyl)-hexa-1,2-diene (87).



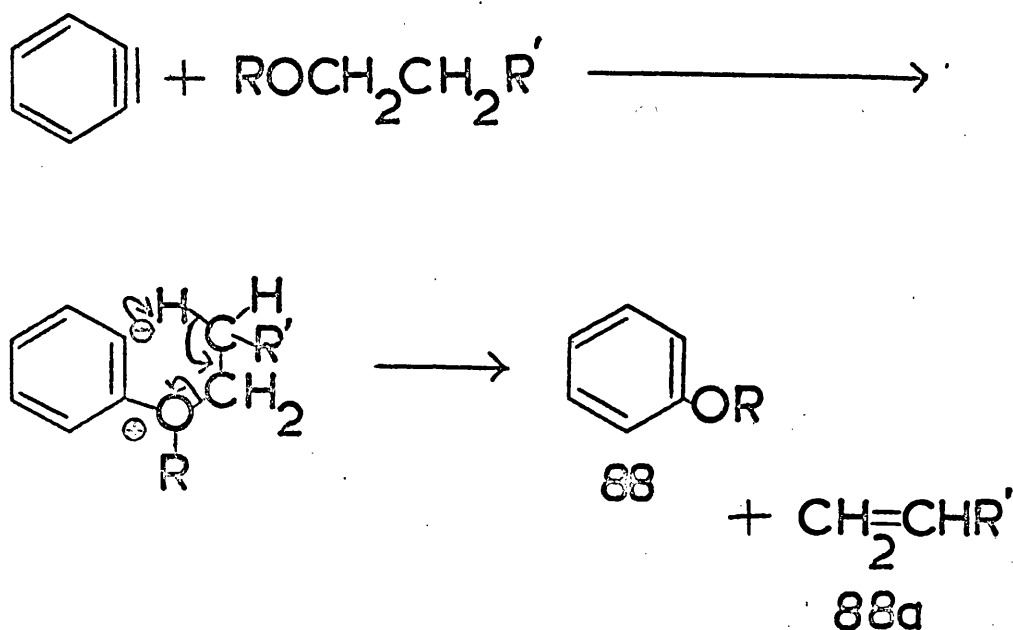
This mixture showed a peak at 1960 cm^{-1} in the i.r. spectrum, and also had a characteristic n.m.r. spectrum. These compounds polymerised slowly at room temperature, and reacted with only one molecule of Br₂ to give dibromo-compounds. The remaining double bond in the molecule was almost inert to bromine. The mass spectrum of the brominated compounds showed a set of parent ions corresponding to two bromine atoms per molecule, and had the correct molecular weight.

It seems that "ene" reactions involving an aryne and a propargyl system occur fairly readily. The marked increase in the yield of such products in going from benzyne to 4-nitrobenzyne is only to be expected on the grounds of the increased electrophilicity of such an aryne. The small, but significant, amounts of phenyl acetate produced from benzyne and acetic acid (or lead tetra-acetate) in the presence of some acetylenes may indicate some sort of interaction between the aryne and the alkyne even though no adduct is isolated.

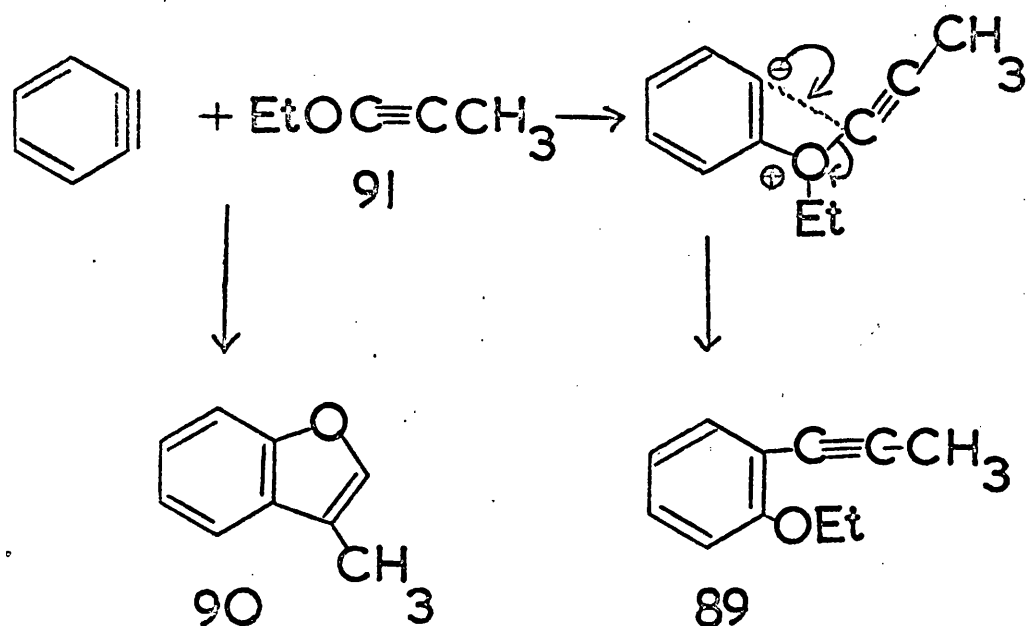
SECTION 7

Reactions of arynes in the presence of ethers.

Attempts to cleave dialkyl ethers with arynes have previously failed; none of the expected olefin (88a) or phenyl ether (88) was isolated in any case. ¹¹⁹ Wassermann ⁹¹ decomposed benzenediazonium



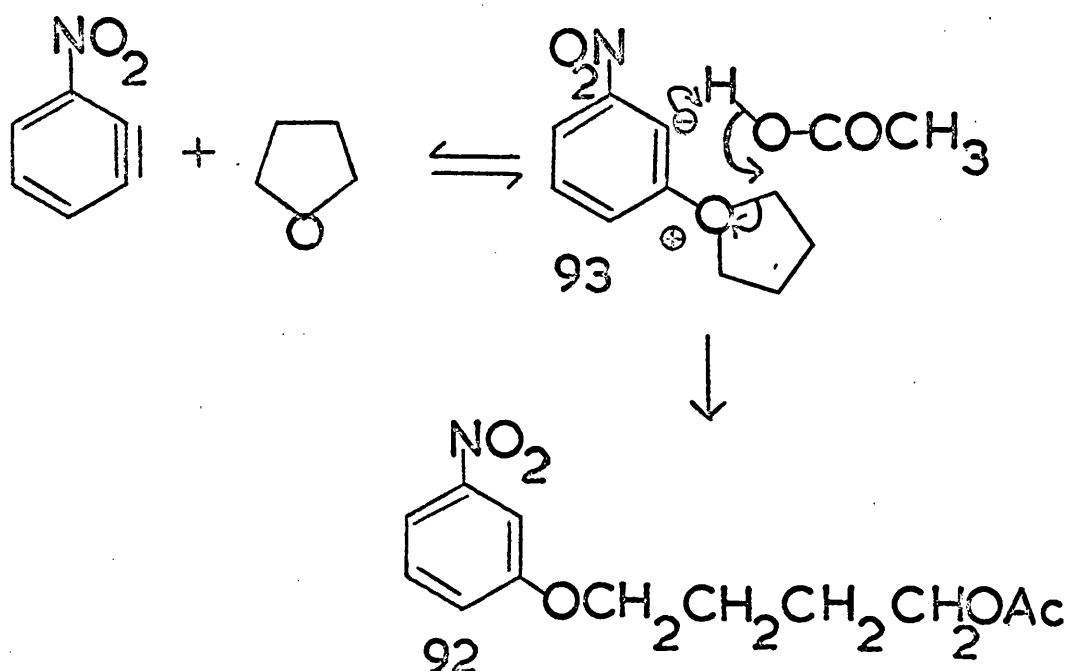
2-carboxylate in the presence of 1-ethoxyprop-1-yne (91), and isolated a series of unusual adducts. Amongst these were two products [(89) and (90)] which were the result of ether cleavage. A series of 1-aminobenzotriazoles was oxidised in diethyl ether with lead tetraacetate in an attempt to cleave the ether, phenetoles being the expected products.



Benzyne itself produced no phenetole when generated in diethyl ether from 1-aminobenzotriazole. Biphenylene (39%) and phenyl acetate (20%) were isolated, the latter compound being produced in exceptionally high yield. 4-Methoxybenzyne, on the other hand, did give a minute yield of a mixture of 3- and 4-ethoxyanisole which was identified by i.r. comparison with the compounds obtained from the reaction of 4-methoxybenzyne and ethanol; 2,6- and 2,7-dimethoxybiphenylenes (29%) and 3- and 4-acetoxyanisoles (5%) were also isolated. 4-Chlorobenzyne gave no phenetoles, affording only a mixture of 2,6- and 2,7-dichlorobiphenylenes (17%) and a mixture of 3- and 4-chlorophenyl acetates (1%). 4-Trifluoromethylbenzyne dimerised in ether to give a mixture of 2,6- and 2,7-bis(trifluoromethyl)-biphenylenes (23%) and a small amount of 3- and 4-trifluoromethylphenyl acetates (5%). A colourless oil, insufficient for structure determination, which might have been the corresponding mixture of phenetoles, was also isolated. However, 3-nitrobenzyne, generated from 1-amino-4-nitro-

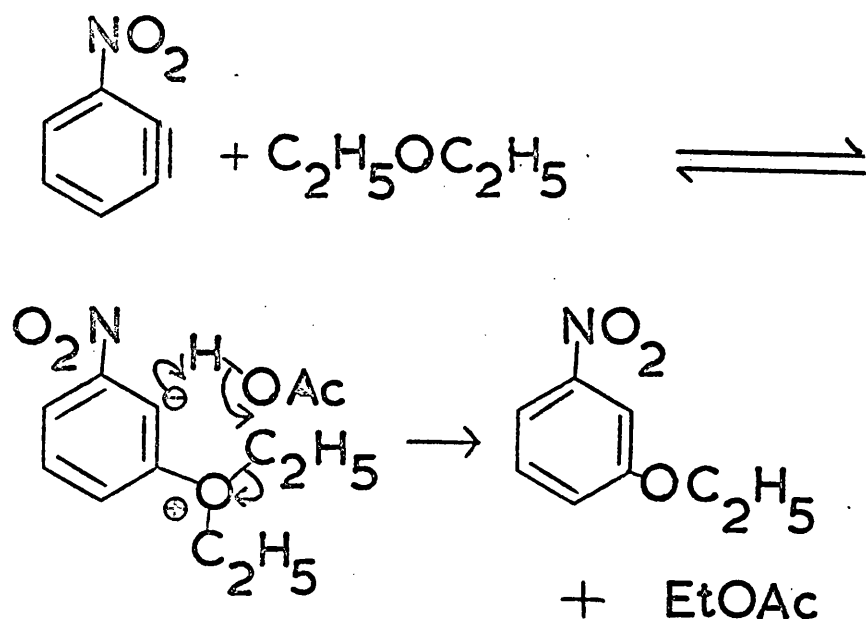
benzotriazole, reacted with diethyl ether to form 3-nitrophenetole (45%), which had all the expected physical properties and spectral data. 3-Nitrophenyl acetate (16%) was also isolated from this reaction.

An analogous experiment with the same aryne, using tetrahydrofuran as the solvent, gave 4-(m-nitrophenoxy)-butyl acetate (92) (54%). This compound was identified by i.r., n.m.r., and mass spectral data, and gave a satisfactory elemental analysis.

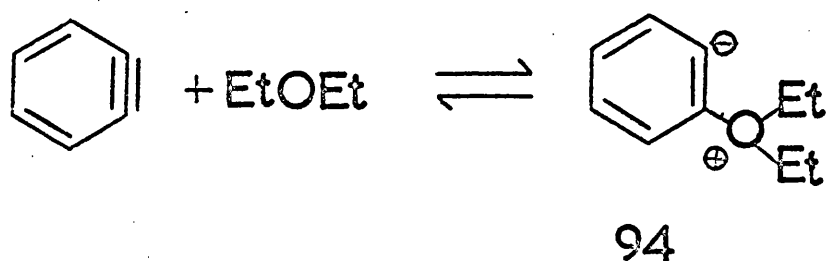


The above mechanism is thought to be the key to what is happening in all the experiments involving arynes and ethers described in this Thesis. The 3-nitrobenzyne is attacked by the oxygen atom of the tetrahydrofuran to give the betaine (93), which can either revert to starting materials or react with acetic acid to give the product (92). The intermediate betaine (93) is stabilised by the fact that it contains a carbanion ortho to a nitro-group and this is thus inductively stabilised, and an oxonium ion, which is a stable entity, as its reactive sites. Hence, the betaine has a relatively long life and thus has a higher chance of reacting with acetic acid.

An analogous mechanism may be drawn for reaction of this species with diethyl ether.

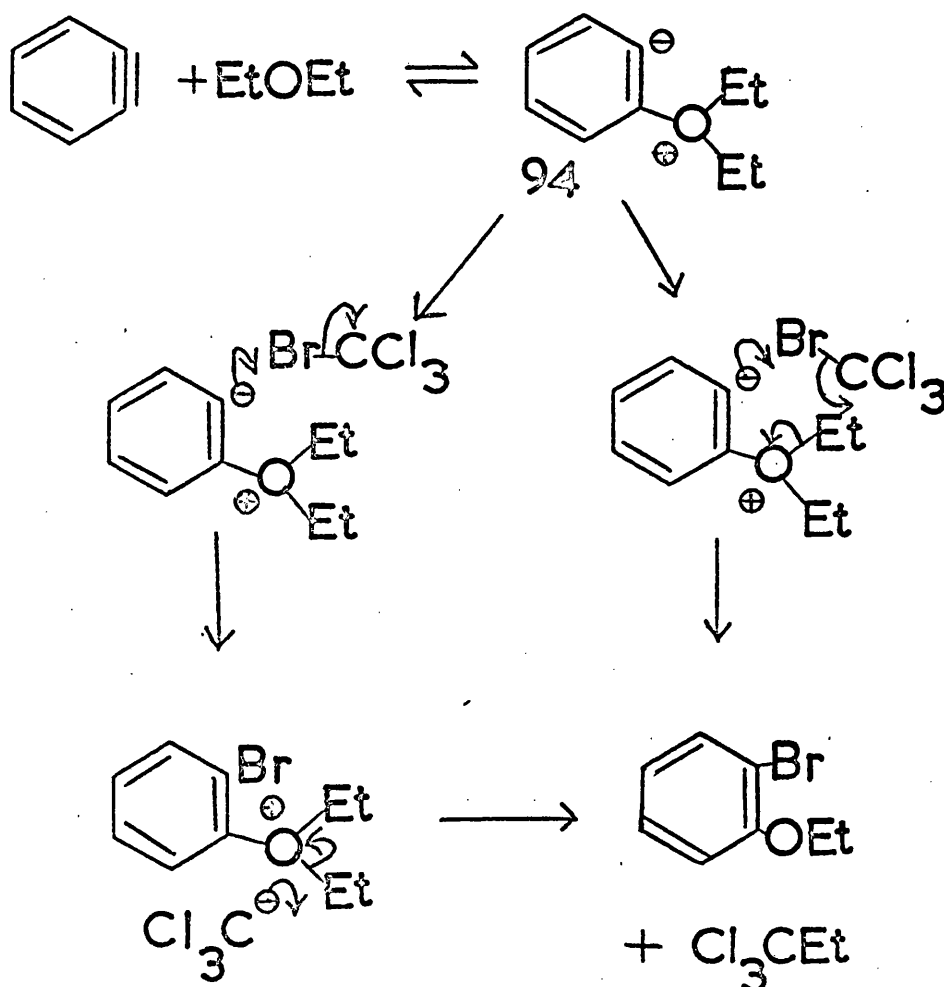


Ethyl acetate, rather than ethylene, is probably formed and gas chromatography of the reaction mixture showed a component with the same retention time as ethyl acetate. If the intermediate was less stable than that involving the o-nitrophenyl carbanion, then the equilibrium would lie more on the side of the starting materials. Hence, benzyne could react with diethyl ether to form the betaine (94) which reverts rapidly to starting materials. The lifetime of (94)

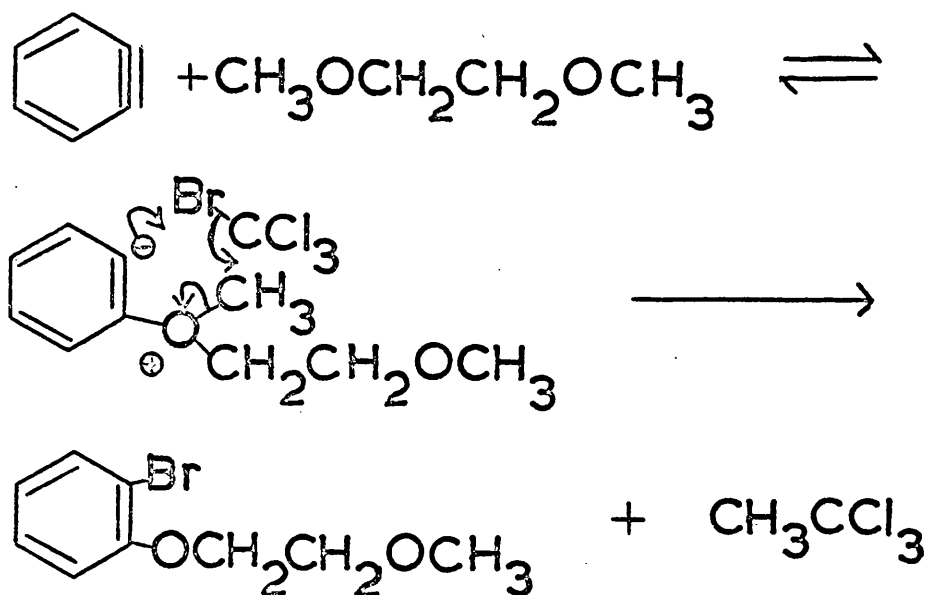


is insufficient for acetic acid to react with the betaine in the exact way necessary for cleavage of the ether, as entropy considerations make this unfavourable.

The existence of the betaine (94) was supported by oxidising 1-aminobenzotriazole in a mixture of ether and bromotrichloromethane. 2-Bromophenetole (16%) was isolated, in addition to the normal benzyne-bromotrichloromethane products. This product was presumably formed by attack of bromotrichloromethane on the betaine (94), via a transition state involving a 6-membered ring, to give 2-bromophenetole and 1,1,1-trichloropropane (which was not isolated). Alternatively, the attack of bromotrichloromethane on the betaine may be stepwise, as shown.



When benzyne was generated from 1,2,3-benzothiadiazole-1,1-dioxide in the same solvent mixture at 40°, 2-bromophenetole (90%) was isolated. Logullo⁹⁴ has performed a similar experiment: benzenediazonium 2-carboxylate was decomposed in 1,2-dimethoxyethane in the presence of bromotrichloromethane; 1-(o-bromophenoxy)-2-methoxyethane was obtained in a similar process to the above.

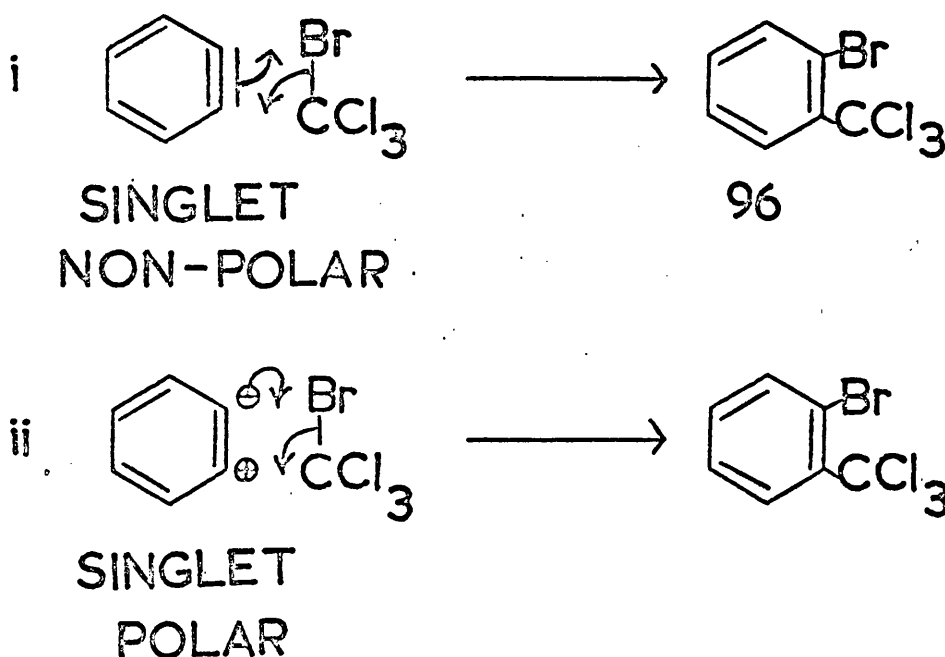


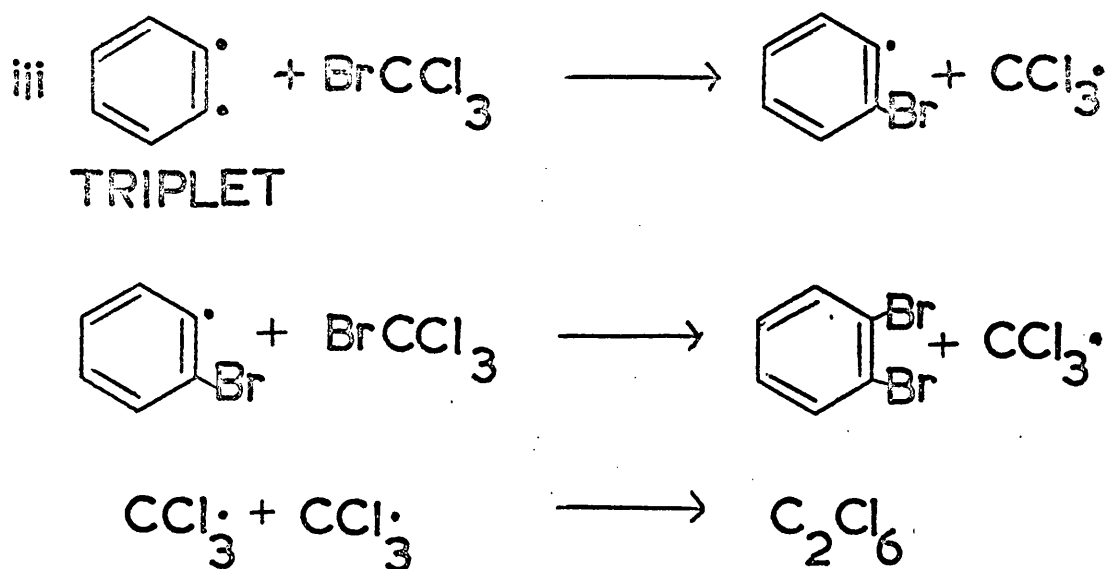
Oxidation of 1-amino-6-nitrobenzotriazole in ethanol with lead tetra-acetate gave a mixture of 3- and 4-nitrophenetoles (43%) and a similar oxidation of 1-amino-6-methoxybenzotriazole gave 3- and 4-ethoxyanisoles (57%).

SECTION 8

Generation of arynes in the presence of bromotrichloromethane.

The weak carbon-bromine bond in bromotrichloromethane is easily ruptured in either a homolytic or a heterolytic process, depending on the reactive species that it encounters. Bromotrichloromethane can be used to trap reactive intermediates, the products depending on the electronic structure of the reactive intermediate. The reaction of bromotrichloromethane with a singlet, ionic species has been reported by Logullo⁹⁴ (see p.152); the reaction with a diradical species has been investigated by Rees and Storr¹⁰¹, who obtained 1,8-dibromonaphthalene from 1,8-dehydronaphthalene by abstraction of bromine atoms from bromotrichloromethane. An extension of these reactions to benzyne would give:



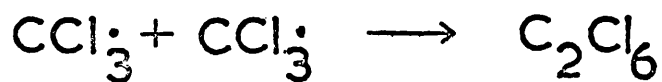
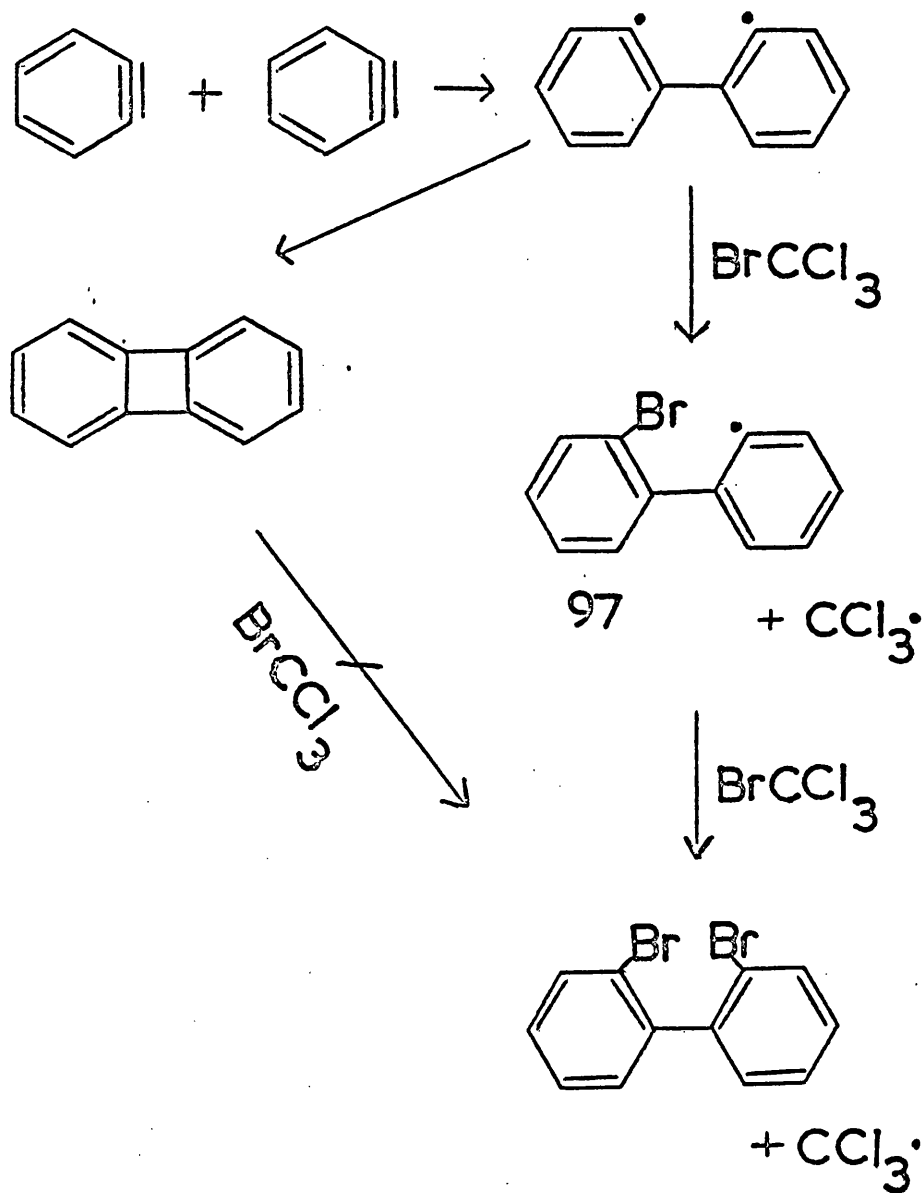


Hence, the singlet state should give 2-bromobenzotrichloride (96), whereas the triplet state should give o-dibromobenzene and hexachloroethane, and so it is possible to distinguish between singlet and triplet arynes by a method independent of stereochemical considerations.⁹²

Oxidation of 1-aminobenzotriazole in pure bromotrichloromethane with lead tetra-acetate proceeded by an exothermic reaction. After chromatography on silica gel, 2-bromobenzotrichloride (12-13%) was obtained, and was identified by i.r., elemental analysis, and conversion to 2-bromobenzoic acid by treatment with concentrated sulphuric acid. No o-dibromobenzene could be detected by i.r. spectroscopy or by TLC, and so the isolation of this compound supports the singlet nature of benzyne. It is to be noted that the addition of bromotrichloromethane to benzyne in the symmetric singlet state cannot be a concerted process on orbital symmetry grounds, but this is, of course, no obstacle to the formation of the addition product.

Hexachloroethane (10%), 2,2'-dibromobiphenyl (6-13%), and biphenylene (10-18%) were also isolated. On the above hypothesis

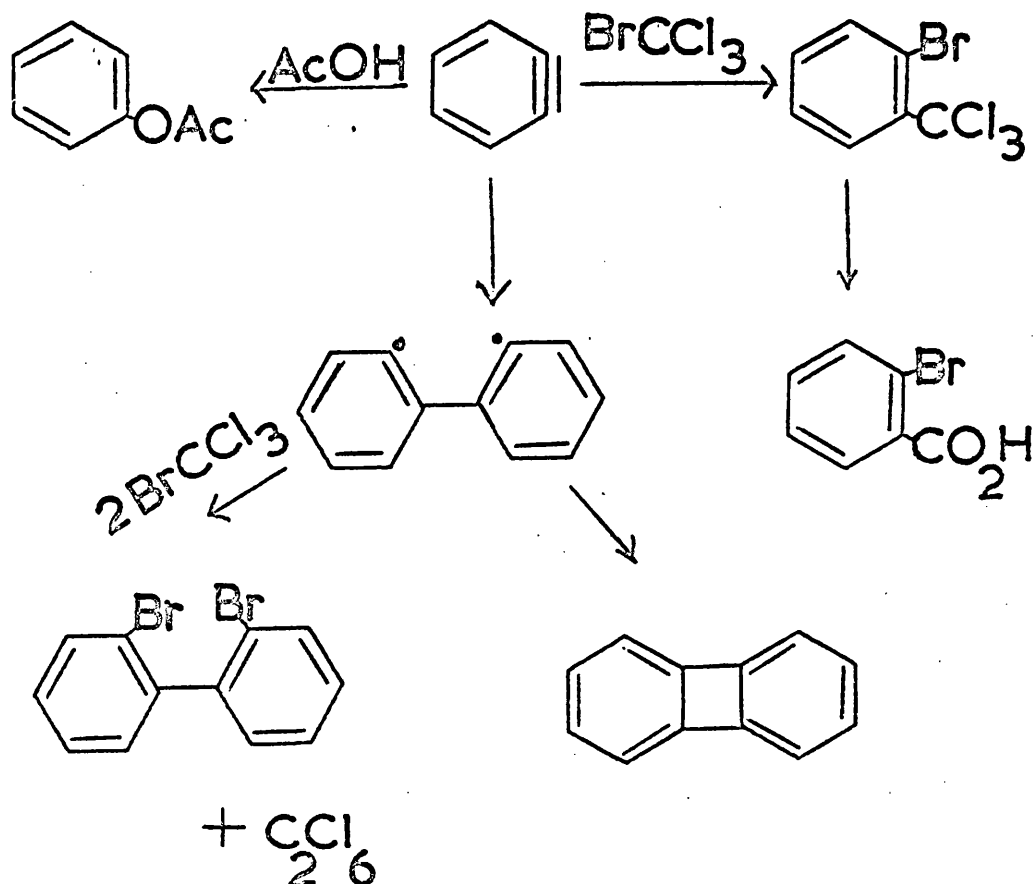
hexachloroethane could not have been formed by the reaction of benzyne with bromotrichloromethane, but may have come from the formation of 2,2'-dibromobiphenyl. This latter compound may have been formed via 2,2'-dehydrobiphenyl, an intermediate in the non-concerted dimerisation of benzyne.



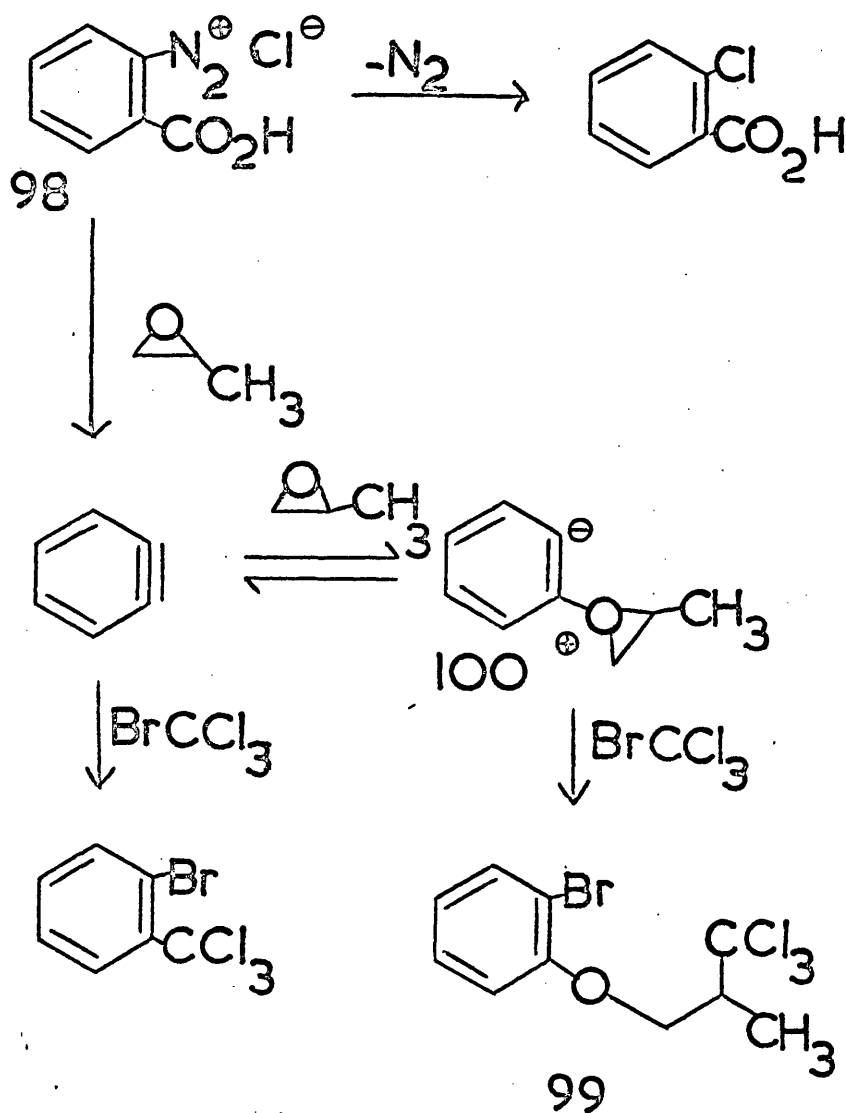
The scheme above outlines a reasonable route to the products.

Benzyne first dimerises to form 2,2'-dehydrobiphenyl, which is a diradical. This diradical then can either collapse to biphenylene, or can react with bromotrichloromethane to give the radical (97), which then further reacts with bromotrichloromethane to give 2,2'-dibromobiphenyl. A blank experiment in which biphenylene was subjected to the reaction environment produced no 2,2'-dibromobiphenyl, and hence this compound was not formed by way of biphenylene, and so this experiment may be regarded as good evidence for the intermediacy of 2,2'-dehydrobiphenyl in the dimerisation of benzyne.

Phenyl acetate (4%) and 2-bromobenzoic acid (1%) were also produced, the latter product probably coming from hydrolysis of o-bromobenzotrichloride during the workup. The reaction scheme is shown below

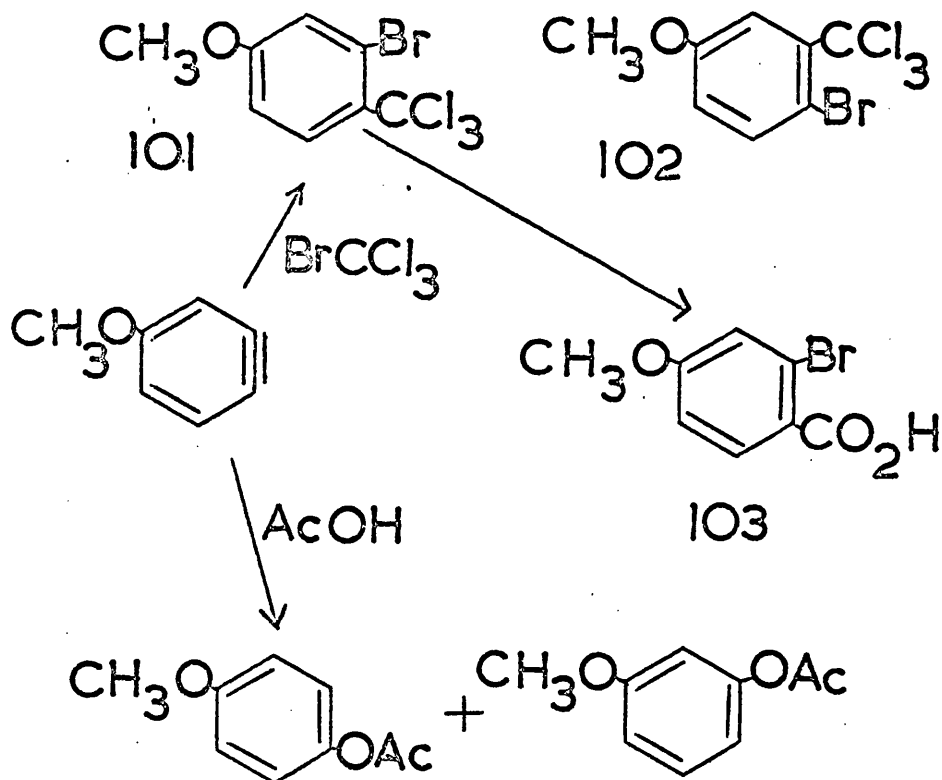


Decomposition of benzenediazonium chloride 2-carboxylic acid (98) in bromotrichloromethane and propylene oxide gave only a trace of 2-bromobenzotrichloride. 2-Chlorobenzoic acid (12%) was produced by loss of nitrogen from the diazonium salt (98). A colourless oil was also isolated, which, from its mass spectrum, was probably compound (99). This could be formed by initial attack of benzyne on propylene oxide to give the betaine (100) which then was intercepted by bromotrichloromethane. A satisfactory analysis could not be obtained for this compound.



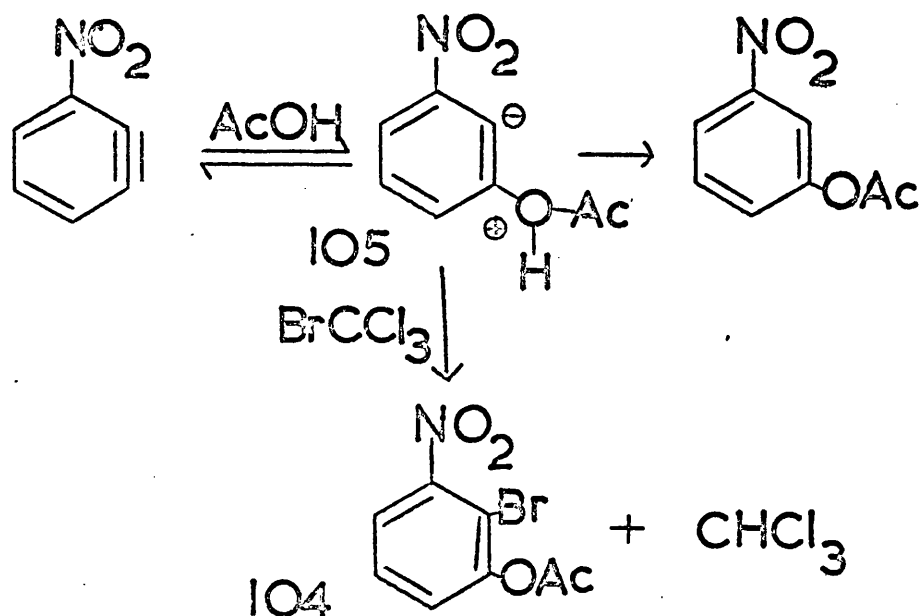
Decomposition of benzenediazonium 2-carboxylate in bromotrichloromethane-benzene-carbon tetrachloride gave only 2-chlorobenzoic acid (2%), together with intractable brown tars.

Oxidation of 1-amino-5-methoxybenzotriazole in bromotrichloromethane gave a mixture of 4- and 5-methoxy-2-bromobenzotrichlorides [(101) and (102)] (12%), which did not give a satisfactory elemental analysis, but was identified by the mass spectrum. 2-Bromo-4-methoxybenzoic acid (103) (2%) was also isolated, and identified by m.p., i.r., and analytical data. This compound arose by hydrolysis during workup of the corresponding benzotrichloride. Hexachloroethane (10%) and a mixture of acetoxyanisoles (9%) were isolated, but no dimethoxybiphenylenes or biphenyls could be detected. The isolation of the 2-bromobenzotrichlorides from this reaction again provides support for the singlet nature of 4-methoxybenzyne.



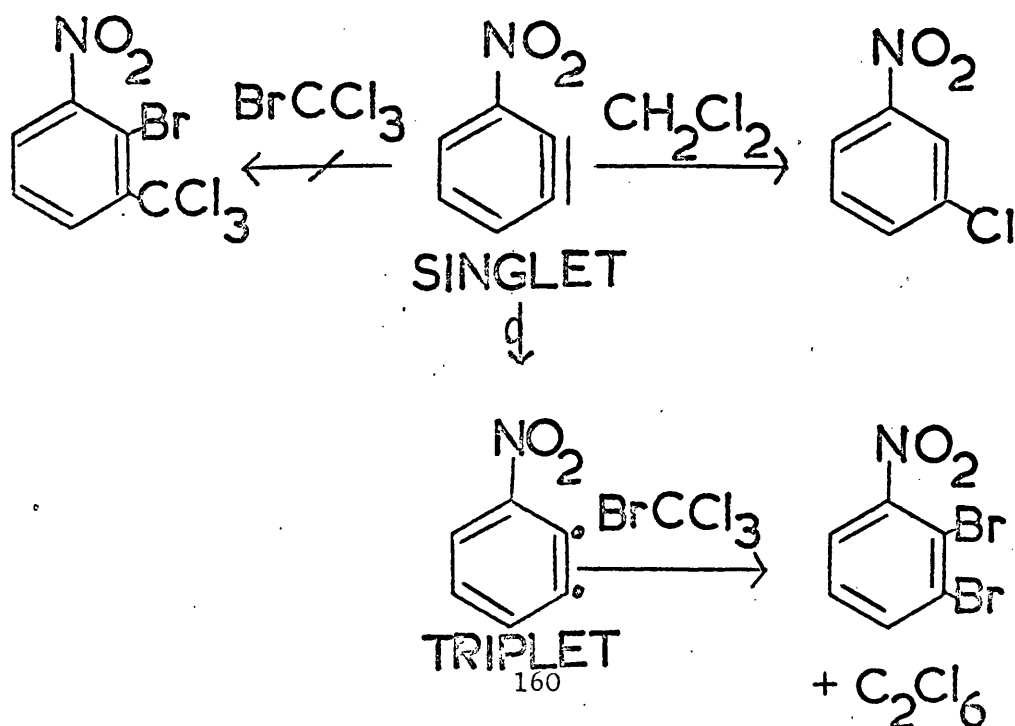
The origin of the hexachloroethane is unknown.

An oxidation of 1-amino-4-nitrobenzotriazole in bromotrichloromethane with lead tetra-acetate gave 3-nitrophenyl acetate (34%), 2-bromo-3-nitrophenyl acetate (8%) and a trace of hexachloroethane. The compound (104) was identified by i.r., n.m.r., and mass spectral data. A satisfactory elemental analysis was obtained. This product is formed by attack of bromotrichloromethane on the betaine (105), which gives the product and an equimolar amount of chloroform, which was not detected.



The very electrophilic 3-nitrobenzyne obviously prefers to attack acetic acid, which is a good nucleophile, rather than bromotrichloromethane, and this must be the reason why no direct 3-nitrobenzyne-bromotrichloromethane products are observed. To remove the possibility of interference by nucleophiles, 1-amino-4-nitrobenzotriazole was oxidised using nickel peroxide in the presence of anhydrous sodium sulphate, using a mixture of methylene chloride and bromotrichloromethane as solvent, in order to increase solubility of the triazole. [No reaction was observed in neat bromotrichloromethane.]

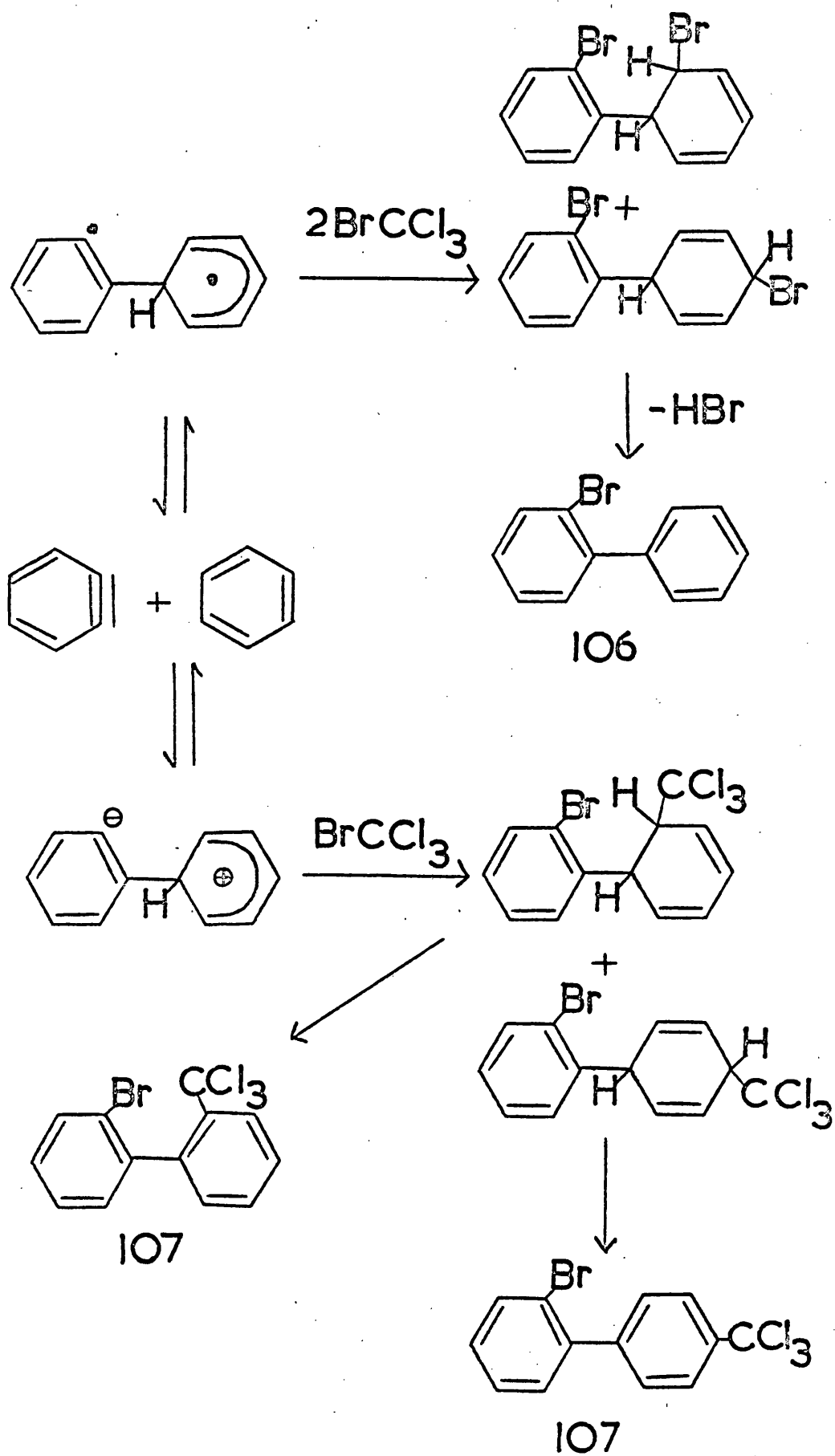
3-Nitrochlorobenzene (18%) was the major product. Small amounts of this compound were formed by oxidation of the same triazole under the same conditions in neat methylene chloride, but this large yield of 3-nitrochlorobenzene is anomalous. As the same batch of methylene chloride was used for all these oxidations, and was free of hydrogen chloride, this increase cannot be due to any impurity in the solvent, and neither is it feasible that the chlorine atom came from the bromotrichloromethane, since the bromine atom is much easier to remove. Moreover, no nitrobromobenzotrichlorides could be detected, but a very small quantity of 2,3-dibromonitrobenzene (1%) was isolated. This compound is the expected product from the reaction of triplet 3-nitrobenzyne with bromotrichloromethane, and is in contrast to all the other reactions of 3-nitrobenzyne. A possible explanation is that a collision between an aryne and bromotrichloromethane might excite the aryne into the triplet state. This explanation, however, is unlikely since the opposite type of process usually occurs in high molecular weight solvents like bromotrichloromethane. Another possibility is that some sort of interaction between the nickel atom and the aryne may stabilise the triplet state, so that it becomes the ground state of the molecule.



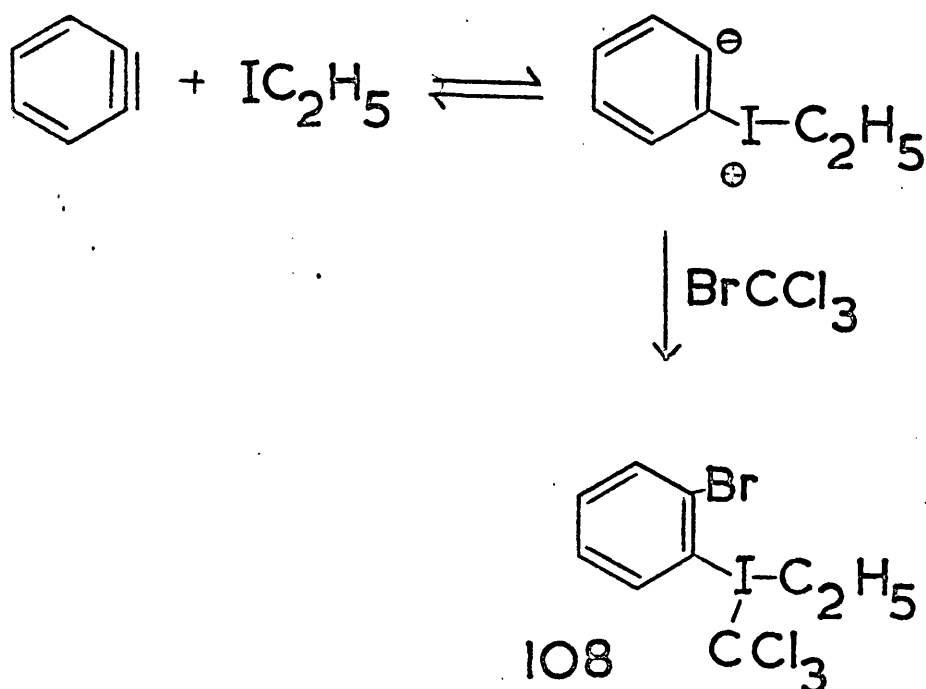
The reason why singlet 3-nitrobenzyne does not react with bromotrichloromethane in the usual manner is not clear, but a steric factor may be involved.

Oxidation of 1-aminobenzotriazole in bromotrichloromethane in the presence of tetracyclone gave 1,2,3,4-tetraphenylnaphthalene (64%), biphenylene (1%), and 2-bromobenzotrichloride (1%). Hence benzyne reacts with tetracyclone much faster than with bromotrichloromethane. Oxidation of 1-aminobenzotriazole with N-bromosuccinimide in bromotrichloromethane gave only o-dibromobenzene, showing that reaction of the aryne⁸⁴ with bromine was faster than reaction with the solvent.

When benzyne is generated from 1-aminobenzotriazole, no adduct with benzene is isolated. In contrast to this observation, other precursors of the aryne give varying yields of benzene adducts. Friedmann⁹⁶ decomposed benzenediazonium 2-carboxylate in benzene, and obtained, inter alia, biphenyl and benzobarrelene, which both arose from attack of benzyne on benzene. To investigate the possibility of an intermediate between benzyne and benzene in the case of the oxidation of 1-aminobenzotriazole, an oxidation was performed in a benzene-bromotrichloromethane mixture. However, the only products isolated were hexachloroethane (2%), 2-bromobenzotrichloride (16%), biphenylene (15%), 2,2'-dibromobiphenyl (15%), and phenyl acetate (10%). No products which could have been compounds resembling the adducts [(106) or (107)] could be detected, and so no intermediate appears to be formed between benzyne and benzene in this case.



Similarly, an oxidation of 1-aminobenzotriazole in bromotrichloromethane-ethyl iodide gave hexachloroethane (~ 10%), 2-bromobenzotrichloride (19%), biphenylene (32%), 2,2'-dibromobiphenyl (18%), phenyl acetate (4%), 2-bromobenzoic acid (2%) and iodine (trace). No trace was found of compound (108) or any apparent decomposition products of this species.



An attempt to ascertain whether 2 + 2 cycloaddition of benzyne and olefins proceeded via a radical or ionic mechanism, also failed. The relevant experiment was performed by oxidising 1-aminobenzotriazole in a mixture of bromotrichloromethane and t-butylethylene. This reaction should have given either product (109) or products [(110) and (111)], depending on the nature of the intermediate. The only products isolated were hexachloroethane (trace), 2-bromobenzotrichloride (7%), biphenylene (26%), 2,2'-dibromobiphenyl (16%), 2-bromobenzoic acid (5%), and a compound of empirical formula, $\text{C}_6\text{H}_{12}\text{Br}_2$. The latter product must

arise by bromination of t-butylethylene with bromotrichloromethane, but was not the dibromo-olefin (112) by i.r. comparison with an authentic sample.

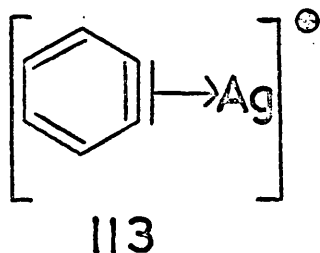
Gassman⁹⁷ has recently shown that the intermediate in the 2 + 2 cycloaddition of benzyne itself with trans-cyclooctene is probably diradical in nature.

SECTION 9

Reactions of 1-aminobenzotriazoles with silver perchlorate or mercuric acetate.

In 1967, Friedmann⁹⁶ decomposed benzenediazonium 2-carboxylate in benzene, in the presence of a catalytic amount of silver ions. A different ratio of the various adducts of benzyne and benzene was produced than in a similar decomposition in the absence of silver ions. Friedmann⁹⁶ concluded that a silver-benzyne complex (113) was an intermediate in this reaction.

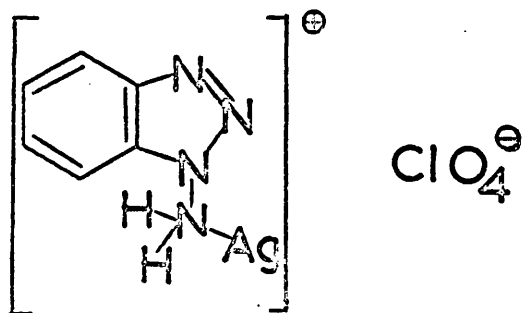
An experiment was carried out under similar conditions, using



1-aminobenzotriazole as the source of benzyne. No benzyne-benzene adducts were found, and the yield of biphenylene was only 9%; no other compound could be identified. It is presumed that benzyne forms a silver complex similar to the complex (113), which, being positively charged, is more electrophilic than unco-ordinated benzyne, and thus has a shorter life-time due to side reactions with nucleophiles in the reaction medium. Consequently, the degree of dimerisation is less than with the unco-ordinated aryne. In this reaction, it was noticed that the benzene containing silver perchlorate and 1-aminobenzotriazole (which are both soluble in benzene) contained a white suspension.

When equimolar quantities of 1-aminobenzotriazole and silver perchlorate were each dissolved in benzene, and the two solutions added

together, a flocculant white precipitate was obtained. This compound gave an elemental analysis which agreed with the formula of 1:1 complex of 1-aminobenzotriazole and silver perchlorate. This complex, which was formed in quantitative yield, had an i.r. spectrum which showed a marked change in the region, $3150-3500\text{ cm}^{-1}$, but hardly any change in the region, $700-800\text{ cm}^{-1}$, when compared with 1-aminobenzotriazole. Hence, it is reasonable to postulate that the silver atom is co-ordinated to the nitrogen of the amino-group, as shown in (114).



114

1-Amino-5-methoxybenzotriazole gave an extremely hygroscopic glass when treated with silver perchlorate in benzene. 1-Amino-6-nitrobenzotriazole, on the other hand, formed a buff complex under the same conditions. This amorphous solid had an elemental analysis commensurate with a 1:1 complex of the amine and silver perchlorate, together with half a molecule of benzene of crystallisation. The yield was nearly quantitative, and the same characteristics in the i.r. spectrum were observed, and so a similar structure to compound (114) is probable.

The complexes decomposed upon slow heating, but very rapid heating caused detonation.

Thermolysis of the 1:1 complex (114) in dimethylformamide, containing tetracyclone, at 156° gave 1,2,3,4-tetraphenylnaphthalene (2%),

showing that oxidation of the amino-group takes place during the decomposition of these complexes.

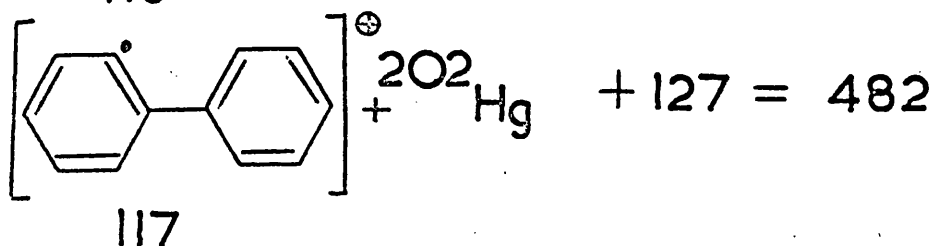
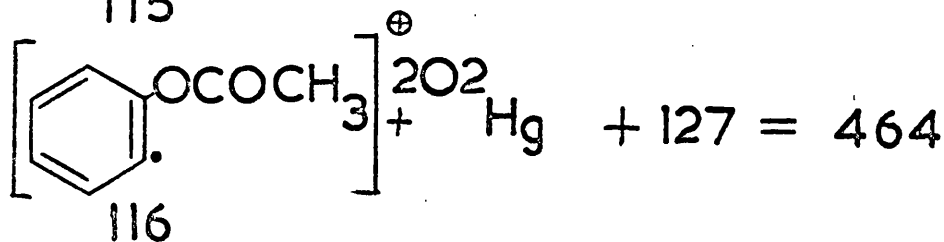
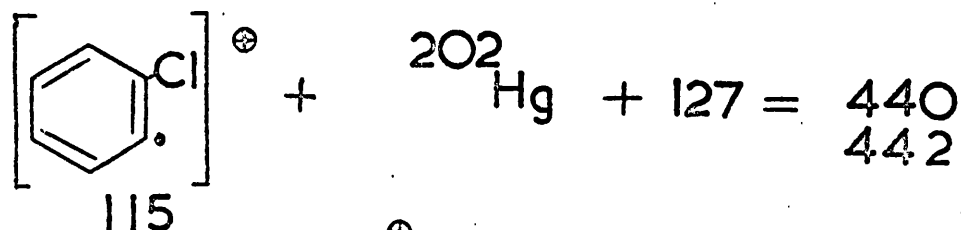
An attempted oxidation of 1-aminobenzotriazole with mercuric acetate in boiling benzene failed; only starting materials were recovered. Oxidations of 1-aminobenzotriazole with lead tetra-acetate in the presence of an excess of mercuric acetate in acetic acid, benzene-acetic acid, or methylene chloride gave no detectable biphenylene. This shows that the benzyne must be intercepted by some species, probably Hg^{II} , which prevents the dimerisation. However, only small amounts of mercury-containing products were isolated by column chromatography. It is possible that some benzyne-mercury compounds were present in the copious, insoluble residues obtained from the reactions, but attempted sublimation of these residues gave only elemental mercury.

When the oxidation was performed in methylene chloride, colourless needles with a green fluorescence were obtained after chromatography on silica gel. This compound had a molecular weight of 429 ± 20 by osmometry, and showed a set of parent ions in the mass spectrum around $\frac{m}{e}$, 440 with a pattern corresponding to the presence of one mercury atom and one chlorine atom in the compound. The infra-red spectrum showed no carbonyl absorption, and the n.m.r. spectrum only aromatic protons. The analysis showed that nitrogen was not present.

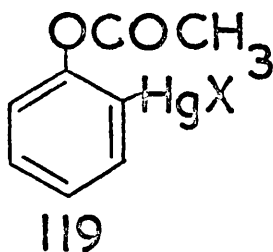
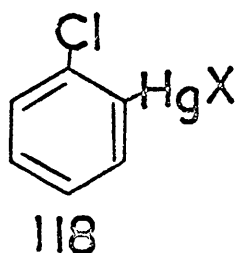
When acetic acid was used as the solvent in the oxidation, colourless blades were obtained after chromatography on silica gel. This compound had a sharp melting point, and elemental analysis showed that nitrogen was absent. The mass spectrum showed a set of parent ions around $\frac{m}{e}$, 464 with a pattern corresponding to the presence of one

mercury atom in the compound. I.r. spectroscopy showed that an acetate group was present. If benzene-acetic acid was used as the solvent for the oxidation, then long feathery needles were obtained after chromatography on silica gel. This compound had a sharp melting point, and elemental analysis showed that nitrogen was absent. The mass spectrum showed a set of parent ions around $\frac{m}{e}$, 482, with a pattern corresponding to the presence of one mercury atom in the compound. The i.r. spectrum showed no recognisable functional group save phenyl and the n.m.r. spectrum showed only aromatic protons.

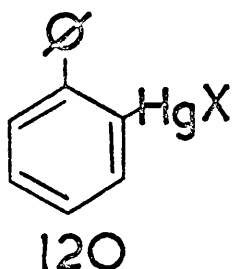
The three compounds above proved to be unidentifiable, but had one mysterious fact in common: that one half of the molecule was the same in all cases. There is a base peak in the mass spectrum of each of these compounds. The first compound, formed in methylene chloride, had a pair of base peaks at $\frac{m}{e}$, 111 and $\frac{m}{e}$ 113 corresponding to the ion (115). The second compound, formed in acetic acid, has a base peak at $\frac{m}{e}$, 135 corresponding to ion (116), and the third compound, formed in benzene-acetic acid, has a base peak at $\frac{m}{e}$, 153 corresponding to ion (117). If an atom of mercury is added to each of these base



peaks, the difference between the mass peak and the base peak plus mercury is 127 in each case. From consideration of the analytical data, this unit of 127 contains three carbon atoms, 2 or 3 hydrogen atoms (which were not detectable in the n.m.r. spectrum) and some other elements. Nitrogen is not one of these elements, and if only oxygen is considered, about eight oxygen atoms would have to be attached to the three carbon atoms, and not one could be as a carbonyl group! The formula of this group, hence, seems a mystery, but there is no doubt that all three samples are homogeneous, so it appears that the formulae of these three compounds are



X is an unknown group.

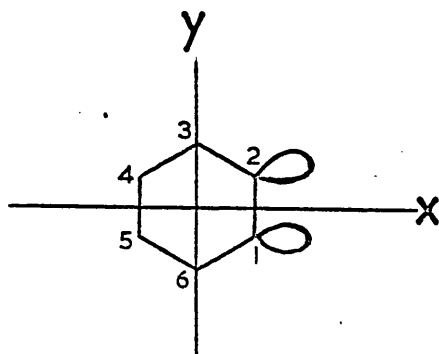


The compound (118) had an i.r. spectrum superimposable upon that of bis(o-chlorophenyl)-mercury and the same m.p. but a mixed m.p. determination showed that these compounds were different.

SECTION 10

Semi-empirical calculations

The extended Hückel treatment, due to Hoffmann⁵⁶ and developed by Claxton⁹⁸, was used to calculate the electronic structure of benzyne. The geometry of benzene was used to calculate the atomic co-ordinates of benzyne, except that a compression along the y axis was used, which shorted the length of the 1,2 and 4,5 bonds from 1.39 Å to 1.32 Å.



This operation was justified in the light of Hoffmann's results⁵⁶, where the overlap population of the 4,5-bond was found to be higher in benzyne than in benzene, and a similar compression was predicted.

It was found that, in the singlet state, the highest occupied molecular orbital was the symmetric combination of the two non-bonded σ -orbitals. In the triplet state, the highest occupied orbital is the antisymmetric combination of the non-bonded σ -orbitals. The energy of the triplet state of benzyne was found to be higher than that of the singlet state by 1.85eV. This difference is sufficient to render benzyne a singlet in the ground state.

The geometry of nitrobenzene was used to calculate the atomic co-ordinates of 3-nitrobenzyne and 4-nitrobenzyne. No compression along any axis was employed.

The highest occupied orbital in the singlet state of 3-nitrobenzyne and 4-nitrobenzyne was found to be the symmetric combination of the non-bonded σ -orbitals. The highest occupied orbital of 3-nitrobenzyne and 4-nitrobenzyne in the triplet state, was, rather surprisingly, found to be an antibonding Π -orbital centred on the three atoms of the nitro-group. The difference in energy between the singlet and triplet states of 3-nitrobenzyne was 0.67eV, and the corresponding figure for 4-nitrobenzyne was 0.56eV. Both these differences are low enough for the ground state of the molecule to be a triplet, if the pairing energy of the electrons is taken into consideration. It is difficult to conceive of a triplet state which has one electron in a σ -orbital and the other electron in a Π^* -orbital. This anomaly may be explained by the fact that electron-electron interactions are ignored in the extended Hückel theory; calculations required to differentiate between different spin states of a molecule must take this effect into account, since electrons with the same spin do not interact with each other in the same way as electrons with opposite spins.

A recent method, which takes such interactions into account in a molecular orbital calculation, is the CNDO (Complete Neglect of Differential Overlap)⁹⁹ method of Pople, Santry and Segal, which is a simplified self-consistent field treatment. A computer programme, recently developed by Dr. T. Claxton¹⁰⁰, was used to calculate the results, using the same atomic co-ordinates as used in the extended Hückel treatment.

Benzyne, 3-nitrobenzyne and 4-nitrobenzyne were all found to have their respective singlet states lower than the triplet states. Furthermore, in all three cases, the highest occupied orbital in the singlet state was found to be the symmetric combination of the two non-bonded σ -orbitals. Hence benzyne, 3-nitrobenzyne, and 4-nitrobenzyne were all calculated to exist in a symmetric singlet ground state.

When these singlet molecules were formally excited to the corresponding triplet molecules, then an interesting phenomenon was observed. In the case of benzyne (Fig. I), the singlet state had a fully occupied symmetric σ -orbital, σ_s , above a fully occupied Π -orbital, Π_1 , with an empty antisymmetric σ -orbital, σ_a , above both these orbitals at virtual energy. If one electron is now promoted from σ_s to σ_a , the orbital, σ_s , drops markedly in energy, Π_1 rises

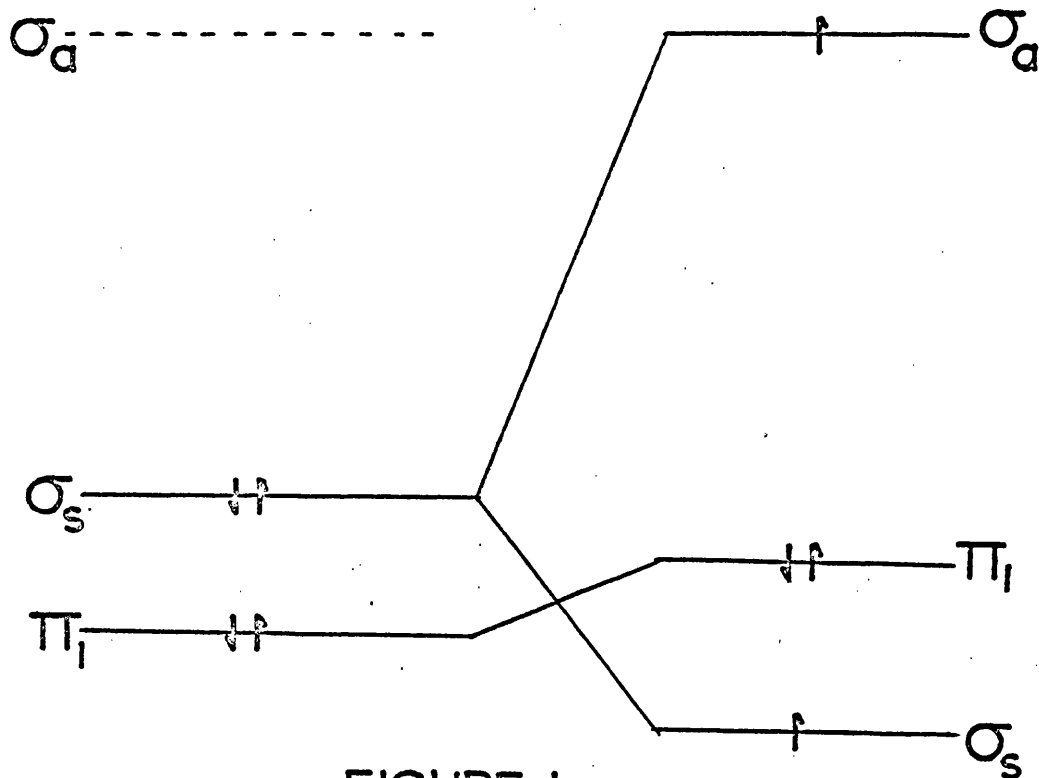


FIGURE I

slightly and σ_a appears at high energy. Hence the electronic configuration of the triplet state of benzyne has the fully occupied orbital, Π_1 , in between the two singly occupied orbitals, σ_a and σ_s .

A similar phenomenon was found with 4-nitrobenzyne (Fig.2). The singlet state had a fully occupied symmetric σ -orbital, σ_s , above a fully occupied Π -orbital, $\Pi_{O_2}^*$, which was identified from the orbital parameters as being an antibonding orbital centred on the oxygen atoms of the nitro-group. (This orbital is not the same as the orbital which was involved in the triplet state of this molecule, as derived from the extended Hückel treatment.) The empty ^{ti}antisymmetric σ -orbital, σ_a , was again at virtual energy. If one electron is promoted

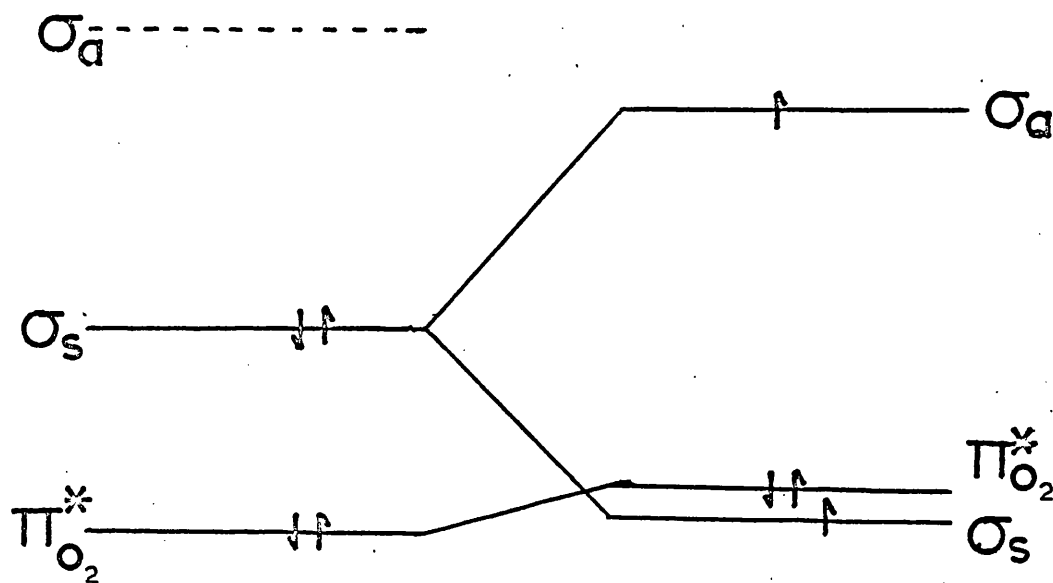


FIGURE 2

from σ_s to σ_a , the orbitals again change in energy in the same way as in benzyne such that the energy of the fully occupied orbital, $\Pi_{O_2}^*$ is in between the two partially filled orbitals, σ_a and σ_s . The Π -orbital involved in this phenomenon is, of course, different to the one involved in the benzyne case, and the relative differences in the energies of the orbitals are not the same.

In the case of 3-nitrobenzyne (Fig. 3.), no crossing of levels is noted in the singlet-triplet excitation process. The ground state singlet of this molecule had the same configuration as that of 4-nitrobenzyne. When one electron is promoted from σ_s to σ_a , σ_s again drops markedly in energy, but the energy of $\Pi_{O_2}^*$, instead of rising as in 4-nitrobenzyne and the Π_1 -orbital of benzyne, drops such that it is still below σ_s . Hence this molecule has a conventional triplet electronic configuration, the two partially occupied orbitals being the two highest occupied orbitals.

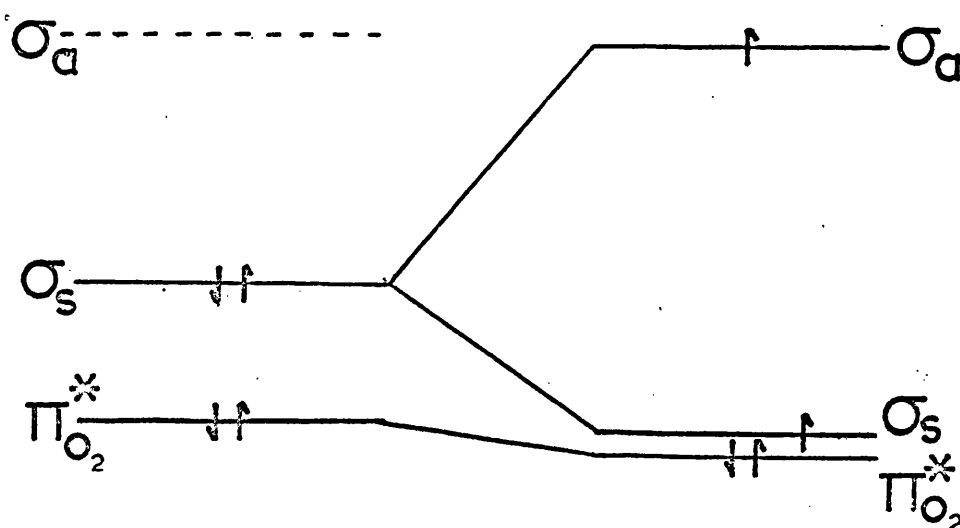
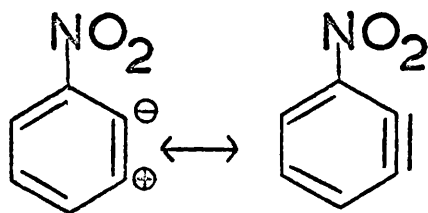


FIGURE 3

A natural consequence of the CNDO2 approach is the calculation of the dipole moment of the molecule in question.

Benzyne had a dipole moment of 1.21D., due to the internal electron withdrawing action of the non-bonding σ -orbitals which tends to increase the atom electron densities on the carbon atoms associated with these orbitals. 4-Nitrobenzyne was found to have a dipole moment of 3.81D., which is near to the sum of the dipole vectors of benzyne and nitrobenzene, taking the relative orientations of these contributors into account. Hence the electronic structure within the two non-bonded σ -orbitals in 4-nitrobenzyne must be similar to that of benzyne itself.

3-Nitrobenzyne, however, had a dipole moment of 6.44D., which is very high for an organic molecule. This high dipole moment far exceeds the sum of the dipole vectors of nitrobenzene and benzyne. The non-bonding σ -orbitals cannot have the same electronic structure as in benzyne, and probably 3-nitrobenzyne exists mainly in the polar form, instead of in the non-polar form.



This polarity between the two non-bonded σ -orbitals is also reflected in the difference between the atom electron densities between the two carbon atoms in question. Benzyne, being symmetrical about these atoms, had no difference in the electron densities at these atoms.

4-Nitrobenzyne showed a small difference (0.05 electron) in the atom electron densities, which shows a small degree of dipolar character between these two orbitals. 3-Nitrobenzyne showed a much larger difference (0.19 electron) between the atom electron densities of the two carbon atoms on which are the non-bonded σ -orbitals. This indicates a considerable dipolar character of the two non-bonded σ -orbitals. The atom electron densities of the three atoms of the nitro-group of 3-nitrobenzyne and 4-nitrobenzyne were not significantly different, showing that through-space interactions from the o-nitro-group of 3-nitrobenzyne are not likely.

Hence, it seems that the main difference between 3-nitrobenzyne and the other two examples, as is demonstrated by these semi-empirical calculations, is that it is a much more polar molecule.

CONCLUSION

Structure and reactivity of arynes

It was shown experimentally that benzyne, 4-methoxybenzyne and 3-nitrobenzyne all have a symmetric singlet ground state. Extended Hückel theory confirmed that the highest occupied orbital in the singlet state is the symmetric . The CND02 treatment again confirms the singlet nature of the benzyne ground state, and also confirms 3-nitrobenzyne to have the same ground state. 4-Nitrobenzyne, using the same method, is predicted to be a symmetric singlet in the ground state. As 5-chlorobenzyne and 5-trifluoromethylbenzyne show experimental properties intermediate between benzyne and 3-nitrobenzyne, it seems reasonable to suppose that the ground state of these two molecules is the symmetric singlet state. 3-Nitrobenzyne underwent a series of reactions which were not found with any other aryne, and the reason for this is generally attributed either to the dipolar character of the aryne, which is confirmed by the CND02 calculations, or to the stability of dipolar intermediates in the reactions of this aryne.

Dimerisation of benzyne was shown to be a non-concerted process, predicted by molecular orbital theory, and also was shown to proceed, in all probability, by a radical intermediate. The relative reduction in the tendency of some arynes to dimerise, compared with benzyne itself, is attributed to the relative efficiency of competing reactions, which remove the aryne from the reaction medium before dimerisation can take place.

The degree of $2 + 2$ cycloaddition with mono-enes is used as a measure of the electrophilicity of the aryne, and the results fit

the expected order of electrophilicity of arynes based on inductive effects alone. In general, it was found that the more electrophilic an aryne was expected to be, upon the grounds of inductive effects only, the more reactive it proved to be.

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