

BENZYNE-PLATINUM  
INTERMEDIATES.

By

FREDERICK JAMES GRAVELING.

A thesis submitted for the degree of Doctor  
of Philosophy at the University of Leicester.

1969

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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. No part of it is concurrently being submitted for any other degree.

October 1966 - August 1969

Signed F. J. Graveling

(F. J. Graveling)



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I should also like to thank the University of Leicester for providing excellent research facilities and the Science Research Council for the award of a Research Studentship.

### ABSTRACT.

The evidence for considering benzyne as a symmetric singlet with a partial  $\pi$  bond between the two one-electron centres is given. Benzyne is compared with strained cyclic acetylenes and a method of stabilizing both systems as  $\sigma\pi$  complexes on a transition metal is illustrated. Other reactions possibly involving benzyne-metal complexes are reviewed.

Two new benzyne precursors are described; the sodium and lithium salts of 1-(toluene-*p*-sulphonamido)benzotriazole (Ia, Ib), and (1-benzotriazolyl)iminotriphenylphosphorane (II) give benzyne on photolysis. For comparison the new cyclohexyne and cycloheptyne precursors, (4,5-tetramethylene-1-triazolyl)iminotriphenylphosphorane (III) and (4,5-pentamethylene-1-triazolyl)iminotriphenylphosphorane (IV) were prepared. It was also found that photolysis at room temperature of cycloheptenocyclopropenone (V) gave cycloheptyne.

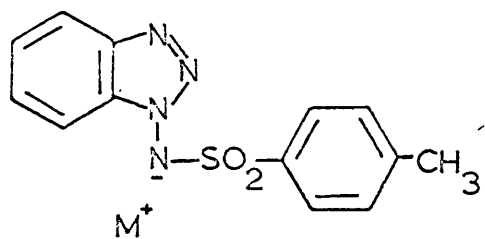
1,2,3-Benzothiadiazole-1,1-dioxides (VI) and benzenediazonium-2-carboxylates (VII) were used as benzyne precursors with tetrakis(triphenylphosphine)platinum(0) (VIII) to prepare benzyne-platinum complexes. Benzyne-platinum intermediates are postulated with 1,2,3-benzothiadiazole-1,1-dioxides in refluxing ether - benzene where cyclotrimerisation of benzyne to triphenylenes (not observed in the absence of platinum) occurs. In cold benzene, 1,2,3-benzothiadiazole-1,1-dioxide is trapped by tetrakis(triphenylphosphine)platinum(0) before it decomposes to benzyne to give the adduct (IX), which when irradiated, is also a new benzyne precursor. The reaction with benzenediazonium-2-carboxylates gives carboxylato-platinum complexes (X) which are not benzyne precursors and no cyclotrimerisation of benzyne was detected.

The oxidation of 1-aminobenzotriazole (XI) in the presence of tetrakis(triphenylphosphine)platinum(0) did not lead to a benzyne-platinum complex and benzyne-platinum intermediates do not appear to be involved. Furthermore the above, new, non-oxidative routes to benzyne with tetrakis(triphenylphosphine)platinum(0) gave no evidence for benzyne-platinum complexes. Analogous cycloalkyne precursors were also explored as routes to cycloalkyne-platinum complexes and cyclooctynebis(triphenylphosphine)-platinum (XII) was isolated.

The lead tetraacetate oxidation of 1-aminobenzotriazole in the presence of ethylenebis(triphenylphosphine)platinum (XIII) does, however, appear to give a benzyne-platinum complex which is stable for 10 minutes in solution. Benzyne was again cyclotrimerised to triphenylene in this reaction.

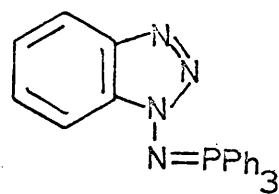
Other attempts to synthesise a benzyne-platinum complex and to stabilize an antiaromatic compound with zerovalent platinum are briefly described.

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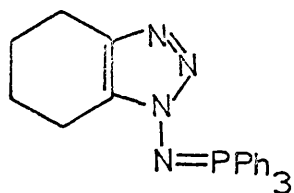


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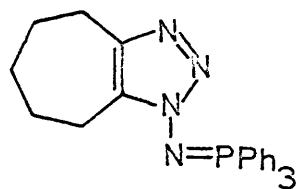
(b)  $M = \text{Li}$



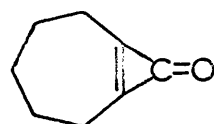
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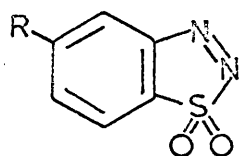
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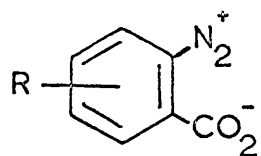
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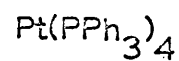
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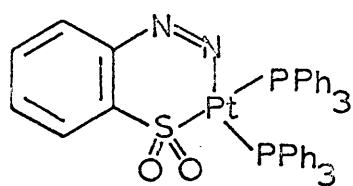
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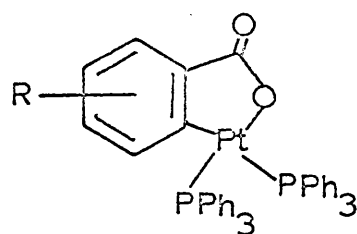
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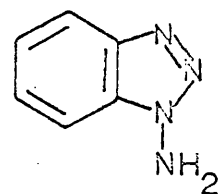
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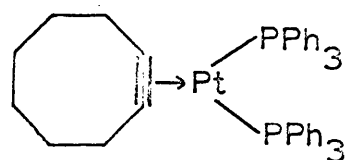
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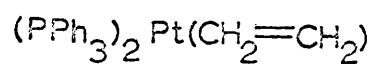
(X)



(XI)



(XII)



(XIII)

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## INTRODUCTION

In 1956 Longuet-Higgins and Orgel<sup>1</sup> predicted that cyclobutadiene would be stabilized by coordination to a transition metal ion. All attempts to isolate a cyclobutadiene species had been unsuccessful upto that time<sup>2</sup>, but this new concept in the hands of the experimental chemist soon proved fruitful and in 1959 Criegee and Schröder<sup>3</sup> isolated a stable cyclobutadiene-nickel complex.

The success of the approach has been extensively exploited by Pettit and co-workers<sup>4,5,6,7</sup> to establish the electronic structure and extend the chemistry of cyclobutadiene. This stimulated efforts with other reactive intermediates<sup>8,9,10,11,12</sup> in the hope that a similar contribution to their chemistry might be achieved.

An application of the approach to benzyne seemed particularly suitable at this time. There is a considerable literature on the chemistry of benzyne<sup>13</sup> and general agreement on its structure. A fairly rational approach to the problem of stabilizing it on a transition metal is therefore possible.

It is the purpose of this introduction to cover those aspects of benzyne and transition metal chemistry which determine the general approach toward a transition metal-benzyne complex. The first two sections cover these considerations. The third section is a review of the very scant literature on the attempts to prepare transition metal complexes of benzyne.

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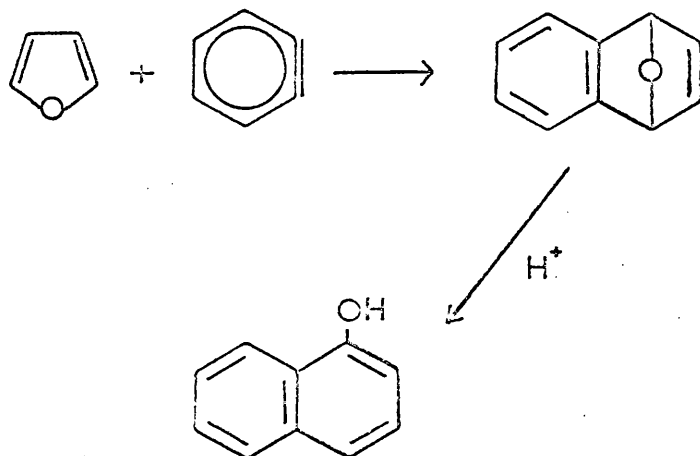
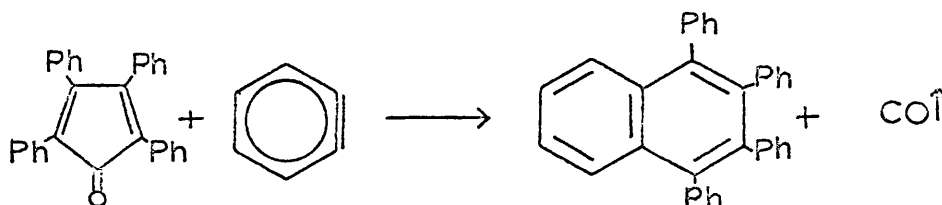
1. STRUCTURE AND REACTIVITY OF BENZYNE. COMPARISON WITH CYCLIC ACETYLENES.



(1)

General methods of preparing benzyne (1) are illustrated in order to provide a background to a discussion on its structure and reactivity. The benzyne precursors are divided into three groups depending upon the reaction conditions required.

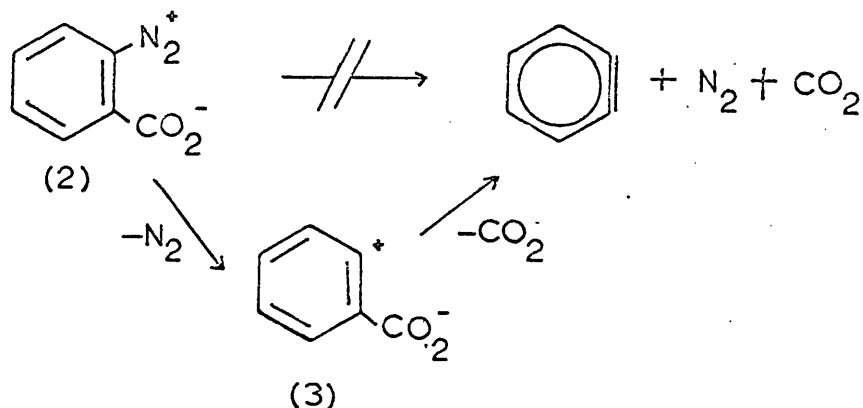
Formation of tetraphenylnaphthalene and 1,4-dihydronaphthalene endoxide from tetraphenylcyclopentadienone (tetracyclone) and furan is accepted as good evidence for the intermediacy of benzyne in a reaction. However for rigorous proof, the symmetrical nature of the reactive site would have to be demonstrated.



Preparation of benzyne.

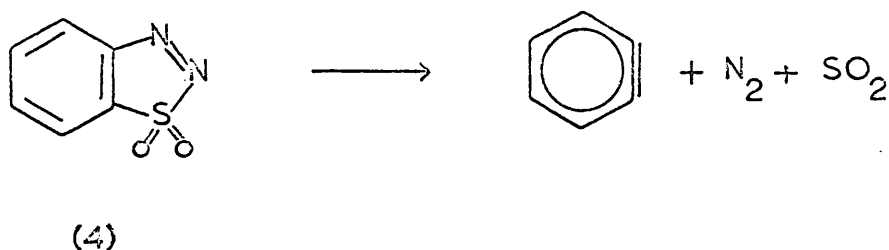
(i) Elimination of stable molecules under ambient conditions.

Decomposition of benzenediazonium-2-carboxylate (2) in benzene at 50° gives nitrogen, carbon dioxide and benzyne which can be trapped in yields approaching 80%.<sup>14,15</sup>



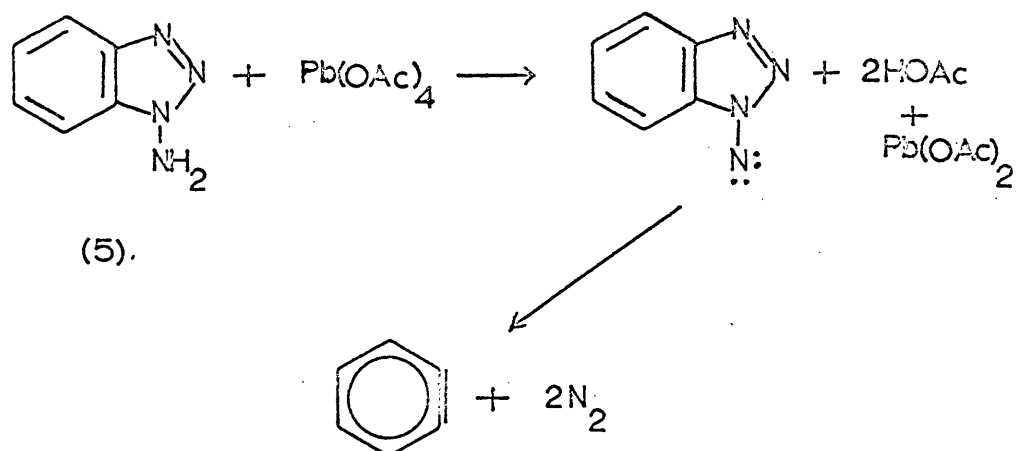
Stepwise decomposition occurs<sup>16</sup> and the intermediate (3) has been trapped with phenylisocyanide and nickelcarbonyl as N-phenylphthalimide and phthalic anhydride<sup>17</sup>. Refluxing 1,2-dichloroethane is the best system for decomposition of this precursor<sup>18</sup>.

Decomposition of 1,2,3-benzothiadiazole-1,1-dioxide (4) at room temperature in a suitable solvent gives benzyne which can be trapped in 50% yield<sup>19,20</sup>. Nitrogen and sulphur dioxide are lost in a concerted fashion<sup>21</sup>.





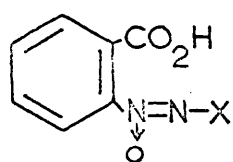
Oxidation of 1-aminobenzotriazole (5) with lead tetraacetate at room temperature in benzene generates the nitrene which fragments immediately to nitrogen and benzyne (trapped in 95% yield)<sup>22</sup>. Slightly lower yields are obtained if the oxidation is carried out in methylene chloride at low temperature ( $-80^{\circ}$ ).



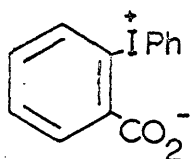
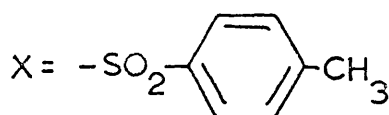
Benzenediazonium-2-carboxylate is easy to prepare (although it cannot be stored) and is the benzyne precursor most frequently used in the literature. It is extremely hazardous to handle<sup>23</sup> and its decomposition is not concerted. 1,2,3-Benzothiadiazole-1,1-dioxide is the 'perfect' benzyne precursor as it fragments to benzyne in a concerted fashion without the aid of an external reagent. However it is so unstable that it has to be freshly prepared for each reaction and its preparation is difficult and tedious. 1-Aminobenzotriazole is a very good benzyne precursor and is a little easier to prepare than compound (4). It can be stored indefinitely, but cannot be used in reactions whose components are sensitive to oxidation.

(ii) Pyrolysis and photolysis of ortho-substituted benzenes.

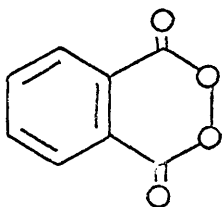
Thermolysis of 2-azoxybenzoic acids (6) for 3 hr. at  $190^{\circ}$  in the presence of tetracyclone gives the benzyne/-tetracyclone adduct in 24% yield<sup>25</sup>.



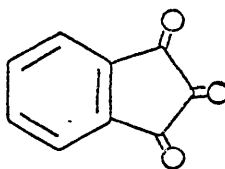
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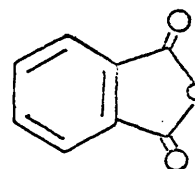
(7)



(8)



(9)



(10)

Decomposition of diphenyliodonium-2-carboxylate (7) in refluxing diglyme ( $160^{\circ}$ ) affords benzyne which can be trapped in 68% yield<sup>24</sup>.

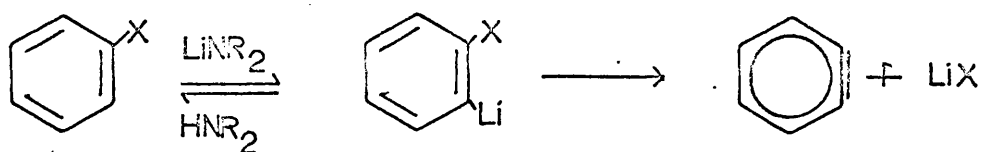
Pyrolysis of phthaloylperoxide (8)<sup>26</sup> and indane-1,2,3-trione (9)<sup>27</sup> at  $600^{\circ}$  gives 27% and 23% biphenylene, a product formed by the dimerisation of benzyne. Photolysis of a benzene solution of phthaloylperoxide in the presence of tetracyclone gave a 7% yield of tetraphenylnaphthalene<sup>26</sup>.

Pyrolysis of phthalic anhydride (10) in benzene at  $690^{\circ}$  leads primarily to products attributable to the reaction of benzyne with benzene<sup>28</sup>, although a small yield of biphenylene (1%) was isolated. Pyrolysis of phthalic anhydride vapour over a Nichrome coil at ca.  $800^{\circ}$  gave biphenylene in 10 - 15% yield<sup>29</sup>.

The fierce reaction conditions have precluded any widespread use of these benzyne precursors.

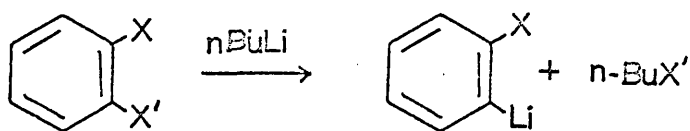
### (iii) Organometallic routes to benzyne.

The objective here is to generate an ortho-metallated phenyl halide which can fragment to benzyne and metal halide. This can be achieved by the action of strong base (e.g. metal amide) on an aryl halide<sup>30</sup> -



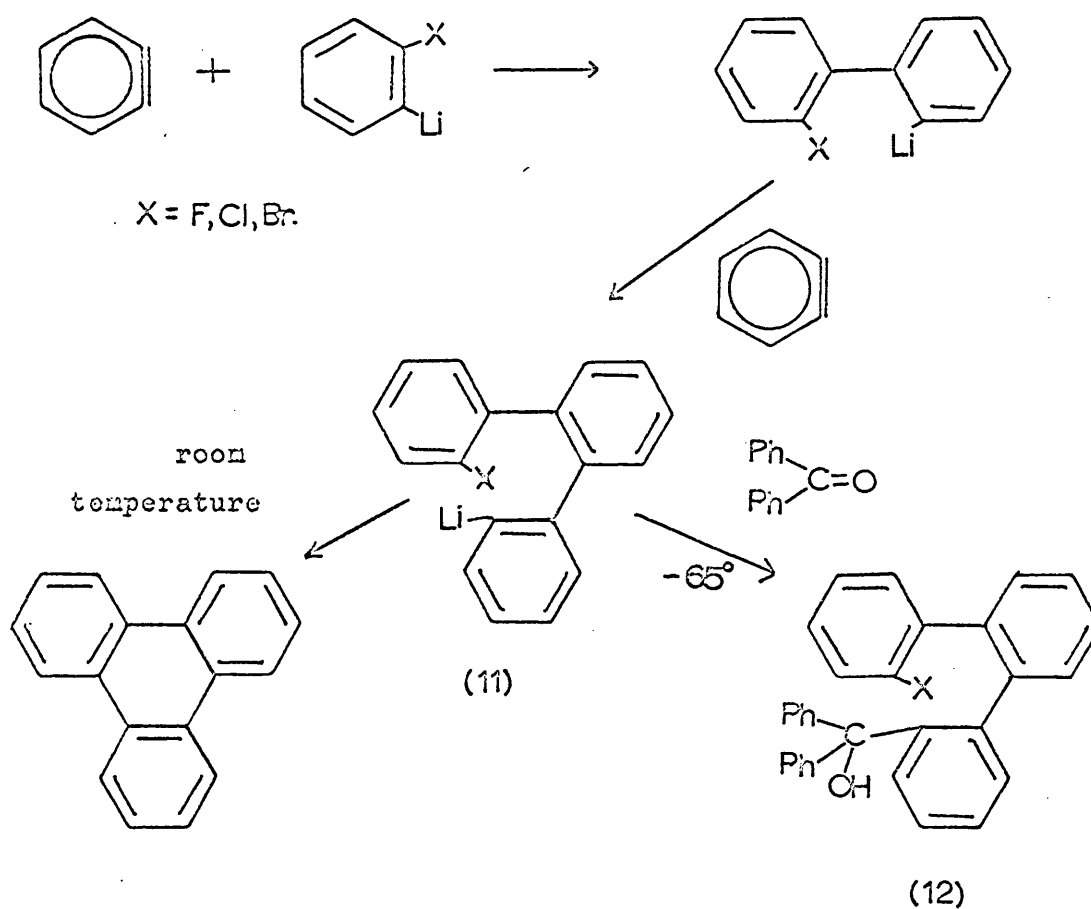
X = F, Cl, Br.

- or by the metallation of aryl dihalides by metal-halogen interconversion reactions<sup>31</sup>.

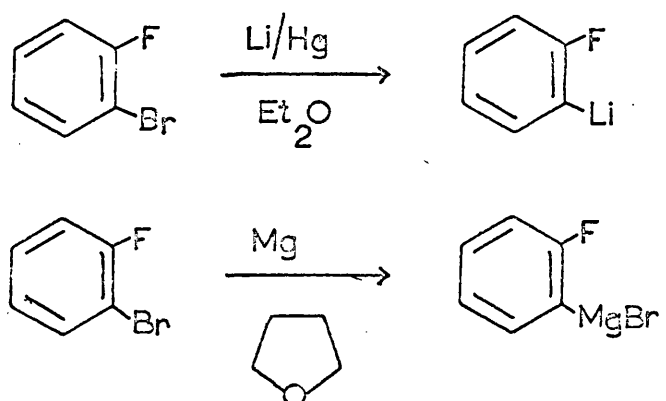


X' - more electropositive halogen

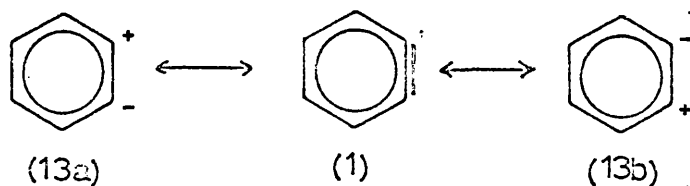
The use of strong organometallic reagents is a disadvantage as it limits the choice of reaction partners for benzyne because side reactions can occur. Thus metal-halogen interconversion can compete with ortho-metallation in aryl halides containing the more electropositive iodide and bromide. Benzyne liberated from these routes can react to give biphenyls and triphenylenes by successive addition to its precursor<sup>31</sup>. Originally it was suggested that triphenylene formation in this situation was due to cyclic trimerisation of benzyne<sup>32</sup>, but the mechanism described below has been clearly confirmed<sup>31</sup> by trapping (11) at low temperature as its benzophenone adduct (12) in yields comparable to that of triphenylene which results from carrying out the reaction at room temperature.



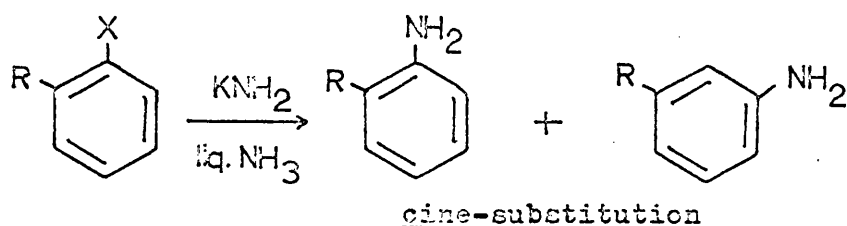
The use of strong organometallic reagents was circumvented by Wittig<sup>30,33</sup> who generated ortho-metallated phenyl halides from 1,2-dihalobenzenes with lithium amalgam or magnesium.



Benzynes as an intermediate.



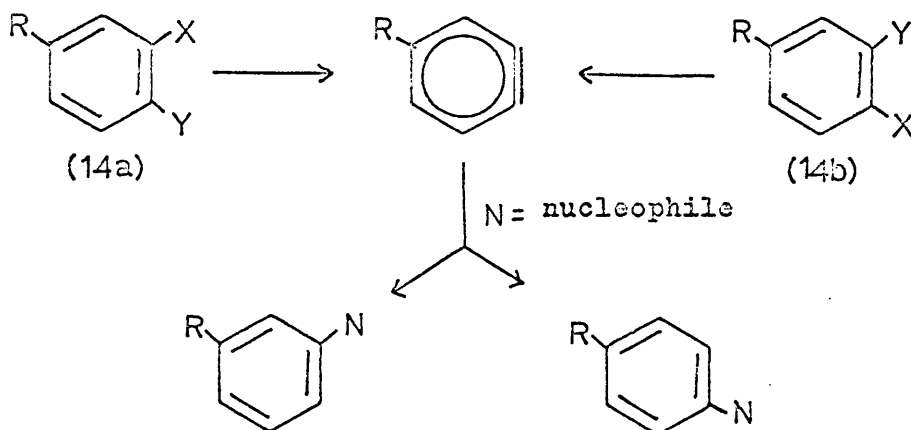
J. D. Roberts suggested benzyne as an intermediate to explain cine-substitution of aryl halides by alkali metal amides<sup>34</sup>. He demonstrated the symmetrical nature of the



intermediate<sup>35</sup>. Information from deuterium and  $^{13}\text{C}$  labelling<sup>36</sup> was consistent with an elimination-addition reaction in which the ortho-hydrogen was removed in the rate determining step.

Benzynes has a significant lifetime which has been demonstrated by reactions in which it selects its reaction partner from among several competitors. Competition experiments between lithium piperidide and phenyllithium<sup>37</sup> and also between lithium chloride, bromide and iodide<sup>38</sup> illustrate this statement. The value of the competition constant remains the same irrespective of the benzyne precursor<sup>39</sup>. The intermediate must therefore be the largest molecular entity common to these precursors which is obviously the  $\text{C}_6\text{H}_4$  unit already suggested by J. D. Roberts.

cine-Substitution occurs when the symmetry of the benzyne intermediate (but not the symmetry of the reactive site) is destroyed by a substituent in the aromatic ring.



The same unsymmetrical intermediate can be generated from two isomeric starting materials. Experiments have shown<sup>15,40</sup> that the ratio of the two products formed is the same from (14a) and (14b). Either the leaving groups X and Y in (14a) and (14b) adopt an identical orientation in the intermediate or they do not form part of it. The latter possibility is a more satisfactory conclusion especially when X and Y are neutral molecules. This has been supported by the observation that product distribution in the reactions of substituted aryl halides via benzyne intermediates is independent on the nature of the halogen<sup>37</sup>.

The existence of a  $C_6H_4$  species in the gas phase has been demonstrated<sup>41,42</sup> by coupling a flash photolysis apparatus to a time of flight mass spectrometer and examining the products of the flash decomposition of benzenediazonium-2-carboxylate. After 50  $\mu$ sec only the masses of nitrogen, carbon dioxide and benzyne were present.

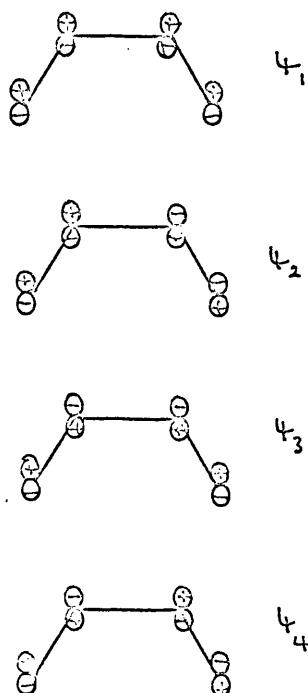
There are two important classes of reaction of benzyne which throw light on its fine structure: (i) cycloaddition reactions (ii) addition of nucleophiles and electrophiles.

#### (i) Cycloaddition reactions.

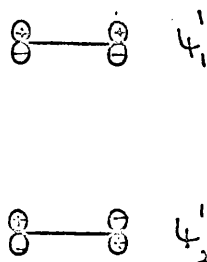
The ability of benzyne to participate in Diels Alder reactions has been known for some time<sup>35</sup>, but the significance in terms of its electronic structure has only recently become apparent.

The mechanism of the Diels Alder addition of olefins (or acetylenes) to 1,3-dienes has been explained by Woodward and Hoffmann<sup>43,44</sup>. The process is envisaged as an interaction between the highest occupied orbital of the olefin and the lowest unoccupied orbital of the diene with a corresponding interaction between the highest occupied orbital of the diene and the lowest unoccupied orbital on the olefin.

Molecular orbitals  
of diene

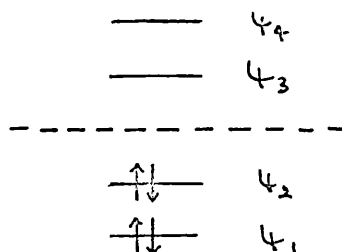


Molecular orbitals  
of olefin

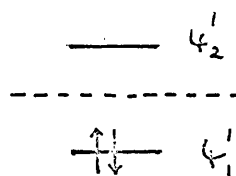


Energy level diagram

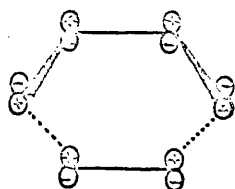
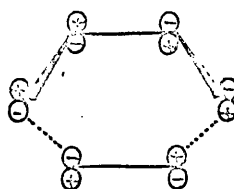
1,3-diene



olefin

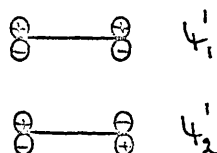


In the Diels Alder reaction  $\psi'_1$  interacts with  $\psi_3$  and  $\psi_2$  with  $\psi'_2$ , the interactions are symmetry allowed and a concerted stereospecific process results.


 $\psi_1/\psi_3$ 

 $\psi_2/\psi_2'$ 

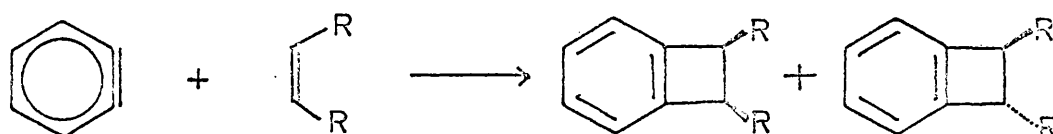
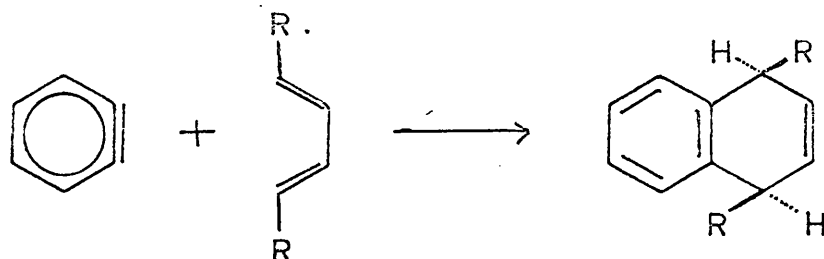
It is apparent from this argument that a similar interaction in a cycloaddition reaction between two olefin molecules would not be symmetry allowed.

no symmetry  
correlation  $\longrightarrow$



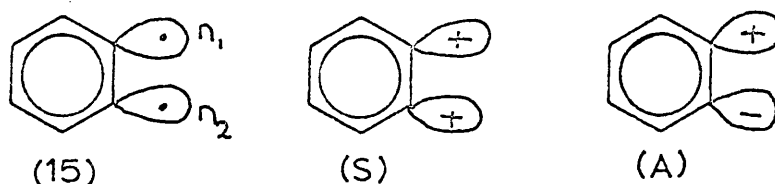
If cycloaddition occurred then it would be a non-concerted and hence non-stereospecific process.

The Diels Alder addition of 1,3-dienes to benzyne is stereospecific<sup>45</sup> and the cycloaddition of olefins is non-stereospecific<sup>46,47,48</sup>. This is precisely the situation expected if the reactive site in benzyne is like the  $\pi$  bond in olefins and acetylenes.

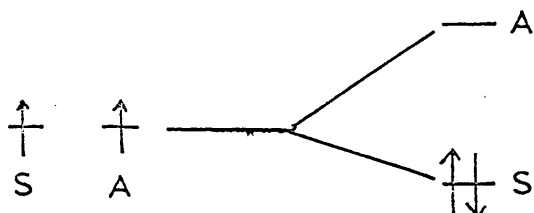




Hoffmann has verified this hypothesis by molecular orbital calculations<sup>49</sup>.  $n_1$  and  $n_2$  (15) are the hybrid orbitals formed by loss of two ortho substituents in the benzyne precursor. The symmetry adapted combinations ( $n_1 + n_2$ )(Symmetric,S) and ( $n_1 - n_2$ )(Antisymmetric,A) are degenerate in the absence of any interaction between  $n_1$  and  $n_2$ . Calculation has shown



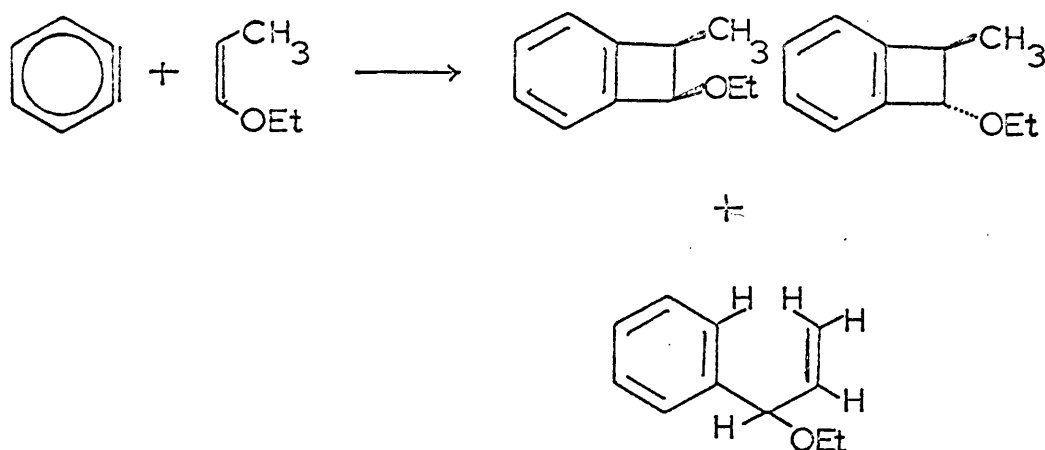
and ( $n_1 - n_2$ )(Antisymmetric,A) are degenerate in the absence of any interaction between  $n_1$  and  $n_2$ . Calculation has shown



that an interaction does occur which manifests itself in a splitting between the energies of (S) and (A) of sufficient magnitude to cause pairing of electrons in the (S) combination. The ground state of benzyne is a symmetric singlet with two electrons in the lower (S) orbital resembling that of a partial  $\pi$  bond.

Diels Alder addition reactions of benzyne are well documented<sup>15</sup> and have become accepted as a diagnostic test for the intermediacy of benzyne in a reaction.

The cycloaddition reactions of olefins with benzyne are non-stereospecific as expected but experiments have shown that they are stereoselective<sup>48</sup>. Thus cis-ethylpropenyl ether afforded the cis and trans butenes in 51% and 3.2% yields together with a product from the 'ene' reaction (see later), ethyl  $\alpha$ -phenylallyl ether (0.9%).

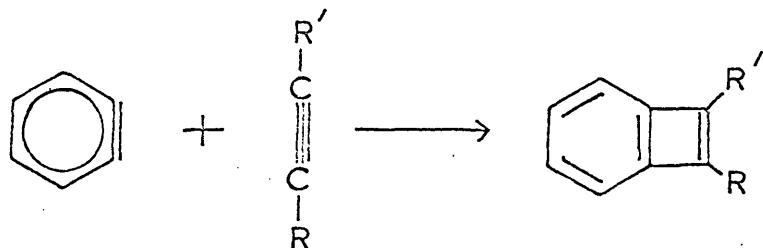


The trans-ethylpropenyl ether gave the corresponding butenes in 8.2% and 31% and the 'ene' product in 14% yield. These results, in which predominant but not exclusive retention of configuration occurs, are consistent with a non-concerted cycloaddition reaction in which bond rotation is relatively slow compared to ring closure. The dependence of the 'ene' product on the stereochemistry of the olefin can be explained by an unfavourable interaction of the bulky groups of the cis-olefin with benzyne.

Formation of biphenylene involves a cycloaddition of benzyne to itself and if the reactive site is a symmetric singlet, the process should be non-concerted. A high stationary concentration of benzyne is necessary for a high collision probability and this requirement has been satisfied by the gas phase flash decomposition of solid 1,2,3-benzothiadiazole-1,1-dioxide(4a)<sup>20</sup> and flash photolysis of benzenediazonium-2-carboxylate(2)<sup>50</sup> where yields of biphenylene approach 60%. Decompositions of these precursors in solution give lower yields of biphenylene and in the case of 1,2,3-benzothiadiazole-1,1-dioxide much lower yields (1-9%).

The very high yields of biphenylene (80%) produced by lead tetraacetate(LTA) oxidation of 1-aminobenzotriazole(5) in solution may be explained by participation of lead in the reaction (see Discussion).

Cycloaddition of acetylenes to benzyne leads to formation of benzocyclobutadienes<sup>51,52</sup> which can react further under these conditions either by dimerisation or addition of a further molecule of benzyne.



The 1,3-dipolar cycloaddition reactions of olefins and acetylenes have been extensively studied in recent years<sup>53</sup> and participation of benzyne<sup>54,55,56</sup> in similar reactions as the 'dipolarophile' is again an indication that the reactive site in benzyne has similar properties to that of a  $\pi$  bond. The mechanism of this reaction has been established by Huisgen<sup>57</sup> after some dispute<sup>58</sup>.

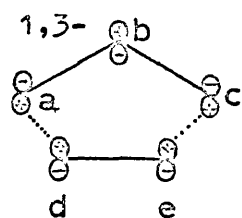
The stereospecificity of the addition has been interpreted in terms of a concerted reaction directly analogous to the Diels Alder reaction, the 1,3-dipole being the four electron component and the dipolarophile (olefin or alkyne) the two electron component. The highest occupied and lowest unoccupied molecular orbitals of the 1,3-dipole (a-b-c) are shown below in the suggested orientation for interaction with corresponding orbitals of the dipolarophile (d-e).

lowest unoccupied

orbital of 1,3-dipole

highest occupied

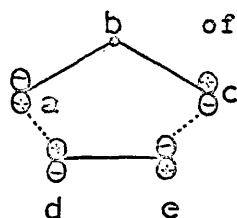
orbital of olefin/-acetylene



highest occupied orbital

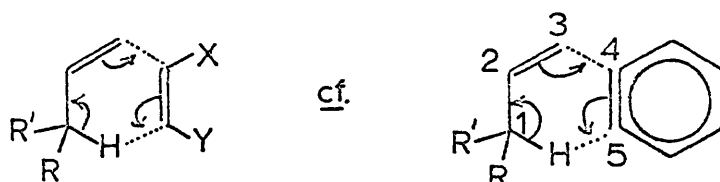
of 1,3-dipole

lowest unoccupied orbital of olefin/-acetylene

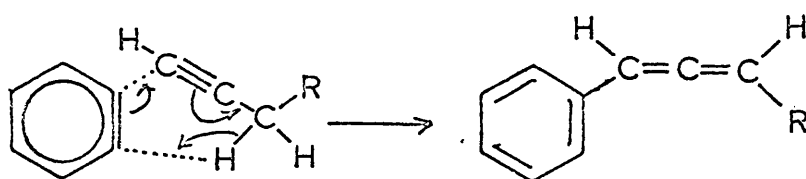


As can be seen from the diagram, the conditions are satisfied for a thermal concerted cycloaddition reaction and when benzyne is the dipolarophile its symmetric (highest occupied) and antisymmetric (lowest unoccupied) molecular orbitals replace those of the dipolarophile.

The 'ene' reaction is a reaction between an activated olefin and an allylic system. It has been shown<sup>59,60</sup> that the reaction is concerted and stereospecific leading to optically active products from an optically active olefin.



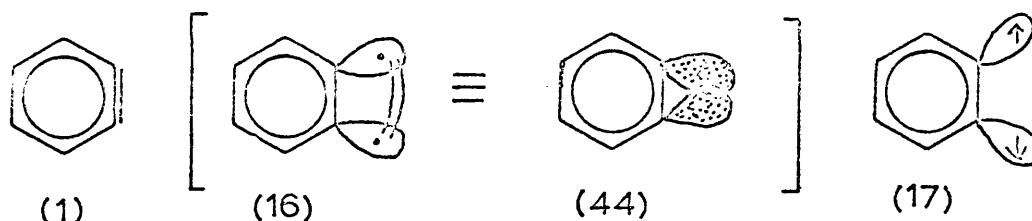
As shown in the diagram, the participation of benzyne in the 'ene' reaction<sup>20,61,62</sup> infers the presence at the reactive site of a  $\pi$  type bond. Benzyne even undergoes the 'ene' reaction with an alkyne to form an allene<sup>13</sup>. These reactions bear a



formal similarity to 1,5-sigmatropic shifts<sup>63,64</sup> which have been described by Woodward and Hoffmann<sup>65</sup> as a suprafacial migration of hydrogen between the ends of a  $\pi$  system.

Cycloaddition reactions provide an insight into the significance of the excited states of molecules in determining the course of a reaction. The electrons of a bond undergoing reaction are deformed and the excited state of that bond describes one possible way in which the electrons can be redistributed<sup>66</sup>. The difference in energy between the ground and excited state determining the ease of the transition, commonly described as the polarisability of the bond.

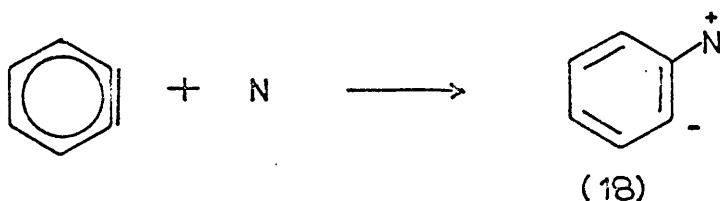
The evidence suggests that benzyne (1) is a ground state singlet in which the pairing energy of the electrons in the partial  $\pi$  bond (16)(44) contribute to its stability. A singlet diradical (17) in which there is no pairing of electrons can be envisaged as one of its possible excited states. There is good evidence for its occurrence when benzyne



is generated by photolytic methods from benzenediazonium-2-carboxylate<sup>50</sup> and 2-iodophenylmercuric iodide<sup>26</sup>. Benzene and biphenyls are reproduced probably by hydrogen abstraction from the solvent - a typical radical reaction.

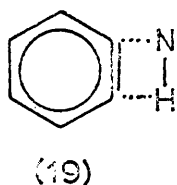
The  $\pi$  bond in benzyne is readily polarised by nucleophiles and electrophiles which can be rationalised on the basis of a small energy difference between (16) and (17). This is a reasonable assumption as the strain in the  $\pi$  bond in (16) is released by excitation to (17) although of course the pairing energy of the electrons is lost.

(ii) Addition of nucleophiles and electrophiles.

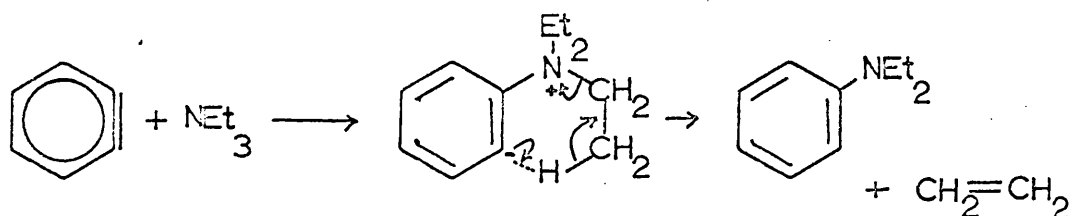


N = nucleophile

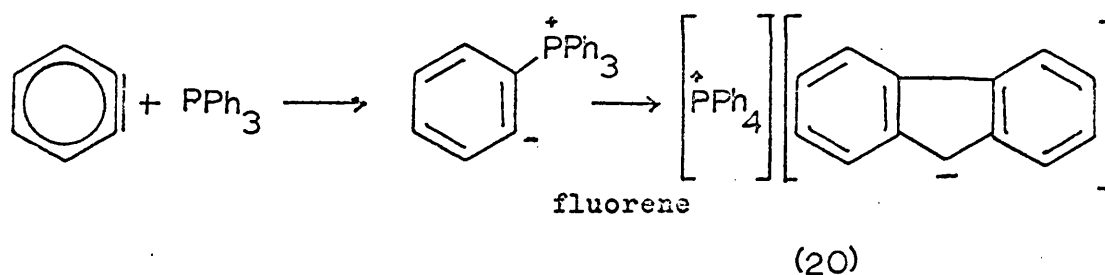
Some examples of nucleophilic addition reactions have already been given in the text to demonstrate the selectivity of the benzyne intermediate. Nucleophiles with an active hydrogen such as primary and secondary amines<sup>67,68</sup> and carboxylic acids<sup>15</sup> would immediately protonate the betaine (18) although it is conceivable that (19) describes the intermediate more satisfactorily in these cases.



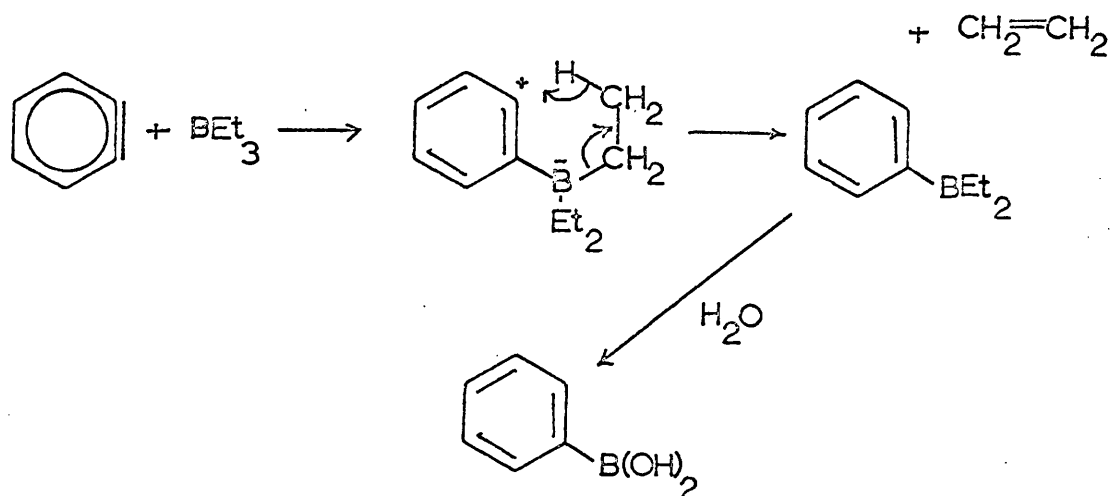
Ethers and tertiary amines<sup>69,70</sup> behave as nucleophiles to give the intermediate (18) which then reacts further by an intramolecular process described below.



The betaine (18) can accept a proton from an external source; thus triphenylphosphine in the presence of fluorene gives the tetraphenyl phosphonium salt (20)<sup>71</sup>.



An example of electrophilic attack is provided by triethyl boron. Hydrolysis of the reaction, yields phenylboronic acid<sup>68</sup>.



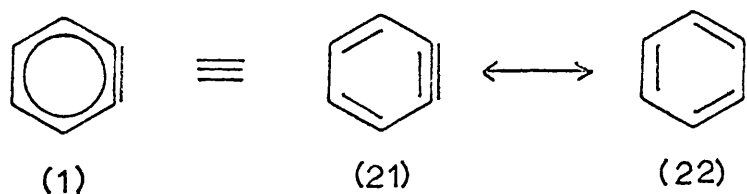
Summary.

The ground state of benzyne is a symmetric singlet in which the reactive site has all the symmetry properties of the  $\pi$  bond in olefins and acetylenes. The  $\pi$  bond is easily polarised. The significant features of the symbol used for benzyne throughout this script are the implicit suggestions that:

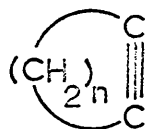
- (i) the aromatic sextet of electrons remains largely undisturbed
- (ii) the two electrons in the (S) orbital interact in such a way as to form a partial  $\pi$  bond which is orthogonal to the  $\pi$  orbital system of the aromatic ring.

Comparison with cyclic acetylenes.

The suffix 'yne' on benzyne infers the existence of a carbon-carbon triple bond in the  $C_6H_4$  species. Coulson suggested<sup>72</sup> that a more effective interaction of the electrons in  $n_1$  and  $n_2$  would be achieved if the  $C_1 - C_2$  bond were shortened and that this would also result in partial bond fixation in the aromatic system (21). However Hoffmann<sup>49</sup> showed by Molecular Orbital calculations that (22) was a sizeable contributor to the structure of benzyne and proposed a resonance hybrid of the two forms (21) and (22).



The 'sp' hybridised carbon atoms of the acetylene triple bond prefer a linear orientation. In cyclic acetylenes



(23)

this preferred orientation becomes increasingly distorted as 'n' (see (23)) decreases. Cyclic acetylenes, therefore exist in a strained conformation and reactions which can relax the strain (conversion of 'sp' to 'sp<sup>2</sup>' hybridised carbon) are favoured. The strain only becomes severe for values of 'n' of five or less, and as a result these systems only have a transitory existence.

Cycloheptyne has a lifetime of 1 hr. at -75° and cyclohexyne a few seconds at -110°<sup>73</sup>. The selectivity of these acetylenes decreases with ring size and cyclohexyne gives the lowest yield of the diphenylisobenzofuran adduct when generated by either the Grignard (43%) or oxidative route (8%)<sup>13</sup>. This observation can be explained in two ways:

- (i) when generated cyclohexyne reacts more indiscriminately than cycloheptyne and larger cyclic acetylenes
- (ii) the cyclohexyne precursor might decompose more slowly than the corresponding cycloheptyne precursor and therefore be susceptible to side reactions (not applicable to oxidative routes).

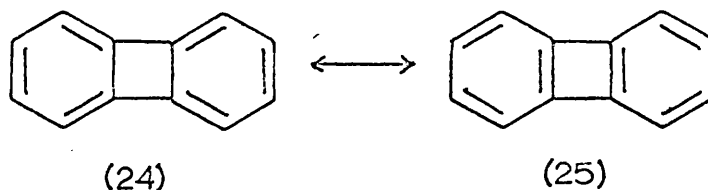
The existence (or not) of a carbon-carbon triple bond in benzyne is irrelevant to a comparison with cyclic acetylenes. It is a relief of strain (which in both systems is a return to 'sp<sup>2</sup>' hybridised carbon) that explains any similarity in their reactivity.

The  $\pi$  component in the carbon-carbon triple bond in acetylenes has the right symmetry to undergo cycloaddition reactions both of the Diels Alder type and with 1,3-dipoles. Cyclic acetylenes readily undergo these cycloaddition reactions<sup>73,74,75</sup> and attack by nucleophiles<sup>13</sup> which also achieves

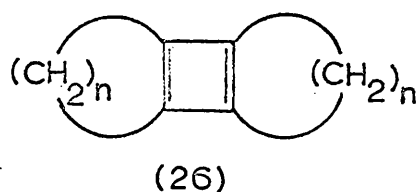


rehybridisation of carbon (to ' $sp^2$ ') at the reactive site.

Benzyne dimerises to biphenylene. The analogous compounds produced by cyclic acetylenes are cyclobutadienes, but they have never been isolated. Biphenylene can be considered as a resonance hybrid of (24) and (25), the dibenzocyclobutadiene (25) being a negligible contributor. The cyclobutadiene ring (26)

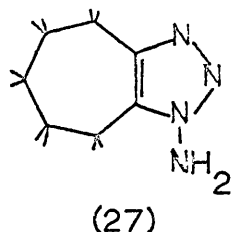


derived by dimerisation of cyclic acetylenes cannot be stabilized in this way and if formed would be extremely reactive.



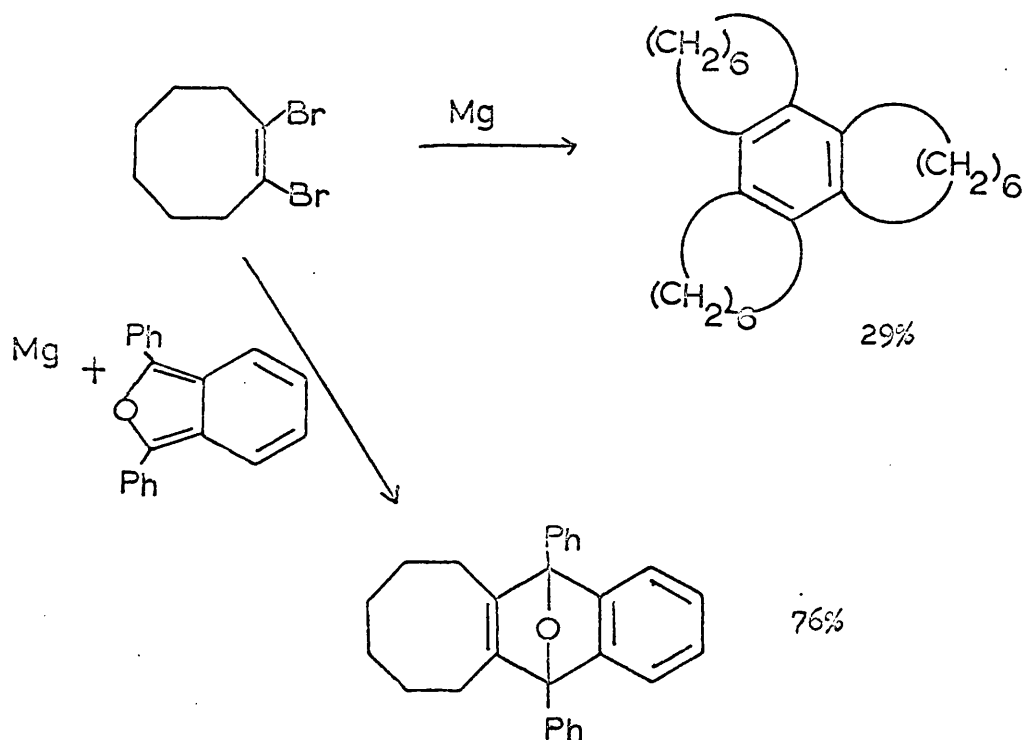
Its formation and subsequent participation in Diels Alder reactions has been used to explain:

- (i) the hexamers produced by the LTA oxidation of 1-amino-4,5-pentamethylenetriazole (27)<sup>76</sup>

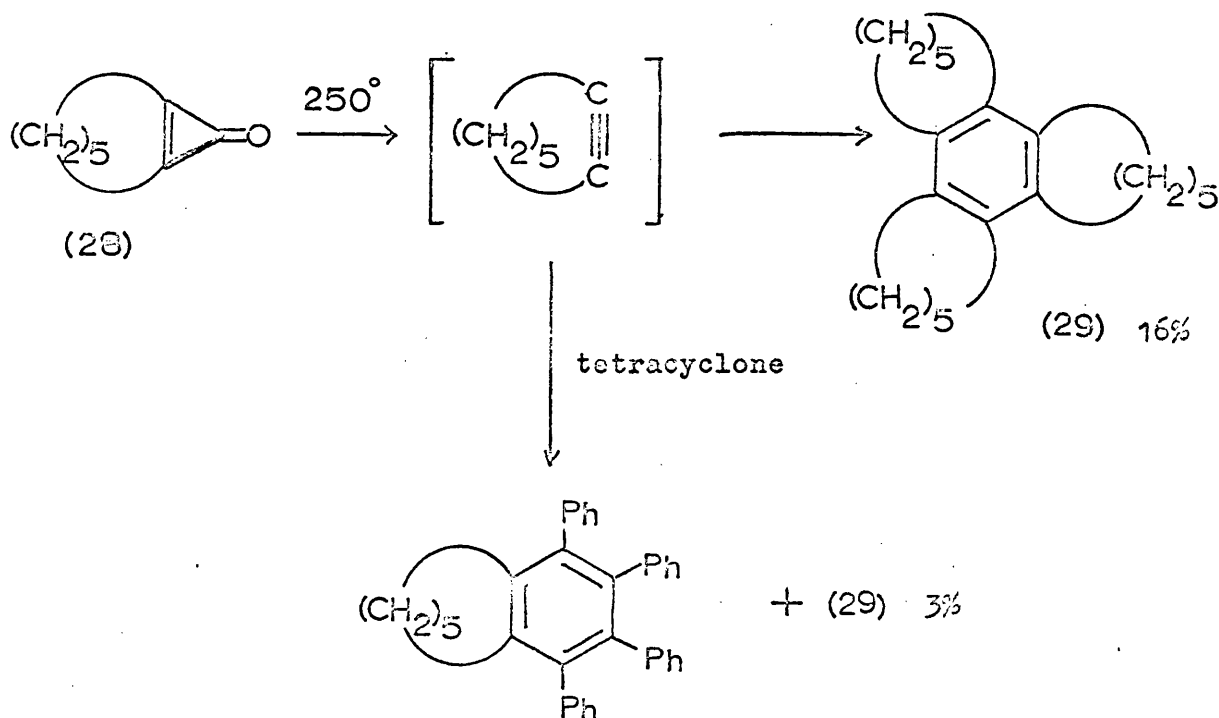


- (ii) the cyclic trimers and tetramers formed by the action of lithium amalgam on 1,2-dihalo-cyclohexenes<sup>77</sup>.

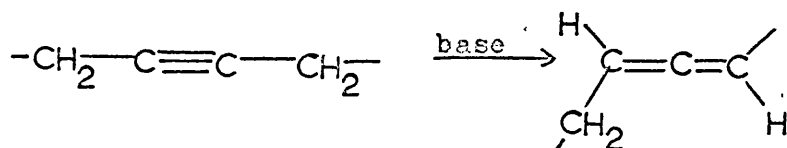
Trimerisation of cyclic acetylenes generated from ortho-metallated precursors may occur by successive addition of the alkyne to the precursor in a mechanism similar to that already described for triphenylene formation. This hypothesis is supported by the observation that thermal trimerisation of cyclooctyne under the identical conditions used to generate it from 1,2-dibromocyclooctene and magnesium cannot account for the high yield of cyclic trimer in this reaction<sup>13</sup>.



This mechanism cannot be used to explain the formation of triscycloheptenobenzene (29) on heating the cyclopropanone (28)<sup>78</sup>.

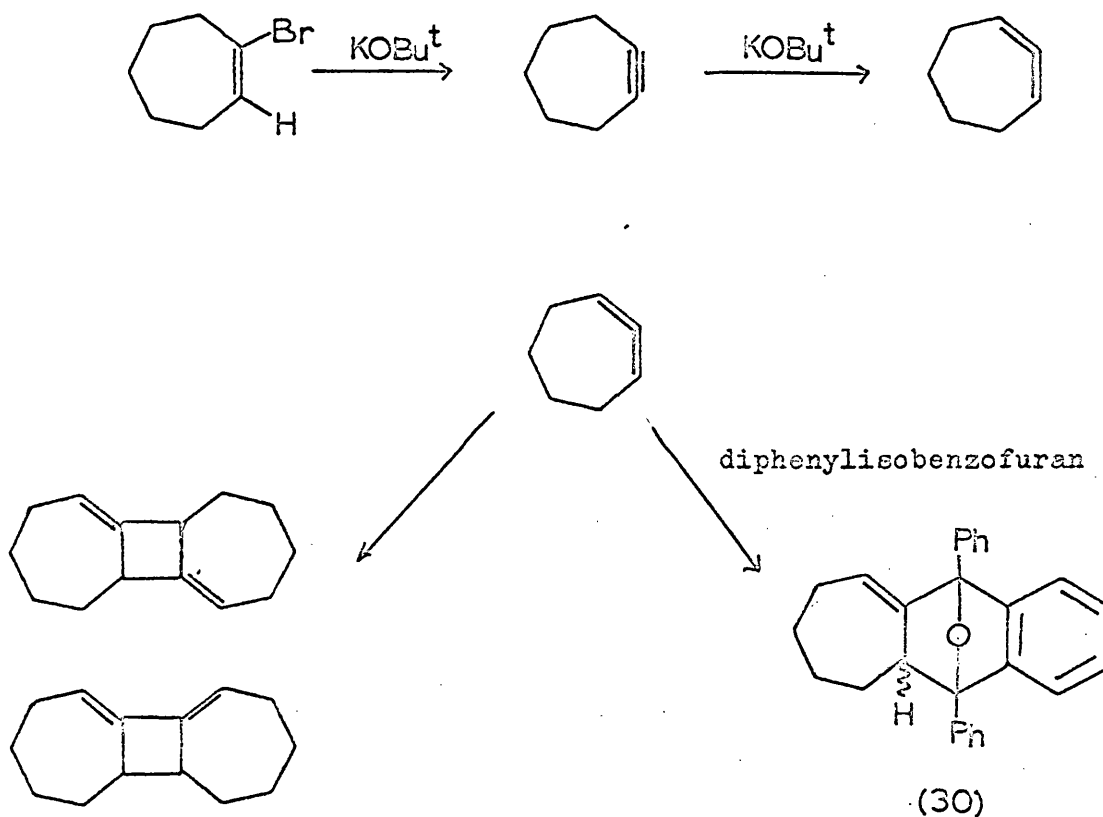


Thermodynamic data has shown that internal acetylenes are more stable than the corresponding allenes obtained by base isomerisation<sup>79</sup>. The unstrained acetylene linkage requires



four colinear atoms, whereas the allene requires only three. An allene therefore, might be expected to become the more stable of the two in small ring systems. This has been demonstrated for a series of cyclic acetylenes ( $n = 7$  to  $9$ )<sup>79</sup>. The ready conversion to allenes of yet smaller cyclic acetylenes ( $n = 6$  to  $4$ ) has been shown in a series of recent papers<sup>80,81,82</sup>.

The formation of the exo and endo isomers of compound (30) by treating 1-bromocycloheptene with potassium tertiary butoxide in the presence of diphenylisobenzofuran and the two hydrocarbons in the absence of the trap has been construed as evidence for the intermediate allene<sup>81</sup>.



Summary.

Highly strained cyclic acetylenes do resemble benzyne in their reactivity and parallel each other's behaviour in cycloaddition reactions and behaviour towards nucleophiles. Cyclic acetylenes, unlike benzyne, can relieve strain by isomerisation to cyclic allenes.

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2. SOME ASPECTS OF TRANSITION METAL CHEMISTRY.

The conditions under which metals form stable complexes of any sort must be considered when designing a transition-metal complex to stabilize a reactive intermediate.

There are two important categories:

- (i) The metal is completely surrounded by ligands. All the 'd', 's' and 'p' valence orbitals are used, making a total of nine orbitals which require 18 electrons to be filled.
- (ii) The metal is in a planar environment in which only eight of the available orbitals are used; the 'p' orbital perpendicular to the molecular plane is of higher energy and remains unfilled.

This restatement of the Inert Gas Rule in molecular orbital terms (modified for planar complexes) can be used to predict the stoichiometry and to a certain extent the geometry of stable transition metal complexes.

Longuet-Higgins and Orgel<sup>1</sup> used this approach in predicting the stability of cyclobutadiene in a transition metal complex, the qualitative approach above being substantiated by Molecular Orbital calculations.

It is necessary to consider the donor - acceptor properties of the ligand in this approach; for example cyclobutadiene has four mobile electrons which can be donated to the transition metal. The success of the approach is exemplified by the series of complexes illustrated below.

Pt(O)

10

6

Ni(II)

8

8

Ni(O)

10

8

Co(O)

9

9

Fe(O)

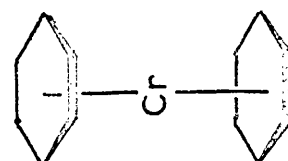
8

10

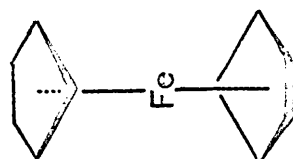
Cr(O)

6

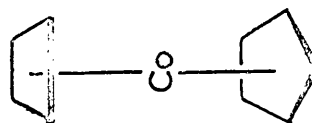
12

Valence  
electronsLigand  
electrons

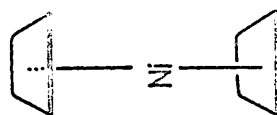
(31)



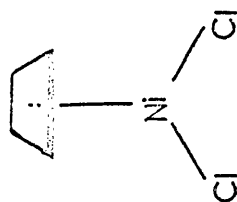
(32)



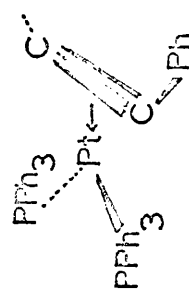
(33)



(34)



(35)



(36)

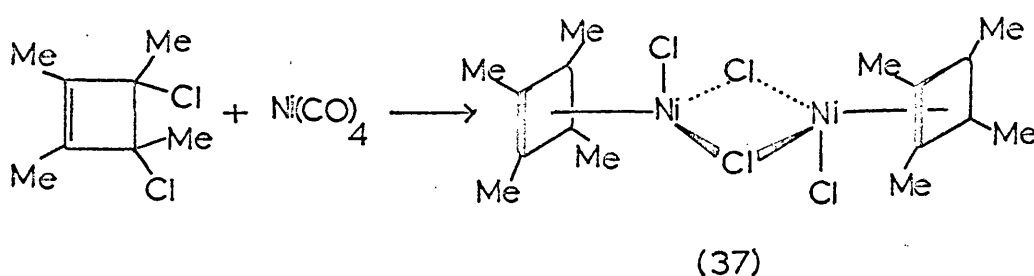
Dibenzenechromium (31): chromium(0) has a total of 24 electrons of which 6 are valence electrons. To form a stable type(i) complex, 12 additional electrons are required by ligand donation. The benzene ligands in dibenzenechromium donate 6 electrons each.

Bis( $\pi$ -cyclopentadienyl)iron (32): iron(0) has eight valence electrons, a type(i) complex is achieved in bis( $\pi$ -cyclopentadienyl)iron in which the cyclopentadienyl radicals donate five electrons each.

( $\pi$ -cyclopentadienyl)( $\pi$ -cyclobutadiene<sup>e</sup>)Cobalt(0) (33): cobalt(0) has nine valence electrons, a type(i) complex is obtained by donation of four electrons from cyclobutadiene and five electrons from the cyclopentadienyl radical.

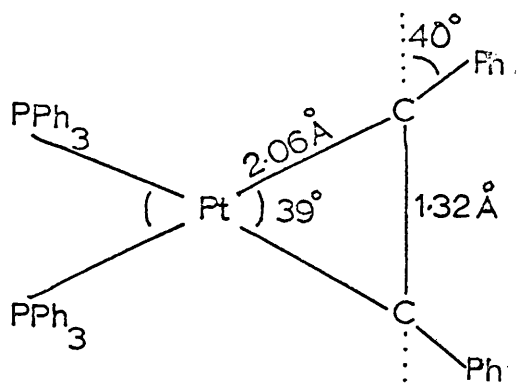
Bis( $\pi$ -tetraphenylcyclobutadiene<sup>e</sup>)nickel (34): it satisfies the conditions for a type(i) complex. It has been postulated as an intermediate<sup>83</sup> in the formation of hexaphenylbenzene from tolan and (dimesityl)nickel in tetrahydrofuran(THF).

$\pi$ -Tetramethylcyclobutadiene<sup>e</sup> dichloronickel(II) (35): this is an example of a type(ii) complex. Nickel(II) has eight valence electrons, donation of two electrons from each of the chlorine ions and four from cyclobutadiene give a total of sixteen electrons. Attempts to prepare this complex<sup>3</sup> resulted in formation of compound (37) in which nickel(II) achieves extra stability in a binuclear complex by sharing a chlorine ion<sup>84</sup>.



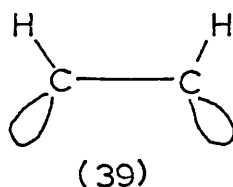
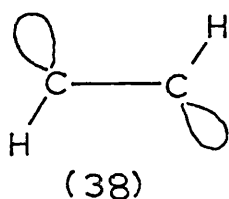
The well known square planar acetylene<sup>85</sup> and olefin<sup>86</sup> complexes of platinum(0) provide many other examples of sixteen electron complexes. In these complexes the olefin or acetylene is behaving as a two electron donor and an analogous benzyne-platinum complex could be formed if benzyne donated two electrons in a similar way.

The precise structure of diphenylacetylenobis(triphenylphosphine)platinum (36) has been established by X-Ray diffraction studies<sup>87</sup> which have shown that diphenylacetylene (tolan) as a ligand is distorted from its normal linear configuration.



This is a very significant result as it illustrates that the bonding process stabilizes the ligand in a similar geometry to that of its excited state.

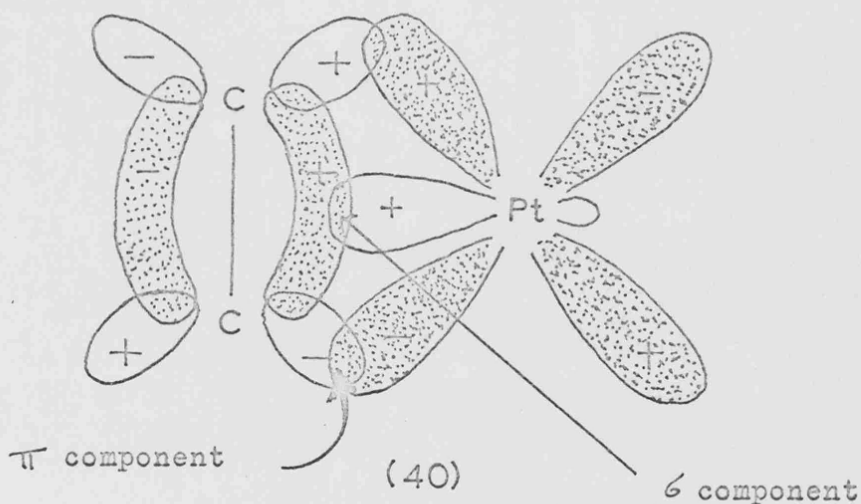
The difference in energy between the two excited states of acetylene shown below is not very great<sup>66,88</sup>. Configuration (39) is of slightly higher energy than (38). The geometry of tolan in the platinum complex (36) corresponds to that of acetylene in configuration (39). The electrons of one



$\pi$  component of the carbon-carbon triple bond have been decoupled and occupy ' $sp^2$ ' type orbitals on carbon.

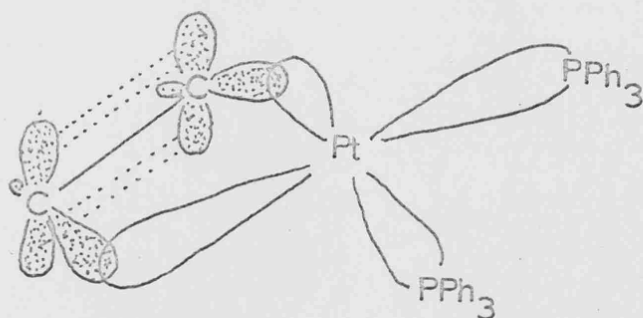
The nature of the bonding in the tolan complex is ambiguous; two extreme viewpoints for the same complex are described in which platinum is regarded as zerovalent or divalent.

1. In the zerovalent platinum complex a  $\sigma$  bond<sup>89</sup> is formed as illustrated in the diagram.



- (a)  $\sigma$  component is formed by donation of electrons from a filled  $\pi$  orbital on acetylene to a vacant ' $sp^2$ ' orbital on platinum.
- (b)  $\pi$  component formed by back donation of electrons from filled 'd' orbitals on platinum to a vacant  $\pi^*$  orbital on acetylene.

2. In the divalent platinum complex each of the acetylenic carbons is  $\sigma$  bonded to ' $dsp^2$ ' hybrid orbitals of the metal by use of approximately ' $sp^2$ ' orbitals thereby reducing the triple bond to a double bond.





The i.r. stretching frequency of the carbon-carbon triple bond in these complexes (viz. compound (36)) is reduced from  $2100\text{ cm}^{-1}$  in the free acetylenes to  $\sim 1750\text{ cm}^{-1}$  in the complexes. This data on first sight favours the situation described in (41).

A similar reduction in the bond order of the carbon-carbon triple bond can be achieved by postulating that in (40) back bonding into the antibonding orbitals is more important to the stability of the complex than  $\sigma$  bonding. A net donation of electrons into the antibonding orbitals will similarly reduce the bond order of the triple bond.

The stability of these complexes depends on two factors:

- (i) the transition metal
- (ii) the nature of the acetylene or olefin.

The most stable complexes of this type are formed by transition metals at the extreme right hand side of the Periodic Table. This observation<sup>90</sup> favours a  $\sigma\pi$  description of the bond as here filled 'd' orbitals are essential for the  $\pi$  component. The stability also increases from first to third row transition metals as the 'd' orbitals become more diffuse and hence more capable of interaction with orbitals on acetylene or olefin.

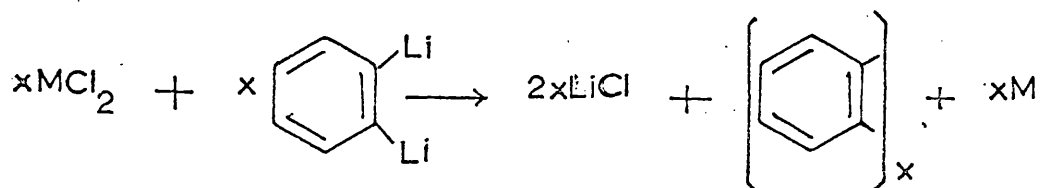
Substituted acetylenes<sup>91</sup> and olefins<sup>86</sup> containing electron-withdrawing groups form the most stable complexes. The donor properties of the olefin and acetylene are therefore not as important as their acceptor properties, an observation which substantiates the bonding situation described in (40) where back-bonding predominates. The energy of the  $\pi^*$  orbitals of the acetylene or olefin is lowered by the electron withdrawing substituent<sup>92</sup>, thus facilitating donation of electrons by the filled 'd' orbitals of the transition metal.

Acetylene complexes are not the only ones examined by X-Ray diffraction which indicate that the ligand is coordinated in its excited state geometry.

The X-ray structure determination of bis( $\pi$ -tetramethylcyclobutadiene) $\mu$ -dichlorodi- $\mu$ -chlorodinickel<sup>84</sup> (37) and tetraphenylcyclobutadienyliron tricarbonyl<sup>95</sup> show the square planar geometry of the coordinated cyclobutadiene moiety. This is the geometry of the triplet (excited) state. When cyclobutadiene is released from its coordination to a transition metal its reactions are those of a singlet<sup>4</sup> in which there are two discrete carbon-carbon double bonds<sup>94</sup>.

### 3. BENZYNE TRANSITION METAL COMPLEXES.

o-Dilithiobenzene reacts with transition metal halides to give biphenyl (plus other open chain polyphenyls), triphenylene, tetraphenylene, hexaphenylene and octaphenylene in varying yields depending upon the transition metal cation<sup>95</sup>. No correlation was found between the hydrocarbon produced and the transition metal cation used. Trapping experiments with diphenylisobenzofuran eliminated the participation of free benzyne in the

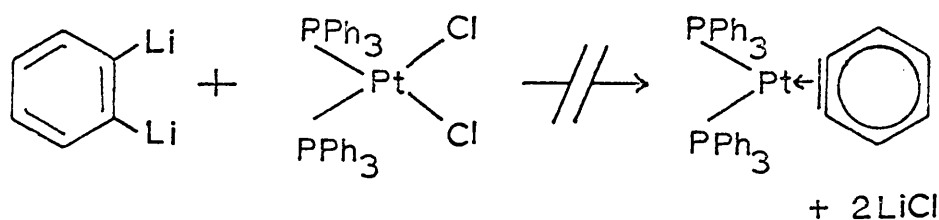


reaction. Small quantities of benzene were found, probably formed by the hydrolysis of the starting material and not by hydrogen abstraction of free phenyl radicals.

No mechanism for the reaction was established, although a coordinated complex involving four benzyne molecules was conceived to explain the formation of tetraphenylene. Today the cyclic trimerisation and tetramerisation of acetylene by transition metals is thought to involve an intermediate in which three and four molecules of acetylene are bonded to the metal<sup>96</sup>. The formation of triphenylene and tetraphenylene is directly analogous to the cyclisation of acetylenes if a benzyne species coordinated to the transition metal is involved. It is

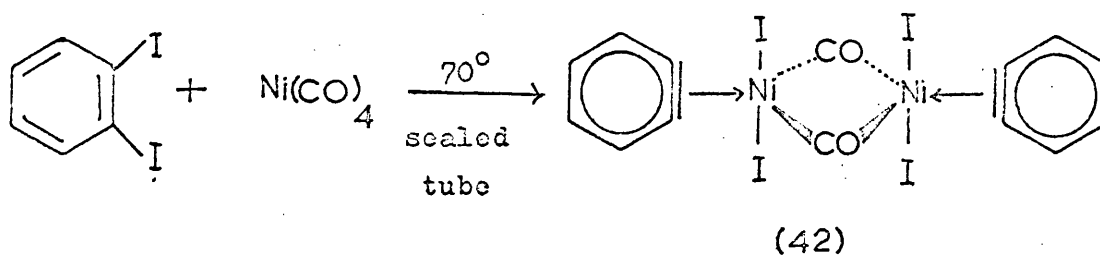
difficult to explain the occurrence of hexaphenylene and octaphenylene in this way, their formation may indicate a stepwise addition reaction which is terminated by ring closure, or hydrolysis to open chain polyphenyls.

The reaction between o-dilithiobenzene and cis-dichloro bis(triphenylphosphine)platinum(II) was investigated<sup>95</sup> in the hope of isolating a platinum-benzyne complex, similar to the tolan-platinum complex (36).



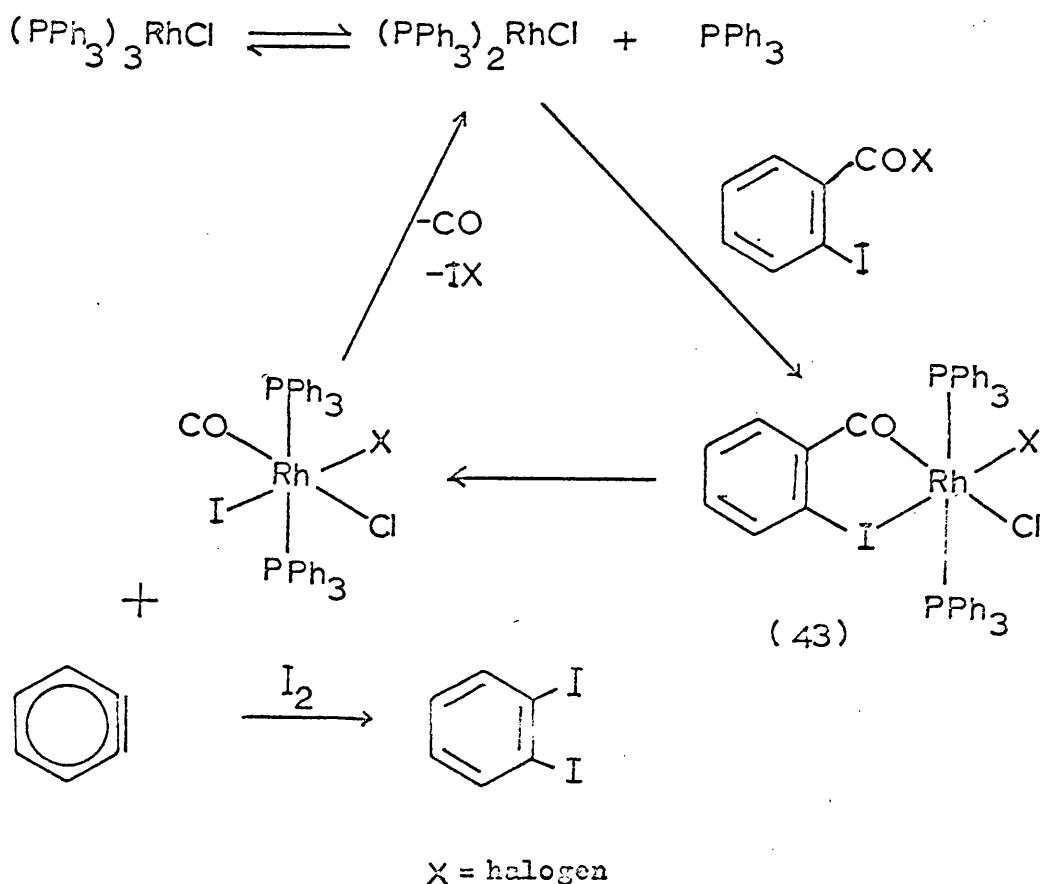
Only triphenylphosphine-platinum complexes could be isolated from the reaction and a 'red laquer' which did not yield benzyne adducts with furan.

A benzyne-nickel complex (42) has been reported in the literature<sup>97</sup>. It is prepared by the action of o-diiodobenzene on nickel carbonyl. The structure of compound (42) in which benzyne is behaving as a two electron donor has not yet been



confirmed. The benzyne complex (42) was reported to be very unstable towards water and yet its NMR spectrum was run in deuteriomethanol.

The high yields of *o*-diiodobenzene obtained by the catalytic decarbonylation of *o*-iodoaryl halides in the presence of iodine and tris(triphenylphosphine)chlororhodium(I) at 175-250° have been explained by a benzyne intermediate generated from compound (43)<sup>98</sup>. The authors expressed doubt about the



mechanism as they could not identify the halogen molecule (IX) by mass spectrometry. No attempt was made to trap benzyne with furan or tetracyclone.

Cook and Jauhal<sup>103</sup> attempted to trap benzyne generated from 1,2,3-benzothiadiazole-1,1-dioxide(4a) and benzenediazonium-2-carboxylate(2) using ethylenebis(triphenylphosphine)platinum(118) as a benzyne trap. They published their results after we had finished our independent study using similar benzyne precursors with tetrakis(triphenylphosphine)platinum(0) (46). The results of Cook and Jauhal supported our findings and are compared with our results in the Discussion.

INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES.

1. Infra red (i.r.) spectra were recorded in the range 4000 - 650  $\text{cm}^{-1}$  using a Perkin Elmer 237 grating spectrometer and a Unicam SP-200 spectrometer. Spectra of solids were taken as Nujol mulls and liquids as thin films between sodium chloride plates. Polystyrene was used as a reference.
2. Ultra violet (u.v.) spectra were recorded in the range 200 - 450 nm using a Unicam SP-800 recording spectrometer.
3. Proton magnetic resonance (NMR) spectra were taken on a Varian A.60 or T.60 instrument.
4. Mass spectra were taken on an A.E.I., M.S.9 instrument.
5. Osmometric molecular weights were determined on a Mechrolab Vapour Phase Osmometer, Model 301A. Two different concentrations of the unknown were used in the molecular weight determination.
6. Melting points (m.p.) were taken on a Kofler Micro Heating Stage and were corrected.
7. Lead tetraacetate (LTA) was commercial material (BDH). Acetic acid was removed by suction and the LTA was then stored over concentrated sulphuric acid.
8. Column chromatography was carried out using silica gel MFC, basic alumina (Spence Type H) and neutral alumina (Woelm, activity grade 1) as supports. The mixture to be separated was absorbed in one of two ways:
  - (A) by evaporation of its solution onto the support using a rotary evaporator (Method A)
  - (B) a concentrated solution of the mixture was poured onto the top of the support and absorbed by allowing 5 min. to elapse before elution was commenced (Method B).

Columns were packed dry except when silica gel was used as a support. They were eluted with mixtures of petrol (b.p. 40 - 60°) and ether, containing a gradually increasing proportion of ether. Ether was then gradually replaced by ethyl acetate and ethyl acetate by ethanol.

9. All experiments, except for certain literature preparations, were performed under a nitrogen atmosphere using dry, oxygen-free solvents. The solvents were purified as follows:

- (i) benzene, toluene and tetrahydrofuran (THF) were dried by refluxing over calcium hydride (24 hr.) followed by distillation in a stream of nitrogen onto sodium wire
- (ii) furan and ether were dried by refluxing over sodium wire (24 hr.) and then distilled onto fresh sodium wire as before
- (iii) dimethylsulphoxide was dried by storage over molecular sieves (Type 4A)
- (iv) chloroform was washed with water to remove ethanol and dried over calcium chloride (48 hr.) followed by distillation in a stream of nitrogen onto fresh calcium chloride.

Nitrogen was purified by passing successively through aqueous sodium hydroxide, concentrated sulphuric acid, sodium hydroxide pellets and silica gel.

10. Three photolysis techniques were used:

- (a) 'Hanovia'. A Hanovia photochemical reactor fitted with quartz jackets was immersed into the solution to be photolysed. A 100 watt medium pressure mercury lamp irradiated at 254, 265, 297, 313 and 336 nm. This method was most frequently used and found superior to the 'Rayonet' method which operated at similar wavelengths.
- (b) 'Rayonet'. The solution in a quartz tube fitted with an 'exit bubbler' to exhaust liberated gases was irradiated by sixteen 21 watt lamps in a Rayonet photochemical reactor. The lamps gave a broad emission spectra between 250 - 360 nm with a maximum at 300 nm.
- (c) 'Sunlamp'. The solution in a quartz round-bottomed flask fitted with a reflux condenser was irradiated externally by a Philips 500 watt sunlamp.

SECTION ONE. EXPERIMENTS WITH 1,2,3-BENZOTHIADIAZOLE  
-1,1-DIOXIDE.

Preparation of 1,2,3-benzothiadiazoic-1,1-dioxide (4a).

The literature preparation<sup>20,99</sup> omits several details which were found necessary to secure good yields. They are incorporated into a modified preparation described below.

(a) 2-Nitrobenzenesulphinic acid.

o-Nitroaniline (13.8 g., 0.1 mole) was dissolved in a hot mixture of concentrated sulphuric acid (75 ml.), concentrated orthophosphoric acid (100 ml.) and water (50 ml.). Diazotisation at 0° was achieved by introducing aqueous (25 ml.) sodium nitrite (8.3 g., 0.12 mole) under the surface of the solution with a pipette. During the addition, the solution was vigorously stirred. The diazonium solution, saturated with sulphur dioxide, was decomposed<sup>100</sup> by a finely ground mixture of ferrous sulphate (hydrated) and freshly prepared copper powder.

One gram quantities of copper powder were prepared by adding zinc dust (1.5 g.) to a solution of copper sulphate (3.6 g.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 50 ml. water). The precipitated copper was washed with hot water and pressed dry.

When gas evolution had ceased, the solution was immediately filtered and the residue extracted with methylene chloride-ether (1 : 1). A pad of Kiesulguhr (BDH acid washed) had to be used in filtration to prevent blockage of the sinter. If filtration was delayed (e.g. overnight) lower yields of o-nitrobenzenesulphinic acid were obtained.

Purification by acidification of an aqueous solution of the ammonium salt, precipitated initially a brown amorphous material which was rejected. Addition of more concentrated hydrochloric acid to the resulting clear yellow solution gave o-nitrobenzenesulphinic acid (12.0 g., 65%) as pale yellow crystals, m.p. 113 - 115°, lit., m.p. 125°, (93.7%),  $\nu_{\text{max}}$  2400, 1530, 1115, 1075, 1045, 1000 and 840  $\text{cm}^{-1}$ .

(b) Sodium 2-aminobenzenesulphinite.

o-Nitrobenzenesulphinic acid (3.4 g., 18.0 mmol.) was used immediately when it had been prepared. It was suspended in water (20 ml.) and titrated with sodium hydroxide solution (approx. 1N) using phenolphthalein as indicator. This solution was hydrogenated using 10% palladium on charcoal (0.2 g.) as a catalyst. When the theoretical amount of hydrogen had been absorbed, the solution was filtered and evaporated to dryness on a rotary evaporator to give the sodium salt of 2-amino-benzenesulphinic acid as a white powder (3.14 g., 97%)

$\nu_{\max}$  3410, 3280, 1615, 1030 and 990  $\text{cm}^{-1}$ .

(c) 1,2,3-Benzothiadiazole-1,1-dioxide (4a)

It was essential at this stage to shield from the sunlight all solutions which might contain compound (4a)

2N Sulphuric acid (20 ml.) and glycerol (28 ml.) were stirred together at  $-20^{\circ}$ . A saturated aqueous solution of sodium 2-aminobenzenesulphinite (1.732 g., 9.7 mmol.) and sodium nitrite (0.665 g., 8.4 mmol.) was slowly added. The mixture was stirred for two hours at  $-20^{\circ}$  and then extracted at  $-6^{\circ}$  by stirring with several small volumes (20 ml.) of ether until the extracts were colourless. The combined extracts at  $-20^{\circ}$  were dried successively with calcium chloride and phosphorous pentoxide. The clear yellow solution was stored at  $-78^{\circ}$  while small volumes of it were evaporated to dryness at  $0^{\circ}$  on a rotary evaporator.

Good yields of 1,2,3-benzothiadiazole-1,1-dioxide (4a) were isolated only if care was taken to protect the reaction from sunlight at all times. Solid 1,2,3-benzothiadiazole-1,1-dioxide exploded violently on one occasion when it was exposed to bright sunlight. It was weighed damp with ether as a precaution against explosion.

$\nu_{\max}$  1605, 1490, 1285, 1180, 1170, 1150, 1120 and 890  $\text{cm}^{-1}$



5-Methyl-1,2,3-benzothiadiazole-1,1-dioxide<sup>101</sup> (4b)  
was prepared similarly:

- (a) 2-nitro-4-methylsulphinic acid(40%), m.p. 113 - 115°,  
lit.<sup>101</sup> m.p. 107 - 108°;  $\nu_{\max}$  3300 - 2200(broad OH),  
1525, 1100 and 1050  $\text{cm}^{-1}$
- (b) sodium 2-amino-4-methylsulphinite (quantitative),  
 $\nu_{\max}$  3400, 3300, 3220, 1645, 1605, 1570, 1030 and 980  $\text{cm}^{-1}$
- (c) 5-methyl-1,2,3-benzothiadiazole-1,1-dioxide (4b)  
was noticeably more sensitive to sunlight than the  
parent compound (4a). Its i.r. spectrum could not  
be recorded.

#### Preparation of platinum complexes.

The literature preparations of tetrakis(triphenylphosphine)  
platinum(0)<sup>102</sup> (46) and ethylenbis(triphenylphosphine)platinum(0)  
<sup>103</sup> (118) were followed exactly.

#### Tolanbis(triphenylphosphine)platinum(0) (36).

The triphenylphosphine-platinum complex (46) (0.5 g., 0.4 mmol.)  
was dissolved in benzene (50 ml.) and tolan (0.5 g., 2.8 mmol.)  
in benzene (25 ml.) was added. The solution was stirred at  
room temperature for 12 hr. and boiled briefly before the solvent  
was exchanged for ethanol. This was achieved by repeatedly  
reducing the volume of the solution by a half on a rotary  
evaporator and then adding the new solvent (ethanol) so that  
the solution attained its original volume. The tolan complex  
(36) crystallised as pale yellow crystals (0.25 g., 70%),  
m.p. 148 - 152°,  $\nu_{\max}$  1765, 1740, 1590, 1435 and 1095  $\text{cm}^{-1}$

An authentic sample was made by the reduction of  
cis-dichlorobis(triphenylphosphine)platinum(II) with hydrazine  
hydrate in the presence of tolan<sup>86</sup>. It had an identical i.r.  
spectrum.

#### Cyclo-octynbis(triphenylphosphine)platinum (102).

Cyclooctyne was prepared from 1,2-dibromocyclooctane  
as described by Wittig and Dorsch<sup>104</sup>. Crude cyclooctyne  
(approx. 1.0 ml.) was added to the triphenylphosphine-platinum  
complex (46) (2.0 g., 1.6 mmol.) in benzene (100 ml.).

The yellow colour slowly faded and after  $2\frac{1}{2}$  hr. the solvent was exchanged for ethanol and the cyclooctyne complex (102) separated as colourless crystals (0.933 g., 70%); and was recrystallised from benzene-ethanol, m.p.  $180 - 182^\circ$ ; (Found: C, 63.8; H, 5.1; P, 7.4.  $C_{44}H_{42}P_2Pt$  requires: C, 63.8; H, 5.1; P, 7.5.)

$\nu_{max}$  1795, 1440 and 1100  $cm^{-1}$

$\tau$  2.5 - 3.0 (multiplet) (15H);  $\tau$  7.8 (multiplet) (4H);

$\tau$  8.4 (broad singlet) (8H).

Reaction between 1,2,3-benzothiadiazole-1,1-dioxide and tetrakis(triphenylphosphine)platinum(0) in chloroform.

Compound (4a) (0.295 g., 1.75 mmol.) was added to the triphenylphosphine-platinum complex (46) (2.02 g., 1.63 mmol.) in chloroform (50 ml.) at  $-20^\circ$ . There was an immediate colour change from yellow to red. The solution was allowed to warm up to room temperature and stirred overnight. A white precipitate of cis-dichlorobis(triphenylphosphine)platinum(II) (47) was filtered off (0.461 g., 35%), recrystallised from chloroform as pale green needles m.p.  $294 - 296^\circ$ , lit.<sup>105</sup> m.p.  $310 - 312^\circ$ ; (Found: C, 54.6; H, 3.7; Cl, 7.2. Calc. for  $C_{36}H_{30}Cl_2P_2Pt$ : C, 54.7; H, 3.8; Cl, 9.0.)

$\nu_{max}$  1590, 1580, 1100 and 1000  $cm^{-1}$

The deep red filtrate was rotary evaporated to give a red oil which was triturated with petrol to remove triphenylphosphine. The brown oily residue was dissolved in benzene and on addition of petrol a yellow precipitate of a phosphine-platinum complex formed (0.286 g.), m.p.  $205 - 220^\circ$ ,  $\nu_{max}$  1590 and 1100  $cm^{-1}$ . The filtrate was chromatographed (Method A) on silica gel. Irreversible adsorption occurred as only a yellow solid (10 mg.), m.p.  $203 - 205^\circ$  was eluted off the column (20% ether in petrol). This was a phosphine-platinum complex (i.r.).

Reaction between tetrakis(triphenylphosphine)platinum(0) (46) and chloroform.

The triphenylphosphine-platinum complex (46) (1.026 g., 0.83 mmol.) was dissolved in chloroform (50 ml.) and stirred overnight at room temperature. The solution changed colour (yellow to green) and a white precipitate of cis-dichlorobis(triphenylphosphine)platinum(II) (47) separated (0.171 g., 26%), m.p. 295 - 296°; i.r. spectrum identical to that of an authentic sample<sup>105</sup>.

Reaction between tetrakis(triphenylphosphine)platinum(0) (46) and chloroform in the presence of cyclohexene.

The triphenylphosphine-platinum complex (46) (2.0 g., 1.6 mmol.) was added to a warm solution of cyclohexene in chloroform and refluxed overnight. The solution was reduced in volume on a rotary evaporator and left to crystallise. cis-Dichlorobis(triphenylphosphine)platinum(II) (47) (0.67 g., 52.5%) was filtered off. The filtrate was examined for the presence of 7-chloronorcaradiene (48)<sup>106</sup> by g.l.c. (Perkin Elmer F.11, Apiezon L, DE 102, 160°). No signal corresponding to 7-chloronorcaradiene was detected.

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Decomposition of 1,2,3-benzothiadiazole-1,1-dioxide (4a) in a cold benzene solution of tetrakis(triphenylphosphine)platinum(0) (46).

The triphenylphosphine-platinum complex (46) (2.0 g., 1.6 mmol.) in benzene (80 ml.) was cooled to 5° in a vessel protected from the light. Freshly prepared (4a) (0.30 g., 1.8 mmol., damp with ether) was added, there was an immediate colour change (yellow to red), and after a few minutes yellow crystals of benzo-3,4-diaza-2-platinothiazine-2,2-bis(triphenylphosphine)-1,1-dioxide (49a) separated (1.13 g., 79%). They were washed with dry benzene and had m.p. 177 - 179°; (Found: C, 56.7; H, 3.7; N, 3.1; P, 6.9; S, 3.6; Pt, 18.7.  $C_{42}H_{34}N_2O_2P_2PtS$  requires: C, 56.8; H, 3.8; N, 3.2; P, 7.0; S, 3.6; Pt, 22.0%);  $\nu_{max}$  1585, 1284, 1210, 1156, 1136, 1093, 950, 850, 765, 740 and 690  $cm^{-1}$ .

6-Methyl-benzo-3,4-diaza-2-platinothiazine-2,2-bis(triphenylphosphine)-1,1-dioxide (49b) was made in the same way (71%), m.p. 177 - 181° (Found: C, 57.4; H, 4.0; N, 2.8; P, 6.8; S, 3.5.  $C_{43}H_{36}N_2O_2P_2SPt$  requires: C, 57.3; H, 4.0; N, 3.1; P, 6.9; S, 3.5%);  $\tau$  2.5 - 3.0 (multiplet) (33H);  $\tau$  8.3 (singlet) (3H)

Addition of two equivalents of (4a) to a benzene solution of the triphenylphosphine-platinum complex (46) gave the azo complex (49a) in 65% yield and products due to the reaction of (4a) with triphenylphosphine.

Experiments with benzo-3,4-diaza-2-platinothiazine-2,2-bis(triphenylphosphine)-1,1-dioxide. (49a)

Thermolysis. (a) in diglyme: The azo complex (49a) (0.302 g., 0.34 mmol.) was suspended in dry diglyme (7 ml.). The temperature of the mixture was gradually increased. Gas evolution occurred mainly between 100 - 120° and was complete at 170°. The evolved gas (8.3 ml., equivalent to 0.41 mmol. nitrogen) was collected over water. The residual mixture was cooled, poured into water, extracted with ether and the ethereal solution chromatographed (Method A) on basic alumina. Biphenyl (1 mg.), identified by its i.r. spectrum was the only compound eluted from the column.

(b) in furan: The azo complex (0.385 g., 0.43 mmol.) was suspended in furan and refluxed for 24 hr.. There was no 1,4-dihydronaphthalene endoxide or  $\alpha$ -naphthol in the solution (t.l.c.). The suspension was left for three weeks and examination by preparative t.l.c. yielded a trace (ca. 1 mg.) of the endoxide (i.r.)

Photolysis. (a) in tetrahydrofuran: The azo complex (49a) (1.6 g., 1.8 mmol.) was dissolved in THF (200 ml.) and irradiated by the 'Sunlamp' method for 24 hr.. The deep red solution was evaporated and the residue chromatographed (Method A) on neutral alumina to give triphenylphosphine (0.063 g., 6.5%) and a yellow solid (0.35 g.), m.p. 253 - 254°, thought to be a dimer of bis(triphenylphosphine)platinum(0). (Found: C, 59.2; H, 4.1; M (osmometric in benzene) 1415.  $C_{36}H_{30}P_2Pt$  requires: C, 60.0; H, 4.2; M, 1458)

(b) in tetrahydrofuran containing furan: The azo complex (49a) (1.7 g., 1.9 mmol.) was dissolved in THF (250 ml.) and furan (30 ml.) was added. The solution was irradiated by the 'Sunlamp' method for 24 hr., evaporated and chromatographed (Method A) on silica gel, to give (with 10% ether in petrol) 1,4-dihydronaphthalene endoxide (52) (0.025 g., 9%), m.p. 53 - 54°, lit.<sup>107</sup> m.p. 55 - 56° and (with 50% ether in petrol)  $\alpha$ -naphthol (53) (0.042 g., 14%)(i.r.).

Irradiation by the 'Rayonet' method for 2 hr. gave  $\alpha$ -naphthol in 4% yield.

(c) in tetrahydrofuran containing tetracyclone: The azo complex (49a) (0.30 g., 0.34 mmol.) and tetracyclone (0.5 g., 1.3 mmol.) were dissolved in THF (80 ml.) and irradiated by the 'Sunlamp' method for 24 hr.. Chromatography (Method A) on basic alumina gave (with 5% ether in petrol) tetraphenylnaphthalene (54) (0.033 g., 22%).

(d) in tetrahydrofuran containing tetrakis-(triphenylphosphine)platinum(0) (46):

The azo complex (49a) (1.0 g., 1.1 mmol.) and the triphenylphosphine-platinum complex (46) (0.483 g., 0.39 mmol.) were dissolved in THF and irradiated by the 'Sunlamp' method for 24 hr.. Sulphatobis(triphenylphosphine)platinum(II) was filtered off (0.17 g., 18.5% based on the azo complex). It had an identical i.r. spectrum to that reported in the literature<sup>108</sup>. The filtrate was chromatographed (Method A) on neutral alumina. No triphenylene or biphenylene was isolated. A colourless crystalline solid (0.010 g.) was eluted with 25% ether in petrol and had m.p. 280 - 283°.(Found: C,60.6; H,4.03%); m/e 262, 202, 147.

A compound with an identical i.r. spectrum was similarly isolated when the 6-methyl-azo complex (49b) was decomposed under these conditions, m.p. 286 - 292°.

#### Reduction.

The azo complex (49a) (0.771 g., 0.87 mmol.) in THF (100 ml.) was hydrogenated with 10% palladium on charcoal (0.2 g.) as catalyst. In 5 hr. at 20°, 53 ml. (2.2 mmol.) of hydrogen was absorbed. The catalyst was filtered off to give a green solution which was chromatographed (Method A) on neutral alumina. Three major compounds were eluted using ethyl acetate in ether as eluant:

- (i) red oil (0.150 g.), difficult to characterise, attempts to crystallise from ether gave small quantities of a crystalline material m.p.  $175 - 190^{\circ}$ , i.r. absorption at  $1220 \text{ cm}^{-1}$  indicating a sulphur-oxygen linkage; this compound was not investigated further.
- (ii) pale violet solid (0.15 g., 19.5%), m.p.  $155 - 160^{\circ}$  (loss of colour at  $145^{\circ}$ )  $\nu_{\text{max}}$  1530, 1205, 1043 and  $1004 \text{ cm}^{-1}$ . Attempts to recrystallise from ethyl acetate resulted in decomposition. The physical properties were very similar to those of 3-platino-3,3-bis(triphenylphosphine)-2,1,4,5-benzoxathia-diazepine-1-oxide<sup>103</sup>: mauve crystals, m.p.  $220 - 223^{\circ}$  (loss of colour between  $120 - 130^{\circ}$ )  $\nu_{\text{max}}$  1527, 1203, 1042 and  $1014 \text{ cm}^{-1}$ .
- (iii) beige coloured amorphous solid (0.1 g.), m.p.  $135 - 150^{\circ}$ ; its i.r. spectrum indicated that it was a phosphine-platinum complex.

#### Chromatography on neutral alumina.

The azo complex (49a) (2.0 g., 2.2 mmol.) was adsorbed onto neutral alumina and chromatographed (Method A). A violet colouration appeared during the initial stages of elution (ethyl acetate - ether) and chromatography was delayed (12 hr.) to allow complete decomposition. Trace amounts of oils were isolated, but on elution with ethyl acetate three major fractions separated, exactly analogous to those found in the 'Reduction' experiment:

- (i) red oil contaminated with violet solid (0.20 g.)
- (ii) violet solid (0.60 g., 33%)
- (iii) phosphine-platinum complex (0.3 g.)

#### Decomposition of 1,2,3-benzothiadiazole-1,1-dioxide in cold benzene.

(a) with tetracyclone. Compound (4a) (0.387 g., 2.3 mmol.) was added to a cold benzene solution of tetracyclone (1.0 g., 2.6 mmol.) and stirred overnight, allowing the reaction to attain room temperature. The products were separated by

chromatography (Method A) on silica gel:

(i) tetraphenyl-naphthalene (0.320 g., 27%), recrystallised from petrol m.p. 202 - 205°, lit.<sup>22</sup> m.p. 204°

(ii) tetracyclone (0.20 g., 20%)

(b) with triphenylphosphine. Recrystallised triphenylphosphine (3.0 g., 11.4 mmol.) was dissolved in benzene (100 ml.) and compound (4a) (1.3 g., 7.75 mmol.) was added. A light brown precipitate (1.99 g.) separated, the supernatant liquor was bright red and small quantities of a gas were evolved. The filtrate was chromatographed (Method A) on neutral alumina:

(i) petrol gave recovered triphenylphosphine (0.841 g., 28%)

(ii) 10% ether in petrol gave triphenylphosphine sulphide (0.021 g., 0.9%), m.p. after sublimation 158 - 160°, lit.<sup>110</sup> m.p. 161°; (Found: C, 73.5; H, 5.0. Calc. for  $C_{18}H_{15}PS$ : C, 73.5; H, 5.1%); i.r. spectrum identical to an authentic specimen.

(iii) 50% ethyl acetate in ether gave triphenylphosphine oxide (0.514 g., 16%), recrystallised from ether-petrol m.p. 155 - 156°, lit.<sup>111</sup> m.p. 156.5 - 157°

(iv) 25% methylene chloride in ether gave a red solid (0.207 g., 10.5%), recrystallised from methylene chloride-ether m.p. 264 - 266° (lost colour ca. 160°) (Found: C, 71.9; H, 5.0; N, 5.1; S, 6.1; P, 7.1; m/e 506, 446, 432, 357, 276, 262, 249, 198, 167, 152.  $C_{30}H_{23}N_2O_2PS$  requires: C, 71.2; H, 4.6; N, 5.5; S, 6.3; P, 6.1%; M 506)  $\nu_{max}$  1580, 1240, 1120 and 870  $cm^{-1}$

The brown precipitate (1.99 g.) was dissolved in methylene chloride and chromatographed (Method A) on silica gel:

(i) A mixture of two amines (0.408 g.) was eluted from the column with 50% ether in petrol. Preparative t.l.c. failed to separate the mixture completely. Solid samples were obtained by rejecting all material in the boundary area between the two amines:

1. m.p. 148 - 153° (36 mg.); m/e 246, 181, 155  
 $\nu_{max}$  3240, 1585, 1490, 1305, 1270, 1180 and 1150  $cm^{-1}$

2. m.p. 95 - 98° (65 mg.); fluoresced under the u.v. lamp; m/e 326, 247\*, 214\*, 185\* (metastable)

168, 167, 154, 139, 140.  $\nu_{\max}$  3290, 3230, 1595  
1585, 1490, 1370, 1310, 1270, 1170, 1150, 1065,  
870  $\text{cm}^{-1}$

$\lambda_{\max}$  (ethanol) 284 nm. ( $\epsilon$  5500), 238 nm. ( $\epsilon$  9950)

(ii) ethyl acetate in ether eluted triphenylphosphine  
oxide (0.975 g., 30%)

(iii) ethanol eluted a red viscous oil which could not  
be characterised.

Thermal decomposition of 1,2,3-benzothiadiazole-1,1-dioxide (4a).

(a) in benzene and ether at 35°.

Tetrakis(triphenylphosphine)platinum(0) (46) (1.0 g.,  
0.8 mmol.) in benzene (50 ml.) and ether (100 ml.) was warmed  
to 35°. Compound (4a) (0.49 g., 2.9 mmol.) was added in three  
portions. There was a rapid evolution of gas at each addition  
and a yellow precipitate separated. After  $\frac{1}{2}$  hr. the mixture  
was allowed to cool to room temperature and stirred overnight.  
The yellow solid was filtered and identified as the azo complex  
(49a) (0.46 g., 64%). The filtrate was chromatographed (Method A)  
on basic alumina to give crude triphenylene (0.086 g., 38% based  
on compound (4a)). Recrystallisation gave triphenylene as  
colourless crystals (0.066 g.), m.p. 192 - 196°, lit.<sup>112</sup> m.p. 198°. No other hydrocarbons were obtained; no biphenylene could be detected.

An identical experiment using the 5-methyl derivative (4b)  
of 1,2,3-benzothiadiazole-1,1-dioxide (1.16 g., 6.35 mmol.) and  
the triphenylphosphine-platinum complex (46) (2.0 g., 1.6 mmol.)  
gave 2,6,11-trimethyltriphenylene (0.20 g., 35%), m.p. 132-  
133°, lit.<sup>113</sup> m.p. 128.5 - 129.5°;  $\tau$  1.6 - 1.8 and 2.6 - 2.8  
(multiplet)(33H);  $\tau$  7.5(singlet)(9H)<sup>114</sup>.

(b) in benzene at 50°.

Compound (4a) (0.25 g., 1.5 mmol.) was added to the  
triphenylphosphine-platinum complex (46) (0.5 g., 0.4 mmol.)  
in benzene (50 ml.) at 50°. The solution rapidly went brown  
in colour and a gas was evolved. After  $\frac{1}{2}$  hr. the solution  
was cooled and sulphatobis(triphenylphosphine)platinum(II)



was filtered off (0.150 g., 45%). The filtrate was chromatographed (Method A) on basic alumina. Triphenylphosphine (0.037 g.), triphenylene (0.013 g., 11.5%) and a phosphine-platinum complex (0.062 g.) were eluted off the column.

(c) with triphenylphosphine alone.

5-Methyl-1,2,3-benzothiadiazole-1,1-dioxide (4b) (0.50 g., 2.75 mmol.) was added to triphenylphosphine (0.5 g., 1.9 mmol) dissolved in ether - benzene (1:1; 100 ml.) at 40°. Chromatography (Method A) on basic alumina gave no trimethyltriphenylene or any other hydrocarbon.

(d) with a catalytic amount of tetrakis(triphenylphosphine) platinum(0) (46)

To the triphenylphosphine-platinum complex (46) (0.10 g., 0.08 mmol.) in benzene (40 ml.) and ether (40 ml.) at 35° was added compound (4a) (0.88 g., 5.2 mmol.). A precipitate (0.136 g.) rapidly appeared. The reaction mixture was cooled after ½ hr., filtered and the filtrate chromatographed (Method A) on basic alumina to give biphenylene (0.040 g., 7%) and triphenylene (0.012 g., 3%).

(e) with the azo complex (49a).

The azo complex (49a) (0.45 g., 0.509 mmol.) was dissolved in THF (50 ml.) at 50° and compound (4a) (1.04 g., 6.2 mmol.) was added. A gas was evolved and the solution darkened in colour. It was allowed to cool to room temperature after ½ hr., stirred overnight and then chromatographed (Method A) on basic alumina to give triphenylene (0.044 g., 9.3%). No other hydrocarbons were obtained.

(f) with ethylenebis(triphenylphosphine)platinum (118).

The ethylene complex (118) (1.5 g., 2 mmol.) was added to a warm (50°) mixture of benzene (30 ml.) and ether (20 ml.). Only part of the complex dissolved, but immediately after compound (4a) (1.1 g., 6.5 mmol.) was added, the solution became homogeneous, darkened rapidly in colour and a gas was simultaneously evolved. A crystalline precipitate separated

(0.635 g.), m.p.  $248 - 250^{\circ}$  (with decomposition),

$\nu_{\max}$  1680, 1285, 1210, 1155, 1100, 1080 and  $885 \text{ cm}^{-1}$ .

Treatment with hot ethanol gave colourless crystals of a

different compound, recrystallised from ethanol - benzene,

m.p.  $293 - 295^{\circ}$ , (Found: C, 52.7; H, 3.8%);  $\nu_{\max}$  1285, 1155 and

$885 \text{ cm}^{-1}$ ; m/e 635, 633, 631\*, 600, 598, 596, 536\*, 455\* (metastable).

The filtrate was chromatographed (Method A) on basic alumina to give triphenylene (0.127 g., 20%), m.p.  $197 - 198^{\circ}$ .

No other hydrocarbon was detected.

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SECTION TWO. EXPERIMENTS WITH BENZENEDIAZONIUM-2-CARBOXYLATE.

Preparation of benzenediazonium-2-carboxylate.

Stiles' method<sup>15</sup> for the preparation of benzenediazonium-2-carboxylate (2) and its derivatives was used in this work except when stated. Two different preparations of this compound were also used:

- (a) Addition of isoamyl nitrite (1 equivalent) to a mixture of anthranilic acid (1 equivalent) and trichloroacetic acid (trace) in THF gave a precipitate of benzenediazonium-2-carboxylate. This method of preparation<sup>115</sup> was found to be extremely hazardous; on one occasion the precipitate exploded while it was still suspended in solution and when it was isolated this tendency was promoted even further.
- (b) The diazonium chloride (1 equivalent) prepared by aprotic diazotisation of anthranilic acid was added to 1,2-dichloroethane at 40° followed by 1,2-epoxypropene (2 equivalents). Subsequent elevation of temperature (70°) generated benzyne without isolation of the explosive benzenediazonium-2-carboxylate<sup>18</sup>.

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Tetrakis(triphenylphosphine)platinum(0) (46) and benzenediazonium-2-carboxylate (2) in benzene.

The triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) was dissolved in benzene (60 ml.) and warmed to 50°. Benzenediazonium-2-carboxylate (2) (0.13 g., 0.88 mmol.) was added. There was a rapid gas evolution as the solid dissolved, imparting a transient reddish tinge of colour to the solution. 3-Platino-3,3-bis(triphenylphosphine)-<sup>1,3-dihydro-</sup>benzo[c]furan-1-one (78) precipitated as colourless crystals (0.38 g., 56%), recrystallised from ethyl acetate m.p. 260 - 264°; (Found: C, 61.3; H, 4.2; P, 7.8.

$C_{43}H_{34}O_2P_2Pt$  requires: C, 61.5; H, 4.1; P, 7.4%);  
 $\nu_{max}$  1655, 1305, 1295 and 1135  $cm^{-1}$

The carboxylato complex (78) (61%) was isolated if the reaction was carried out in cold benzene.

By the same method the following analogous compounds were prepared:

- 1,3-dihydro-

5-Nitro-3-platino-3,3-bis(triphenylphosphine)-benzo [c] furan-1-one.  
 (79) (60%); m.p. 285 - 287°; (Found: C, 58.2; H, 3.8; N, 1.6; P, 6.9.  $C_{43}H_{33}NO_4P_2Pt$  requires: C, 58.3; H, 3.7; N, 1.6; P, 7.0%)  
 $\nu_{max}$  1655, 1510, 1300, 1135  $cm^{-1}$   
 $\lambda_{max}$  249 nm. ( $\epsilon$  31500), shoulders at 261 and 275 nm.

- 1,3-dihydro-

6-Methyl-3-platino-3,3-bis(triphenylphosphine)-benzo [c] furan-1-one.  
 (80) (36%); m.p. 261 - 262°; (Found: C, 61.7; H, 4.4; P, 7.4.  $C_{44}H_{36}O_2P_2Pt$  requires: C, 61.9; H, 4.2; P, 7.3%)  
 $\nu_{max}$  1650 and 1305  $cm^{-1}$   
 $\lambda_{max}$  247 nm. ( $\epsilon$  29000), shoulders at 269 and 276 nm.

4-Methylanthranilic acid was prepared by a procedure analogous to that described in the literature<sup>117</sup>. The literature preparation of 4-methoxyanthranilic acid<sup>118</sup> could not be repeated.

- 1,3-dihydro-

5-Chloro-3-platino-3,3-bis(triphenylphosphine)-benzo [c] furan-1-one.  
 (82) (37%); m.p. 268 - 270°; (Found: C, 59.0; H, 3.8; Cl, 3.9; P, 7.3.  $C_{43}H_{33}ClO_2P_2Pt$  requires: C, 59.1; H, 3.8; Cl, 4.1; P, 7.1%)  
 $\nu_{max}$  1650, 1575, 1305 and 1135  $cm^{-1}$   
 $\lambda_{max}$  246 nm. ( $\epsilon$  35700), shoulders at 268 and 276 nm.

- 1,3-dihydro-

6-Chloro-3-platino-3,3-bis(triphenylphosphine)-benzo [c] furan-1-one.  
 (81) (60%); m.p. 270 - 272°; (Found: C, 58.9; H, 3.6; Cl, 3.9; P, 6.9%)  
 $\nu_{max}$  1650, 1295 and 1145  $cm^{-1}$   
 $\lambda_{max}$  247 nm. ( $\epsilon$  32300), shoulders at 268 and 276 nm.

Tetrakis(triphenylphosphine)platinum(0) (46) and benzenediazonium-2-sulphonate<sup>119</sup>.

By a procedure exactly analogous to that for the diazonium carboxylates, the sulphato complex (83) <sup>4,3-dithyano-</sup> 3-platino-3,3-bis(triphenylphosphine)-1-thia-benzo(c)furan-1,1-dioxide (91%) was prepared, m.p. 245 - 246°; (Found: C, 57.8; H, 4.0; S, 3.6; P, 7.3.  $C_{42}H_{34}O_3S_2Pt$  requires: C, 57.6; H, 3.9; S, 3.7; P, 7.1%)  
 $\nu_{max}$  1274, 1160, 1128 and 1095  $cm^{-1}$

Tetrakis(triphenylphosphine)platinum(0) (46) and benzenediazonium-2-carboxylate in 1,2-dichloroethane.

The triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) was dissolved in dry ( $P_2O_5$ ), oxygen-free, refluxing 1,2-dichloroethane and benzenediazonium-2-carboxylate (0.15 g., 1.0 mmol.) was added immediately. There was a rapid gas evolution, the solution showing a transient red colouration. After two minutes the solvent was removed on a rotary evaporator and replaced with benzene. The carboxylato complex (78) (0.604 g., 89%) was precipitated; no biphenylene or triphenylene were detected (t.l.c.).

4-Methylbenzenediazonium-2-carboxylate decomposed under these conditions gave the 6-methyl-carboxylato complex (80) in 33% yield.

When decomposed on its own under these conditions benzenediazonium-2-carboxylate gave biphenylene (5.5%) and no other hydrocarbon.

The triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) was dissolved in 1,2-dichloroethane and refluxed for 24 hr.. The solvent was exchanged for benzene and cis-dichlorobis(triphenylphosphine)platinum(II) (47) (0.364 g., 56%) was precipitated.

The carboxylato complex (78) (0.516 g.) was dissolved in 1,2-dichloroethane and refluxed for 5 hr.. It was recovered unchanged (0.354 g., 68%) by exchanging the solvent for benzene.

The triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) was added to refluxing 1,2-dichloroethane (70 ml.) and benzenediazonium-2-carboxylate (0.15 g., 1.0 mmol.) was added after ca. 5 min.. The solution was allowed to cool overnight. The carboxylato complex (78) (0.325 g., 48%) was isolated and a new compound (0.20 g.), m.p. 230 - 240°;

$\nu_{\max}$  1680, 1640, 1630, 1585 and 1330  $\text{cm}^{-1}$

This compound decomposed on recrystallisation from methylene chloride - ethyl acetate to another off white crystalline compound (0.044 g.), m.p. 274 - 275° (colour change to yellow 265 - 270°); (Found: C, 60.5; H, 4.0; P, 6.9%)

$\nu_{\max}$  1640, 1630, 1585 and 1330  $\text{cm}^{-1}$

$\lambda_{\max}$  275 nm. ( $\epsilon$  11100, assuming molecular weight 900)

268 nm. ( $\epsilon$  13000), 246 nm. ( $\epsilon$  19000)

m/e 294, 262, 250, 210, 183, 177, 152, 137, 122, 115, 108, 104, 91.

Reaction between trans-hydrido-chlorobis(triphenylphosphine) platinum(II) (85) and benzenediazonium-2-carboxylate.

Benzenediazonium-2-carboxylate (0.4 g., 2.7 mmol.) was added to a benzene solution of the hydrido-complex<sup>105</sup> (85) (1.150 g., 1.52 mmol.). A gas was evolved for 15 min. and the solution developed a faint pink colouration. After 1½ hr. the solution was reduced in volume on a rotary evaporator to yield recovered starting material (0.455 g., 40%) and three other compounds partially separated by fractional crystallisation:

(i) a trans-substituted platinum-phosphine complex

(0.05 g.), recrystallised from ethanol - methylene chloride m.p. 249 - 254°; (Found: C, 58.5; H, 4.2;

N, 0; Cl, 5.6%);  $\nu_{\max}$  1660, 1570, 1540, 1300, 1260, 1100  $\text{cm}^{-1}$

(ii) (0.285 g.), m.p. 170 - 220°, recrystallised from

hot ethanol as colourless stout needles m.p. 240 -

260° (became opaque 180 - 190°); (Found: C, 59.6;

H, 4.5; N, 0; Cl, 2.2%);  $\nu_{\max}$  3300, 1635 (shoulder 1620),

1320 and 1100  $\text{cm}^{-1}$ , (Possibly (88))

( $\text{C}_{43}\text{H}_{35}\text{ClO}_2\text{P}_2\text{Pt}$  requires: C, 59.2; H, 4.0; Cl, 4.0%)

The impurity in this material was not isolated; it had an absorption in the i.r. spectrum at 2240 and 2260  $\text{cm}^{-1}$

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Reaction between phenylacetylene and benzyne.

Benzenediazonium-2-carboxylate contaminated with silver ions was prepared by Stiles' method from anthranilic acid (2.8 g., 2 mmol.). Addition to phenylacetylene (7 ml., 6.56 g., 6.4 mmol.) in refluxing 1,2-dichloroethane (100 ml.) gave phenanthrene (91) (0.130 g., 3.6% based on anthranilic acid) and 5,6-diphenyldibenzocyclooctatetraene (92) (0.493 g., 13.7%) m.p. 196°, lit.<sup>51</sup> m.p. 195.5 - 196°. They were isolated by chromatography (Method A) on basic alumina after removing excess phenylacetylene by distillation under reduced pressure.

Benzenediazonium-2-carboxylate free from silver ions was generated in situ from anthranilic acid (2.74 g., 2 mmol.) as follows. The diazonium chloride (prepared by aprotic diazotisation) was added to phenylacetylene (10 ml., 9.37 g., 9.2 mmol.) and 1,2-epoxypropene (3 ml., 2.49 g., 4.2 mmol.) in 1,2-dichloroethane (100 ml.) at 40°. The temperature of the solution was increased until gas evolution started (70°). When the reaction was completed, phenanthrene (91) (0.520 g., 14.6%) and 5,6-diphenyldibenzocyclooctatetraene (92) (0.87 g., 24%) were isolated as before.

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SECTION THREE. EXPERIMENTS WITH 1-AMINO BENZOTRIAZOLE.Preparation of 1-aminobenzotriazole.

1-Aminobenzotriazole (5) was prepared<sup>22</sup> in a three stage synthesis from o-nitroaniline. It was recrystallised from benzene - hexane and had m.p. 83 - 84°, lit.<sup>22</sup> m.p. 84°.

Preparation of 1-(toluene-p-sulphonamido)benzotriazole. (99)

1-Aminobenzotriazole (5) (3.03 g., 2.26 mmol.) and recrystallised toluene-p-sulphonyl chloride (6.3 g., 3.3 mmol.) were dissolved in dry pyridine (30 ml.) and refluxed for  $\frac{1}{2}$  hr.. The mixture was poured into water (30 ml.) and the precipitate filtered off and recrystallised from hot ethanol as colourless prisms of 1-(N,N-di(toluene-p-sulphonyl))aminobenzotriazole (100) (1.7 g., 23%), m.p. 165 - 165.5°; (Found: C, 54.4; H, 4.3; N, 12.4.  $C_{20}H_{18}N_4O_2S$  requires: C, 54.3; H, 4.1; N, 12.7%);  $\nu_{max}$  1595, 1375, 1180, 1040, 1080, 890, 850, 815, and 745  $cm^{-1}$

The filtrate on acidification with hydrochloric acid gave 1-(toluene-p-sulphonamido)benzotriazole (99) (2.2 g., 34% based on 1-aminobenzotriazole), recrystallised from ethanol - water as colourless crystals m.p. 181 - 182°; (Found: C, 54.6; H, 3.8; N, 19.3.  $C_{13}H_{12}N_4O_2S$  requires: C, 54.3; H, 4.2; N, 19.4; M 288); m/e 288, 155, 133.

$\nu_{max}$  2900(broad), 1600, 1360, 1160, 1085  $cm^{-1}$

Compound (100) (1.7 g.) was hydrolysed by refluxing sodium ethoxide in ethanol (sodium 1.0 g., in ethanol 20 ml.). After 15 min. the ethanol was removed and the residue dissolved in the minimum of water. Filtration, followed by acidification gave compound (99) (0.802 g., 73%).

Better overall yields of (99) were achieved if (100) was prepared as an intermediate. Thus 1-aminobenzotriazole (8.0 g., 6 mmol.) and toluene-p-sulphonyl chloride (23.0 g. 12 mmol.) reacted as before in pyridine gave compound (99)



(13.6 g., 66%). Compound (100) was not purified before hydrolysis.

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The sodium and lithium salts of 1-(toluene-p-sulphonamido)-benzotriazole. (98a) (98b)

Preparation.

Sodium N(1-benzotriazolyl)toluene-p-sulphonamide (98a) was prepared by the addition of one equivalent of sodium ethoxide to a 'super' dry ethanol solution of compound (99)  $\nu_{\max}$  3450 and 1650  $\text{cm}^{-1}$  (broad, due to absorbed water), 1275, 1240, 1140, 1085, 945 and 915  $\text{cm}^{-1}$

Lithium N(1-benzotriazolyl)toluene-p-sulphonamide (98b) was prepared by addition of one equivalent of butyllithium to a solution of compound (99) in THF at room temperature. It had an identical i.r. spectrum to that of the sodium salt.

(a) Photolysis of the sodium salt. (98a)

The sodium salt (98a) (0.47 g.) was dissolved in dry dimethylsulphoxide (10 ml.) and furan (10 ml.) was added. The solution was irradiated by the 'Rayonet' method for 15 hr.; the resulting brown solution was poured into water (50 ml.) acidified with dilute hydrochloric acid and ether extracted. Recovered compound (99) (0.125 g., 29%) and  $\alpha$ -naphthol (0.04 g., 18%) were separated by fractional crystallisation. The 3,5-dinitrobenzoyl derivative of the isolated  $\alpha$ -naphthol was prepared (0.020 g.), m.p. 180 - 190°, lit. m.p. 217°; it had an identical i.r. spectrum to that of an authentic specimen.

A suspension of the sodium salt (98a) (0.4 g.) in benzene (40 ml.) and furan (10 ml.) irradiated under the same conditions gave no  $\alpha$ -naphthol or 1,4-naphthalene endoxide.

(b) Photolysis of the lithium salt. (98b)

(i) Furan (10 ml.) was added to the lithium salt (98b) (0.586 g.) in THF and irradiated by the 'Rayonet' method for 20 hr.. The solvent was removed by rotary evaporation and the residue hydrolysed by a refluxing solution of concentrated hydrochloric acid (5 ml.) in methanol (10 ml.) for 5 min..

$\alpha$ -Naphthol (0.150 g., 52%) was isolated by base extraction.

(ii) The lithium salt (1.0 g., 3.4 mmol.) and tetracyclone (2.5 g., 6.5 mmol.) were dissolved in THF (100 ml.) and irradiated by the 'Hanovia' method for 20 hr.. The reaction mixture was poured into a large volume of water and extracted with ether. Chromatography (Method A) of the ether extracts on basic alumina gave tetraphenylnaphthalene (0.33 g., 22%). The aqueous layer was acidified (hydrochloric acid) and ether extracted to give an oil (0.53 g.) which was not characterised.

An identical experiment using furan (10 ml.) as the benzyne trap gave 1,4-naphthalene endoxide (0.087 g., 17%) and recovered compound (99) (0.225 g., 23%).

(iii) The lithium salt (98b) (0.6 g., 2 mmol.) and the triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) in THF were irradiated by the 'Rayonet' method for 20 hr.. The solvent was removed and the brown oil triturated with ether to remove triphenylphosphine. Crystallisation did not occur. The mixture was chromatographed on neutral alumina prepared by the addition of 10% (by weight) of 20% acetic acid to basic alumina. Elution with benzene gave triphenylphosphine (0.041 g.), triphenylphosphine oxide (0.416 g., 49%) and an oil (0.175 g.) containing phosphine-platinum species(i.r.)

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Chromatography of 1-(toluene-p-sulphonamido)benzotriazole. (99)

Compound (99) (0.747 g., 2.6 mmol.) and tetracyclone (1.47 g., 3.8 mmol.) were dissolved in benzene - ether and the solution shaken with basic alumina (10 g.) for two days. The mixture was separated by chromatography (Method A) on basic alumina; no tetraphenyl-naphthalene was detected in any of the fractions (t.l.c.). Tetracyclone (1.16 g., 80%) was recovered but not compound (99), even with 100% ethanol.

Iminophosphorane of 1-aminobenzotriazole.Preparation.

Bromine (2.4 g., 0.77 ml., 15 mmol.) in benzene (10 ml.) was added to recrystallised triphenylphosphine (3.9 g., 15 mmol.) in cold benzene (50 ml.). Triethylamine (3.0 g., 4.1 ml., 29.6 mmol.) was added to the resulting suspension of triphenylphosphine dibromide in benzene, followed by 1-amino-benzotriazole (2.0 g., 15 mmol.) in benzene. The solution was refluxed for 1 hr. and filtered. The precipitate was a mixture of triethylamine hydrobromide and the iminophosphorane (103). It was separated by treatment with aqueous sodium carbonate until basic, followed by extraction with methylene chloride - benzene (1:1) to give the iminophosphorane (103) (1.8 g.). The filtrate gave pure iminophosphorane (103) (2.93 g.) on evaporation. Total yield of (1-benzotriazolyl)-iminotriphenylphosphorane (103) (4.7 g., 80%); recrystallised from benzene - hexane m.p. 172 - 174°, from ethyl acetate m.p. 174 - 175°; (Found: C, 73.2; H, 4.7; N, 14.2.  $C_{24}H_{19}N_4P$  requires: C, 73.2; H, 4.8; N, 14.2%; M 394).

Molecular weight (osmometric in benzene), 7.6 g./litre 434; 14.9 g./litre 412.

m/e 394, 366, 338, 276, 262, 183, 153, 131.

$\nu_{max}$  1440, 1435, 1410, 1215, 1180, 1120, 1107, 1090  
975 and 700 - 800  $cm^{-1}$  (complex)

$\lambda_{max}$  312 nm. ( $\epsilon$  5150); 267.5 nm. ( $\epsilon$  7900) shoulders at  
261, 275, 283.5 nm.

Photolysis of (1-benzotriazolyl)iminotriphenylphosphorane. (103)

(a) 'Rayonet' method.

(i) The iminophosphorane (103) (0.494 g.) in THF (100 ml.) and furan (10 ml.) were irradiated for 20 hr. and the reaction mixture then chromatographed (Method A) on silica gel to yield a mixture of 1,4-naphthalene endoxide and  $\alpha$ -naphthol (0.016 g., 9%) which was not separated.

(ii) The iminophosphorane (103) (0.492 g., 1.25 mmol.) and tetracyclone (0.7 g., 1.8 mmol.) in benzene (100 ml.) were irradiated for 20 hr. and the reaction mixture chromatographed (Method A) on basic alumina to yield triphenylphosphine (0.026 g., 7.6%); tetraphenylnaphthalene (0.055 g., 10%); tetracyclone (0.556 g., 80%) and the iminophosphorane (103) (0.10 g., 20%)

(iii) The iminophosphorane (103) (0.635 g., 1.6 mmol.) and the triphenylphosphine-platinum complex (46) (0.70 g., 0.56 mmol.) in benzene (100 ml.) were irradiated for 20 hr.. The resulting red solution was reduced in volume and the solvent exchanged for ethanol. A precipitate (0.10 g.) of a phosphine-platinum complex (i.r.) separated. The filtrate was chromatographed (Method A) on basic alumina, no hydrocarbon was eluted, no biphenylene or triphenylene was detected (t.l.c.).

(b) 'Sunlamp' method.

(i) The iminophosphorane (103) (0.507 g., 1.28 mmol.) and tetracyclone (0.612 g., 1.6 mmol.) in benzene were irradiated for 20 hr. and the products separated by chromatography (Method A) on basic alumina. Triphenylphosphine (0.137 g., 40%); tetraphenylnaphthalene (0.126 g., 23%); tetracyclone (0.436 g., 70%); trace amounts of 1-aminobenzotriazole, and triphenylphosphine oxide (0.132 g., 37%) were eluted and characterised by i.r. spectra.

(ii) The iminophosphorane (103) (0.574 g., 1.45 mmol.) was dissolved in benzene (30 ml.) and irradiated for 20 hr., the products were separated as before. Biphenyl (0.031 g., 13% assuming solvent involved); triphenylphosphine (0.250 g., 65%) and triphenylphosphine oxide (0.10 g., 25%) were eluted and characterised by i.r. spectra.

(iii) The iminophosphorane (103) (0.531 g., 1.35 mmol.) and the triphenylphosphine-platinum complex (46) (0.59 g., 0.47 mmol.) in benzene (30 ml.) were irradiated for 20 hr.. The solution was reduced in volume on a rotary evaporator and left to crystallise. Only triphenylphosphine oxide (0.05 g.) separated. The filtrate was evaporated to dryness, dissolved in methylene chloride and its solution i.r. spectrum examined. There were no absorptions in the range 2900 - 1600  $\text{cm}^{-1}$ .

(c) 'Hanovia' method.

(i) The iminophosphorane (103) (0.57 g., 1.45 mmol.) and tetracyclone (0.624 g., 1.6 mmol.) in benzene were irradiated for 12 hr.; the products were separated by chromatography (Method A) on basic alumina. Biphenyl (0.007 g., 3%); tetraphenylnaphthalene (0.153 g., 25%); triphenylphosphine (0.10 g., 26%); 2,3,4,5-tetraphenylcyclopentenone (0.060 g., 9.5%), m.p. 150 - 155°, lit.<sup>120</sup> m.p. 160 - 162°; tetracyclone (0.30 g., 48%); a brown solid derived from tetracyclone (0.11 g.),  $\nu_{\text{max}}$  1700 and 1120  $\text{cm}^{-1}$ ; and triphenylphosphine oxide (0.25 g., 66%) were isolated.

(ii) The iminophosphorane (103) (0.543 g., 1.38 mmol.) and tetracyclone (0.601 g., 1.56 mmol.) in THF were irradiated for 12 hr. and the products then separated by chromatography (Method A) on basic alumina. Tetraphenylnaphthalene (0.08 g., 13.6%); a dark oil showing a carbonyl absorption in the i.r. spectrum, presumably derived from tetracyclone (0.315 g.); and an oil (0.40 g.) containing triphenylphosphine oxide were eluted.

(iii) The iminophosphorane (103) (0.7 g., 1.8 mmol.) and furan (20 ml.) in benzene (80 ml.) were irradiated for 20 hr.; the products were separated by chromatography (Method A) on basic alumina. Triphenylphosphine (0.10 g., 21%); 1,4-naphthalene endoxide (0.042 g., 16.5%) were eluted and identified by i.r. spectra.

(iv) The iminophosphorane (103) (0.573 g., 1.46 mmol.) and anthracene (0.514 g., 2.9 mmol.) in benzene were irradiated for 12 hr.. Dianthrane (0.344 g., 67%) crystallised out of

the solution, the filtrate was chromatographed (Method A) on basic alumina. Biphenyl (0.026 g., 11%) and anthracene (0.02 g.) were eluted; the column was terminated with 100% ether as eluant.

(v) The iminophosphorane (103) (0.516 g., 1.3 mmol.) in benzene was irradiated for 12 hr. and the products separated by chromatography (Method A) on basic alumina. Biphenyl (0.04 g., 18.5%); triphenylphosphine (0.046 g., 13.5%); triphenylphosphine oxide (0.241 g., 71%) were eluted and characterised by i.r. spectra.

(vi) The iminophosphorane (103) (0.550 g., 1.4 mmol.) in toluene was irradiated for 22 hr. and the products separated by chromatography (Method A) on basic alumina. No biphenyl was detected (t.l.c.) but a colourless oil (0.055 g.) which was a mixture of triphenylphosphine and a hydrocarbon was isolated. It was partially separated into an oil (0.025 g.) by sublimation,  $\nu_{\max}$  1495, 1455  $\text{cm}^{-1}$ ;  $\tau$  2.5 - 3.5 (multiplet) (12 units),  $\tau$  7.15 (singlet) (0.8 units),  $\tau$  7.62 (singlet) (1.2 units),  $\tau$  8.7 (multiplet) (8.0 units).

(vii) Triphenylphosphine (0.695 g.) was irradiated in benzene (100 ml.) for 12 hr. and the products separated by chromatography (Method A) on basic alumina. A mixture (0.045 g.) of biphenyl and a phosphine oxide; and the phosphine oxide (0.052 g.),  $\nu_{\max}$  1440, 1195, 1125 and 945  $\text{cm}^{-1}$ , were eluted with petrol.

The mixture was separated by rechromatography (Method A) on basic alumina and gave pure (one spot on t.l.c.) biphenyl (0.015 g., 3.7%)

#### Photolysis of tolan-bis(triphenylphosphine)platinum. (36)

The tolan complex (36) (0.720 g.) in benzene (100 ml.) was irradiated by the 'Hanovia' method for 12 hr. and recovered by crystallisation (0.33 g., 45%). The filtrate was chromatographed (Method B) on basic alumina and gave tolan (0.023 g.) and the tolan complex (36) (0.03 g.).

Reaction of (1-benzotriazolyl)iminotriphenylphosphorane (103)  
with carbon dioxide.

(i) The iminophosphorane (103) (1.5 g., 3.8 mmol.) was dissolved in chloroform (50 ml.) at room temperature and dry carbon dioxide was passed through the solution. Solution i.r. spectra (chloroform) revealed the formation of an absorption at  $2330\text{ cm.}^{-1}$  which also occurred when carbon dioxide was passed through chloroform only. To half of the solution was added *p*-toluidine, evaporation and dilution with ether precipitated the iminophosphorane (103). The other half was evaporated and the solvent exchanged for benzene, a colourless crystalline sample of compound (112) separated, contaminated by a compound which had an absorption in the i.r. spectrum at  $1660\text{ cm.}^{-1}$

(ii) The iminophosphorane (103) (1.1 g., 2.8 mmol.) and tetracyclone (1.2 g., 3.1 mmol.) in benzene (150 ml.) were irradiated by the 'Hanovia' method for 4 hr. while a stream of dry carbon dioxide was bubbled through the solution. A colourless crystalline solid, compound (112) (0.180 g., 24%) separated overnight. It was insoluble in benzene, ether and ethyl acetate but soluble in chloroform to give a lime green solution. Recrystallised from benzene - chloroform as colourless needles m.p.  $203 - 204^{\circ}$ ; (Found: C, 66.2; H, 4.1; N, 24.7.  $\text{C}_{30}\text{H}_{25}\text{N}_8\text{P}$  requires: C, 68.5; H, 4.4; N, 21.4; M 526)  $\nu_{\text{max}}$  1600, 1585, 1440, 1300, 1275, 1110 and  $1035\text{ cm.}^{-1}$

$\lambda_{\text{max}}$  (assuming M = 526), 295 nm. ( $\epsilon$  10300), 276 nm. ( $\epsilon$  13300), 263 nm. (17000)

m/e at 70 ev., 366, 337, 277, 262, 202, 183, 152, 153, 131, 119, 108, 91.

at 10 ev., mass peak 366 increased in intensity.

Osmometric molecular weight in chloroform; 10.1 g./litre, 560; 21.7 g./litre, 620.

The filtrate was chromatographed (Method A) on basic alumina. Triphenylphosphine (0.05 g., 6.8%); tetraphenyl-naphthalene (0.10 g., 8.3%); tetracyclone (0.84 g., 70%);

the iminophosphorane (103) (0.11 g., 10%); triphenylphosphine oxide (0.424 g., 55%); and a mixture (0.10 g.) of triphenylphosphine oxide and 1-aminobenzotriazole, were eluted and identified by i.r. spectra.

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Reaction of (1-benzotriazolyl)iminotriphenylphosphorane (103) with nitrous oxide.

(i) Dry nitrous oxide was passed through a solution of the iminophosphorane (103) (1.0 g., 2.54 mmol.) in chloroform. Solution spectra revealed the appearance of an absorption at  $2210\text{ cm.}^{-1}$  which was also observed when nitrous oxide was passed through chloroform only. After  $1\frac{3}{4}$  hr. the solvent was exchanged for benzene and evaporated to small bulk when the iminophosphorane (103) (0.824 g., 82%) was recovered.

(ii) The iminophosphorane (103) (0.985 g., 2.5 mmol.) and tetracyclone (1.0 g., 2.6 mmol.) in benzene (150 ml.) were irradiated by the 'Hanovia' method for 8 hr. while a stream of dry nitrous oxide was bubbled through the solution. No precipitate separated. The solution was chromatographed (Method A) on basic alumina. Triphenylphosphine (0.08 g., 11%); tetraphenyl-naphthalene (0.120 g., 11%); tetracyclone (0.73 g., 73%); the iminophosphorane (103) (0.43 g., 44%); triphenylphosphine oxide (0.10 g., 14.5%); a mixture (0.172 g.) of triphenylphosphine oxide and 1-aminobenzotriazole; and 1-aminobenzotriazole (0.037 g., 11%) were eluted and identified by i.r. spectra.

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Pyrolysis of (1-benzotriazolyl)iminotriphenylphosphorane. (103)

(a) in dimethylsulphoxide. The iminophosphorane (103) (0.3 g.) in DMSO (5 ml.) was heated at  $180^{\circ}$  for 1 hr.. The pale yellow solution was poured into water (50 ml.) and extracted with chloroform to give a brown oil which gave the iminophosphorane (103) (0.150 g., 50%) on trituration with ether.



(b) with tetracyclone. The iminophosphorane (103) (0.30 g., 0.76 mmol.) and tetracyclone (0.60 g., 1.55 mmol.) were dissolved in benzene and evaporated to dryness. The mixture was heated at  $240^{\circ}$  for  $\frac{1}{2}$  hr. and a gas was evolved. The reaction mixture was chromatographed (Method A) on basic alumina and gave tetracyclone (0.40 g., 66%); crude triphenylphosphine oxide (0.22 g.) and a black oil (0.060 g.). No tetraphenyl-naphthalene was detected in any of the fractions.

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#### Oxidation of 1-aminobenzotriazole.

(a) using tetrakis(triphenylphosphine)platinum(0) (46)  
as the benzyne trap.

(i) To 1-aminobenzotriazole (0.054 g., 0.4 mmol.), the triphenylphosphine-platinum complex (46) (0.5 g., 0.4 mmol.) and excess potassium carbonate in cold benzene (40 ml.) was added lead tetraacetate (LTA). A gas was evolved and the original yellow solution went brown in colour. The lead and potassium salts were filtered off and the filtrate evaporated to dryness to yield a partially crystalline oil. This residue was dissolved in benzene and crystallisation effected by adding petrol. cis-Diacetatobis(triphenylphosphine)platinum(II) separated, m.p.  $185 - 195^{\circ}$ ; (Found: C, 56.8; H, 4.3; P, 7.2.  $C_{40}H_{36}O_4P_2Pt$  requires: C, 57.3; H, 4.3; P, 7.4%);  $\tau$  8.6 (singlet) (6H);  $\nu_{max}$  1635, 1315 and 1100  $cm^{-1}$

The filtrate contained a trace of biphenylene (t.l.c.)

(ii) Anhydrous potassium carbonate (2.0 g., 14.5 mmol.) was suspended in a benzene (50 ml.) solution of the triphenylphosphine-platinum complex (46) (1.7 g., 1.35 mmol.) and 1-aminobenzotriazole (0.36 g., 2.68 mmol.). A gas was evolved as LTA (1.0 g., 2.25 mmol.) was added in small portions. The reaction mixture was stirred for 15 min. until there was no gas evolution, and then tetracyclone (0.8 g., 2.1 mmol.) in benzene (20 ml.) was added and the solution refluxed for 15 min. The concentrated reaction mixture was chromatographed (Method B) on basic alumina using benzene as eluant. Recovered tetracyclone

(0.76 g., 95%); triphenylphosphine (0.22 g., 15%); a brown oil (0.567 g.) containing triphenylphosphine oxide (0.280 g., 18.5%) and carbonatobis(triphenylphosphine)platinum(II) (0.29 g., 27%) were isolated but no biphenylene, triphenylene, or tetraphenyl-naphthalene was detected in any of the fractions.

(b) using ethylenebis(triphenylphosphine)platinum(0) (118)  
as a benzyne trap.

(i) The ethylene complex (118) (1.0 g., 1.35 mmol.) and 1-aminobenzotriazole (0.36 g., 2.7 mmol.) were dissolved in cold benzene (50 ml.) and LTA (1.0 g., 2.25 mmol.) added in small portions. After 15 min. (no gas evolution) the precipitate of lead diacetate (0.684 g., 93%) was filtered off and the filtrate left to crystallise overnight. No crystals appeared and so the filtrate was chromatographed (Method B) on basic alumina using benzene - ethanol as eluant. Carbonatobis(triphenylphosphine)platinum(II) (0.250 g., 24%), m.p. 203 - 204°, lit.<sup>121</sup> n.p. 202 - 205°,  $\nu_{\max}$  1680, 1100  $\text{cm}^{-1}$ ; a brown oil (0.250 g.) containing triphenylphosphine oxide, 1-amino-benzotriazole and a phosphine-platinum complex m.p. 177 - 180° (dec.)  $\nu_{\max}$  1100  $\text{cm}^{-1}$  were isolated, but no triphenylene or biphenylene was detected (t.l.c.) in any of the fractions.

(ii) To a suspension of anhydrous potassium carbonate (2.0 g., 14.5 mmol.) in a solution of the ethylene complex (118) (1.0 g., 1.35 mmol.) and 1-aminobenzotriazole (0.36 g., 2.7 mmol.) in cold benzene (50 ml.) was added LTA (1.0 g., 2.25 mmol.). The potassium carbonate coagulated towards the end of the addition. After 15 min. the solution was refluxed (15 min.), filtered and chromatographed (Method A) on basic alumina. A trace (less than 1 mg.) of biphenylene; triphenylene (0.006 g. 3.5%); and a yellow phosphine-platinum complex (0.015 g.) m.p. 200 - 202°(dec.) were eluted.

(iii) To a vigorously stirred suspension of potassium carbonate (2.0 g., 14.5 mmol.) in a solution of the ethylene complex (118) (1.0 g., 1.35 mmol.) and 1-aminobenzotriazole (0.36 g., 2.7 mmol.) in cold benzene (50 ml.) was added LTA (1.0 g., 2.25 mmol.). After 10 min. when no more gas was evolved, tetracyclone (0.8 g., 2.1 mmol.) in benzene (20 ml.)

was added and the solution refluxed for 15 min. and then left to stir at room temperature overnight. The lead and potassium salts were filtered off and the filtrate chromatographed (Method B) on basic alumina using benzene as eluant. Rechromatography (Method A) on basic alumina was necessary to separate tetracyclone and triphenylene. Recovered tetracyclone (0.457 g., 57%); triphenylene (0.045 g., 25% based on oxidised 1-aminobenzotriazole) m.p. 197 - 198°; and tetracyclonebis(triphenylphosphine)-platinum (119), recrystallised from benzene - ethanol as red prisms m.p. 170°, (Found: C, 71.4; H, 4.8; P, 5.96.  $C_{65}H_{50}OP_2Pt$  requires: C, 70.7; H, 4.5; P, 5.62; M 1103) Osmometric molecular weight in benzene: 15.2 g./litre, 981; 18.5 g./litre, 974. m/e 384, 356, 262, 183, 178.

$\nu_{max}$  1660  $cm^{-1}$

and also a phosphine-platinum complex m.p. 162 - 165° (i.r.) were isolated. 1-Aminobenzotriazole but no biphenylene or tetraphenylnaphthalene were detected (t.l.c.).

The ethylene complex (118) (0.832 g., 1.08 mmol.) and tetracyclone (0.9 g., 2.35 mmol.) were dissolved in benzene and heated at 60° for 15 min.. The reaction mixture was chromatographed (Method B) on basic alumina using benzene as eluant. Recovered tetracyclone (0.566 g., 64%) and tetracyclonebis(triphenylphosphine)platinum (119) (0.54 g., 43%) were isolated.

(iv) The experimental details were identical to those reported in (iii) except that 5-methyl-1-aminobenzotriazole (0.36 g., 2.43 mmol.) was used. Recovered tetracyclone (0.546 g., 68%); 2,6,11-trimethyltriphenylene (0.08 g., 13%), m.p. 132 - 133°; 6-methyl-1,2,3,4-tetraphenylnaphthalene (0.010 g., 2%), m.p. 195 - 220°, lit.<sup>122</sup> m.p. 222 - 223°; tetracyclonebis(triphenylphosphine)platinum (119) (0.30 g., 21%); a brown oil (0.50 g.) from which was isolated a phosphine-platinum complex (i.r.), m.p. 167 - 170°; 5-methyl-1-aminobenzotriazole was detected (t.l.c.) in the filtrates; carbonatobis(triphenylphosphine)platinum(II) (0.132 g., 12%) were isolated.

(v) To a vigorously stirred suspension of anhydrous potassium carbonate (2.0 g., 14.5 mmol.) in a solution of the ethylene complex (118) (1.0 g., 1.35 mmol.) and 1-amino-benzotriazole (0.36 g., 2.7 mmol.) in cold benzene was added LTA (1.0 g., 2.25 mmol.). After 15 min., triphenylene was detected (t.l.c.), triphenylphosphine (0.71 g., 0.27 mmol.) was added and the reaction mixture refluxed for 15 min.. The solution was left overnight, filtered and chromatographed (Method A) on basic alumina. Recovered triphenylphosphine (0.435 g., 60%) and triphenylene (0.004 g., 2%) were isolated.

(vi) The experimental details were identical to those reported in (v) except that bromine (0.2 ml., 3.9 mmol.) instead of triphenylphosphine was added. Chromatography (Method A) on basic alumina gave o-dibromobenzene (0.092 g., 84% based on excess 1-aminobenzotriazole); an oil (0.013 g.) which was a mixture of four compounds (t.l.c.):  
n/c 387 (3Br), 310 (2Br), 232 (1Br);  
and triphenylene (0.004 g., 2%) were isolated.

Addition of bromine (0.25 ml., 4.9 mmol.) to 1-amino-benzotriazole (0.2 g., 1.48 mmol.) and potassium carbonate (2.0 g.) gave after chromatography (Method A) using petrol as eluant, o-dibromobenzene (0.161 g., 45%) only.

(vii) To a vigorously stirred suspension of potassium carbonate (1.0 g., 7.25 mmol.) in a solution of the ethylene complex (118) (1.0 g., 1.35 mmol.) and 1-aminobenzotriazole (0.36 g., 2.7 mmol.) in dry methylene chloride at room temperature was added LTA (1.0 g., 2.25 mmol.) in small portions. There was a very vigorous gas evolution and the solution became brown/red in colour. A solution i.r. spectrum was taken at this point,  $\nu_{\max}$  1710  $\text{cm}^{-1}$ , shoulder at 1755  $\text{cm}^{-1}$ . After 15 min., tetracyclone (0.8 g., 2.1 mmol.) was added, the solution was refluxed (15 min.) and left at room temperature overnight and then chromatographed (Method B) on basic alumina. Tetraphenyl-naphthalene (0.005 g., 0.5%); triphenylene (0.009 g., 4.5%); tetracyclone (0.36 g., 45%) and a brown oil which could not be characterised were eluted with benzene - ethanol mixtures.

(viii) Conditions identical to those in (vii) were employed except that benzene was used as a solvent. Before tetracyclone was added efforts were made to encourage crystallisation of the filtrate by reducing the volume of the solution on a rotary evaporator, but crystallisation did not occur. The residue of lead and potassium salts was refluxed in benzene and the solvent examined on t.l.c.. No hydrocarbons were detected.

As crystallisation had not occurred, the filtrate was divided and one half evaporated to dryness and triturated with ether to yield diacetatobis(triphenylphosphine)platinum(II) (0.15 g., 13.7%). The filtrates were combined with the other half of the solution, refluxed with tetracyclone for  $1\frac{1}{2}$  hr. and chromatographed (Method A) on basic alumina to yield triphenylene (0.013 g., 6%).

(c) using tolanbis(triphenylphosphine)platinum as a benzyne trap.

LTA (0.5 g., 1.1 mmol.) was added in small portions to a benzene (20 ml.) solution of 1-aminobenzotriazole (0.144 g., 1.08 mmol.) and the tolan complex (36) (0.9 g., 1.0 mmol.). After gas evolution had ceased, the precipitate of lead diacetate (0.25 g., 70%) was filtered off and the filtrate reduced in volume and left to crystallise to yield the tolan complex (36) (0.2 g., 22%). The filtrate was chromatographed (Method A) on basic alumina to yield tolan (0.065 g., 36%) and the tolan complex (36) (0.10 g., 11%). No triphenylene or biphenylene was detected (t.l.c.) in any of the fractions.

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Attempted oxidation of 1-aminobenzotriazole by oxygenbis(triphenylphosphine)platinum.

1-Aminobenzotriazole (0.11 g., 0.82 mmol.) was added to a solution of oxygenbis(triphenylphosphine)platinum<sup>103,130</sup> (117) (0.3 g., 0.4 mmol.) in benzene (50 ml.). After refluxing for 1 hr. the yellow solution became black in colour. It was reduced in volume on a rotary evaporator but no crystals appeared on standing. The reaction mixture was chromatographed on Fluorsil (BDH). Trace amounts of unidentified oils and recovered 1-aminobenzotriazole were eluted and triphenylphosphine oxide (0.072 g.) was isolated.

1-Aminobenzotriazole (0.107 g., 0.8 mmol.) was added to a benzene solution of the triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.). Dry oxygen was passed through the solution at room temperature for 3 hr.. The solution was left standing for 60 hr. and a precipitate (0.04 g.) of carbonato-bis(triphenylphosphine)platinum(II)<sup>121,131</sup> was isolated. Addition of ethyl acetate followed by reduction in volume on a rotary evaporator precipitated a dark brown solid (0.125 g.), m.p. 250 -280° after reprecipitation from ethyl acetate - methylene chloride. Its i.r. spectrum indicated a phosphine-platinum complex. Chromatography of the filtrates on basic alumina gave oils (traces) and triphenylphosphine oxide (0.477 g., 53%).

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Oxidation of 1-aminobenzotriazole with silver (II) oxide.

Oxygenbis(triphenylphosphine)platinum (117) (0.533 g., 0.71 mmol.) was dissolved in benzene (50 ml.) at 45°. Silver (II) oxide<sup>132</sup> (7.0 g., 56.5 mmol.) was added. 1-Aminobenzotriazole (0.30 g., 2.24 mmol.) in ether was added dropwise. The mixture was heated at 60° for 20 min. and then the silver residues removed by filtration. A brown solid (0.13 g.) was isolated from the filtrate by dilution with ether. Its i.r. spectrum was poorly resolved and it was rejected. The filtrates were chromatographed (Method A) on basic alumina to yield biphenyl (0.012 g., 7%) only.

Silver (II) oxide (6.643 g., 53.5 mmol.) was heated at 70° in benzene (50 ml.) and an ether solution of 1-amino-benzotriazole (0.3 g., 2.24 mmol.) was added dropwise. The silver residues were filtered off and treated with 50% nitric acid. Ether extraction gave a trace (~0.1 mg.) of a brown oil.

The filtrate was chromatographed as before to yield biphenyl (0.01 g., 6%) only.

Attempted preparation of the dimethylsulphoxide and dimethylsulphide adducts of 1-aminobenzotriazole.

(a) Dimethylsulphoxide.

Bromine (0.4 ml., 7.8 mmol.) in benzene (5 ml.) was added to dimethylsulphoxide (0.54 ml., 7.5 mmol.) in benzene. A red oil separated and a white gas was evolved when triethylamine (2.1 ml., 15 mmol.) was added. 1-Aminobenzotriazole (1.0 g., 7.8 mmol.) in ether - benzene was added and the solution refluxed for 1 hr. and left to cool overnight. Triethylamine hydrobromide (2.48 g., 88%) was filtered off and the bright red filtrate was reduced in volume on a rotary evaporator and treated with ethyl acetate. It gave a bright yellow compound (0.04 g.) recrystallised from ethyl acetate m.p. 210-214°

$\nu_{\max}$  2485, 1305, 1295, 1245, 1160, 1145, 1030  $\text{cm}^{-1}$

A similar reaction using chlorine in carbon tetrachloride gave no yellow compound. Chromatography (Method A) on basic alumina gave recovered 1-aminobenzotriazole (0.72 g., 72%) and dimethyl sulphoxide (0.20 g., 40%).

(b) Dimethylsulphide.

Bromine (0.4 ml., 7.8 mmol.) in benzene (5 ml.) was added to dimethylsulphide (0.4 ml., 7.5 mmol.) in cold benzene. A yellow precipitate separated and triethylamine (2.1 ml., 15 mmol.) was added followed by 1-aminobenzotriazole (1.0 g., 7.8 mmol.). The mixture was stirred at room temperature for  $\frac{1}{2}$  hr. and then filtered to yield triethylaminehydrobromide (1.667 g., 60%). The filtrate was evaporated to small bulk and gave 1-amino-benzotriazole (0.42 g., 42%). Exchange of the solvent for

ethyl acetate gave a yellow crystalline compound (0.02 g.)

m.p. 210 - 217°;

$\nu_{\max}$  2480, 1300, 1285, 1155 and 1025  $\text{cm}^{-1}$

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Reaction between toluene-p-sulphonyl azide and benzotriazole.

An attempt to prepare 1-(toluene-p-sulphonamido)benzotriazole.

Toluene-p-sulphonyl azide was prepared by the addition of an acetone solution of toluene-p-sulphonyl chloride (10.0 g., 52.5 mmol.) to sodium azide (3.5 g., 54 mmol.) in water. The reaction mixture was diluted with water until an oil separated which was ether extracted to yield pure azide.

No reaction occurred when the azide (4.0 g., 20 mmol.) and benzotriazole (2.0 g., 17 mmol.) were refluxed in benzene (50 ml.) for 4 hr.. The reaction was repeated in refluxing xylene (145°) and gave a black oil which was rejected.

Benzotriazole (3.0 g., 25.2 mmol.) and the azide (5.2 g., 25.4 mmol.) were refluxed in chlorobenzene at 135° for 20 hr. and the products separated by chromatography (Method A) on silica gel. Two compounds were characterised:

- (i) toluene-p-sulphonyl-o-chloroanilide (0.32 g., 4.3%), m.p. 104 - 105°, lit. m.p. 105°; it had an identical i.r. spectrum to that of an authentic specimen prepared from o-chloroaniline and toluene-p-sulphonyl chloride.
  - (ii) toluene-p-sulphonyl-p-chloroanilide (0.51 g., 7%), m.p. 76.5 - 78°, lit. m.p. 95°, mixed m.p. 93 - 96°; it had an identical i.r. spectrum to that of an authentic specimen prepared from p-chloroaniline and toluene-p-sulphonyl chloride.
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SECTION FOUR. EXPERIMENTS WITH CYCLIC ACETYLENES.1. CYCLOHEXYNE.Preparation of 1-(toluene-p-sulphonamido)-4,5-tetramethylenetriazole.

A solution of cyclohexanedione<sup>123</sup> (5.6 g., 5 mmol.), toluene-p-sulphonyl hydrazide (18.6 g., 10 mmol.) in methanol (40 ml.) and one drop of concentrated hydrochloric acid was refluxed for 2 hr.. The reaction mixture was evaporated to dryness and the residual oil triturated with ether to give a yellow solid, recrystallised from ethanol as colourless crystals of 1-(toluene-p-sulphonamido)-4,5-tetramethylenetriazole, m.p. 212 - 213°; (Found: C, 50.7; H, 5.4; N, 17.4. Calc. for  $C_{13}H_{16}N_4O_2S$  : C, 53.5; H, 5.5; N, 19.3%).  
 $\nu_{\max}$  3000  $\text{cm}^{-1}$  (broad), 1600, 1370, 1170 and 1040  $\text{cm}^{-1}$

Lithium N(4,5-tetramethylene-1-triazolyl)toluene-p-sulphonamide was prepared in an analogous fashion to the lithium salt of 1-(toluene-p-sulphonamido)benzotriazole.  
 $\nu_{\max}$  3500 and 1650  $\text{cm}^{-1}$  (broad due to absorbed water).  
 1280, 1150, 1095, 950  $\text{cm}^{-1}$

Photolysis of the lithium salt.

The lithium salt (0.4 g., 1.35 mmol.) and the triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) in dioxan (50 ml.) were irradiated for 20 hr. by the 'Rayonet' method. Afterwards the solvent was exchanged for ethanol, but no precipitate appeared until ether was added. A flocculent yellow precipitate with a poorly resolved i.r. spectrum separated.

The iminophosphorane of 1-amino-4,5-tetramethylenetriazole.Preparation.

Bromine (3.75 g., 1.2 ml., 23.4 mmol.) in benzene (10 ml.) was added to a benzene solution of triphenylphosphine (5.65 g.,

21.5 mmol.). Triethylamine (4.35 g., 6 ml., 43.0 mmol.) was added to a suspension followed by recrystallised 1-amino-4,5-tetramethylenetriazole<sup>124</sup> (2.9 g., 21 mmol.) in benzene (80 ml.). The reaction mixture was refluxed for 1½ hr., cooled, and the precipitate of triethylamine hydrobromide filtered off. The filtrate gave (4,5-tetramethylene-1-triazolyl)imino-triphenylphosphorane (107) as pale brown crystals, m.p. 202 - 203°, recrystallised from methylene chloride - benzene as light-sensitive colourless plates (5.0 g., 60%), m.p. 203 - 204°; (Found: C, 72.4; H, 5.6; N, 14.1. C<sub>24</sub>H<sub>23</sub>N<sub>4</sub>P requires: C, 72.5; H, 5.8; N, 14.1%)  
 $\nu_{\max}$  1490, 1440, 1430, 1200, 1160, 1120, 1110, 1090 and 990 cm.<sup>-1</sup>.  
 $\lambda_{\max}$  335 nm. ( $\epsilon$  12800), 260 nm. ( $\epsilon$  5500), 267 nm. ( $\epsilon$  5100), 274 nm. ( $\epsilon$  4100).  
 $\tau$  2.0 - 2.7(multiplet)(15H),  $\tau$  7.2 - 7.75(multiplet)(4H),  
 $\tau$  8.2 - 8.5(multiplet)(4H).

Photolysis of (4,5-tetramethylene-1-triazolyl)imino-triphenylphosphorane.

(a) 'Sunlamp' method.

(i) The iminophosphorane (107) (0.513 g., 1.29 mmol.) and tetracyclone (0.591 g., 1.54 mmol.) in THF (50 ml.) were irradiated for 24 hr. and the products separated by chromatography (Method A) on basic alumina. 1,2,3,4-Tetrahydro-5,6,7,8-tetraphenylnaphthalene recrystallised from ethanol (0.04 g., 7%) m.p. 277°, lit.<sup>125</sup> m.p. 271 - 272° or lit.<sup>124</sup> m.p. 284 - 286°; tetracyclone (0.50 g., 85%) and triphenylphosphine oxide (0.10 g., 28%) were isolated.

(ii) The iminophosphorane (107) (0.513 g., 1.29 mmol.) and the triphenylphosphine-platinum complex (46) (0.624 g., 0.5 mmol.) in THF were irradiated for 24 hr.. The solvent was exchanged for a small volume of benzene and the iminophosphorane (107) (0.17 g., 33%) was recovered. The solution was evaporated to dryness and triturated with petrol to give a brown solid (0.66 g.) containing triphenylphosphine oxide which was extracted with ether to leave a residue containing triphenylphosphine-platinum species (i.r.).

(b) 'Hanovia' method.

(i) The iminophosphorane (107) (0.504 g., 1.27 mmol.) and tetracyclone (0.629 g., 1.63 mmol.) in THF were irradiated using a pyrex filter for 48 hr. and the products separated by chromatography (Method A) on basic alumina. The cyclohexyne adduct (0.018 g., 3%); tetracyclone (0.50 g., 80%); the iminophosphorane (107) (0.14 g., 36%) and triphenylphosphine oxide (0.19 g., 55%) were isolated.

(ii) The iminophosphorane (107) (0.667 g., 1.67 mmol.) and tetracyclone (0.626 g., 1.63 mmol.) in THF were irradiated for 12 hr. and the products separated as before. The cyclohexyne adduct (0.085 g., 11.5%); tetracyclone (0.493 g., 80%); triphenylphosphine oxide (0.439 g., 95%) were isolated.

2. CYCLOHEPTYNE.

1-Amino-4,5-pentamethylenetriazole (27) was prepared as described in the literature<sup>76,126</sup>.

Oxidation.

(i) LTA (0.75 g., 1.65 mmol.) in methylene chloride (20 ml.) was added dropwise to a methylene chloride solution of the amine (27) (0.24 g., 1.58 mmol.) at  $-78^{\circ}$ . Immediately after gas evolution had ceased (15 sec.) a methylene chloride - benzene solution of the triphenylphosphine-platinum complex (46) (2.0 g., 1.6 mmol.) was added. The solution was allowed to warm up to room temperature and the solvent exchanged for benzene. A yellow precipitate (0.22 g.) of a phosphine-platinum complex (i.r.) separated and when the volume of the solution was reduced, cis-diacetatobis(triphenylphosphine)platinum(II) (0.285 g., 24%). The filtrates were chromatographed (Method A) on silica gel, but no hydrocarbons were isolated.

(ii) LTA (1.0 g., 2.2 mmol.) was added in small portions to a suspension of potassium carbonate (2.0 g., 14.5 mmol.) in a benzene solution of the ethylene complex (118) (1.0 g., 1.33 mmol.) and the amine (27) (0.4 g., 2.63 mmol.). After gas evolution had ceased, the lead and potassium salts were filtered off and the filtrate evaporated to small bulk. No crystallisation occurred when ethanol was added, the solvent was removed and the oil triturated with ether. It gave a brown solid which

was a phosphine-platinum complex (i.r.). Trace quantities of brown oils, triphenylphosphine, and triphenylphosphine oxide were eluted when the filtrate was chromatographed (Method A) on basic alumina.

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The iminophosphorane of 1-amino-4,5-pentamethylenetriazole.

This compound (108) was prepared (16%) in an exactly similar way to the iminophosphorane of 1-amino-4,5-tetramethylenetriazole.

After recrystallisation from ethyl acetate  
(4,5-pentamethylene-1-triazolyl)iminotriphenylphosphorane (108)  
 was obtained as pale brown plates m.p.  $164 - 166^{\circ}$ ;  
 (Found: C, 72.6; H, 6.2; N, 13.5.  $C_{25}H_{25}N_4P$  requires: C, 73.0;  
 H, 6.1; N, 13.6%)  
 $\nu_{max}$  1215, 1205, 1110 and 980  $cm^{-1}$

$\tau$  2.0 - 3.0 (multiplet) (15H),  $\tau$  7.3 (multiplet) (4H),  
 $\tau$  8.4 (multiplet) (6H).

Photolysis of (4,5-pentamethylene-1-triazolyl)imino-  
triphenylphosphorane.

The iminophosphorane (108) (0.347 g., 0.845 mmol.) and tetracyclone (0.40 g., 1.04 mmol.) in benzene (100 ml.) were irradiated for 20 hr. by the 'Hanovia' method, the products were separated by chromatography (Method A) on basic alumina. The products were biphenyl (0.01 g.) and crude 1,2-pentamethylene-3,4,5,6-tetraphenylbenzene (0.21 g., 55%) recrystallised from petrol (0.14 g., 36%), m.p.  $221 - 222^{\circ}$ , lit.<sup>124</sup> m.p.  $225 - 226^{\circ}$ .

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Cycloheptenocyclopropenone.Photolysis.

Crude cycloheptenocyclopropenone<sup>127</sup> and tetracyclone (0.516 g.) in benzene (100 ml.) were irradiated for 20 hr. by the 'Hanovia' method and gave 1,2-pentamethylene-3,4,5,6-tetraphenylbenzene (0.094 g.), recrystallised from ethanol m.p. 220 - 225° and tetracyclone (crude 0.5 g.)

Reaction with tris(triphenylphosphine)chlororhodium(I).

Tris(triphenylphosphine)chlororhodium(I)<sup>128</sup> (0.5 g., 0.54 mmol.) in benzene (20 ml.) was added to a warm (50°) benzene (50 ml.) solution of the triphenylphosphine-platinum complex (46) (1.0 g., 0.8 mmol.) and crude cycloheptenocyclopropenone (28) (0.2 g., 1.16 mmol.). After 12 hr. at 50° the solution was reduced in volume and trans-bis(triphenylphosphine)carbonylchlororhodium(I)<sup>129</sup> precipitated as yellow crystals  $\nu_{\max}$  2960 and 1100  $\text{cm}^{-1}$ . The filtrate was diluted with ethanol and gave yellow crystals (0.23 g.),  $\nu_{\max}$  1655, 1095 and 805  $\text{cm}^{-1}$  which recrystallised poorly from ethanol - benzene. The filtrates were diluted with ether and gave a light brown precipitate of a phosphine-metal complex  $\nu_{\max}$  1440 and 1105  $\text{cm}^{-1}$ .

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## SECTION FIVE. MISCELLANEOUS EXPERIMENTS.

### o-Fluorobromobenzene with magnesium and tetrakis(triphenylphosphine)platinum(0)

o-Fluorobromobenzene (0.28 g., 1.6 mmol.) and magnesium (0.08 g., 3.2 mmol.) were reacted in dry ether (10 ml.) to form the Grignard derivative and the mixture was cooled to 0°. The triphenylphosphine-platinum complex (46) (2.0 g., 1.6 mmol.) in benzene (40 ml.) was added. There was an immediate precipitation of a yellow solid. After 2 hr. the mixture was filtered. The filtrate was evaporated to small bulk to give crystals (0.42 g.), m.p. 100 - 125°, the i.r. spectrum was identical to the triphenylphosphine-platinum complex (46). The precipitate and isolated crystals were combined and heated under reflux for 2 hr. with furan (20 ml.). Neither 1,4-dihydronaphthalene endoxide nor  $\alpha$ -naphthol could be detected (t.l.c.).

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### Attempted stepwise synthesis of a benzyne complex.

#### (i) 2-Bromophenylazochlorobis(triphenylphosphine)platinum(II).

A slurry of cis-hydrido-chlorobis(triphenylphosphine)platinum(II) (4.55 g., 6 mmol.) in ethanol was added to a stirred suspension of o-bromobenzenediazonium fluoroborate (1.7 g., 6.3 mmol. damp with ether) in ethanol. The mixture rapidly became homogeneous and then yellow crystals of the fluoroborate salt (120) (2.62 g., 2.55 mmol., 41%) were deposited, m.p. 195 - 230°. It was suspended in methanol (100 ml.) at 0° and a solution of sodium acetate trihydrate (0.36 g., 2.65 mmol.) in methanol added. Almost immediately the suspension took on a violet colouration and after 5 min. the solution was filtered to give lilac crystals of 2-bromophenylazochlorobis(triphenylphosphine)platinum(II) (121) (2.34 g., 97%), m.p. 250 - 254° after recrystallisation from

benzene - hexane; (Found: C, 54.8; H, 3.6; N, 2.8.  $C_{42}H_{34}N_2BrClP_2Pt$  requires: C, 55.7; H, 3.6; N, 3.0%)

(ii) 2-Bromophenylchlorobis(triphenylphosphine)platinum(II).

The azo complex (121) (0.613 g.) in benzene was poured onto a short column of neutral alumina and rapidly eluted with 10% ether in benzene to give colourless needles of 2-bromophenylchlorobis(triphenylphosphine)platinum(II) (122) (0.065 g., 11%) m.p. 278 - 282°; (Found: C, 55.1; H, 3.6; Br, 9.5.  $C_{42}H_{34}BrClP_2Pt$  requires: C, 55.4; H, 3.7; Br, 8.8%). Modifications of this procedure gave even lower yields of compound (122).

(iii) Reaction between 2-bromophenylazochlorobis(triphenylphosphine)platinum(II) and lithium.

Compound (121) (1.36 g., 1.45 mmol.) and lithium shavings (0.07 g., 7 mmol.) were suspended in dry THF (15 ml.). The reaction was initiated by adding a small piece of potassium. A gas appeared to be evolved during the reaction. After 2 hr. at reflux, the reaction mixture was cooled and ethanol added to destroy the excess lithium. A yellow precipitate (0.34 g.) was filtered off. It consisted of lithium salts and a platinum complex (i.r.) but nothing crystalline could be obtained from it. Similarly the filtrate yielded no crystalline compounds after evaporation.

There was no reaction when compound (121) (1.1 g., 1.17 mmol.) in benzene - THF (50 ml.) was added to magnesium turnings (0.07 g., 2.9 mmol.) in THF (10 ml.).

Oxidation of N-aminophthalimide in the presence of tolanbis(triphenylphosphine)platinum.

LTA (0.8 g., 1.8 mmol.) was added in small portions to a suspension of N-aminophthalimide (0.3 g., 2.0 mmol.) and the tolan complex (36) (0.8 g., 1.0 mmol.) in benzene (20 ml.)

a small quantity of a gas was evolved and the solution went brown in colour. The solution was filtered and the residue (0.54 g.) was a mixture of lead diacetate and N-aminophthalimide (i.r.). The filtrate was treated with hexane until precipitation occurred. A solid separated,  $\nu_{\max}$  2050, 1725, 1680 and 1310  $\text{cm}^{-1}$ , which was boiled with benzene - hexane and gave two crops of crystals:

(i) m.p. 147 - 160°

$\nu_{\max}$  2050, 1725, 1670 and 1310  $\text{cm}^{-1}$

(ii) m.p. 148 - 152°

$\nu_{\max}$  2050(weak), 1670(shoulder at 1640), 1310, 1125 and 1105  $\text{cm}^{-1}$

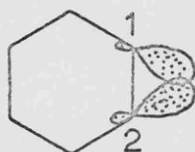
Chromatography (Method A) of the filtrate on basic alumina gave tolan (0.064 g., 40%) and a colourless crystalline compound, recrystallised from ether - petrol m.p. 177 - 180°,  $\nu_{\max}$  1740, 1630, 1300, 1225, 1200 and 1100  $\text{cm}^{-1}$ .

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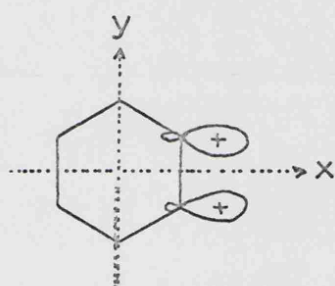
# DISCUSSION.

The evidence for considering benzyne as a symmetric singlet has been discussed in the Introduction. The selectivity of benzyne has been explained by postulating that the molecule is stabilized by a bonding interaction between the two electrons on  $C_1$  and  $C_2$ . Partial  $\pi$  bond formation may be demonstrated pictorially as (44)<sup>133</sup>. The approximate geometry of the (S) and

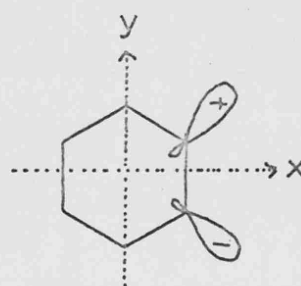


(44)

(A) orbitals have been calculated<sup>69</sup> and are illustrated below.

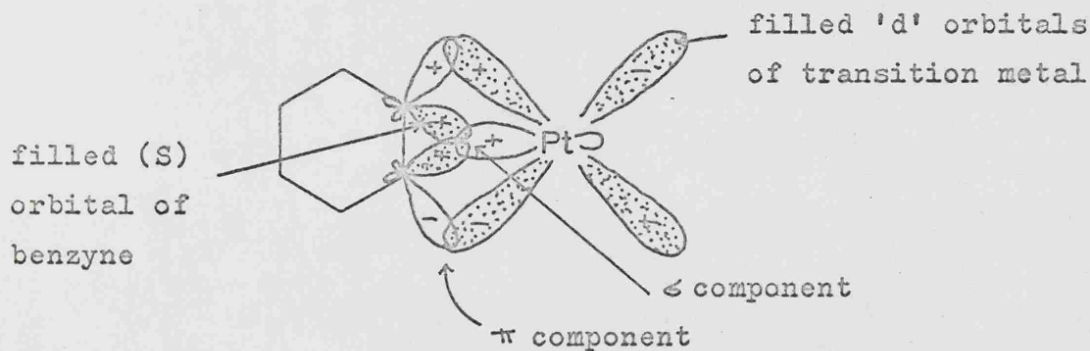


(S)



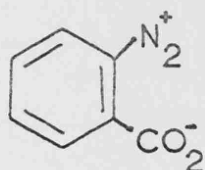
(A)

If these ideas concerning the electronic structure of benzyne are correct then it should be possible to prepare a  $\sigma\pi$  complex of benzyne (45) analogous to the transition metal complexes of olefins and acetylenes. Several attempts depending upon this concept have been described in the Introduction.

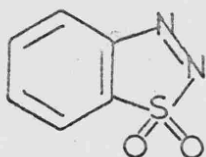


(45)

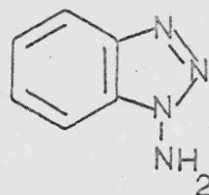
In this work it was decided to generate benzyne from an organic precursor in the presence of a transition metal capable of stabilizing it as a  $\pi$ -complex. Examination of the literature<sup>134</sup> at the time when this work was started revealed that platinum(0) formed very stable monoacetylene and olefin complexes and the decomposition of the benzyne precursors, benzenediazonium-2-carboxylate (2), 1,2,3-benzothiadiazole-1,1-dioxide (4) and 1-aminobenzotriazole (5) were investigated



(2)



(4)



(5)

in its presence in the hope of isolating a benzyne-platinum complex.

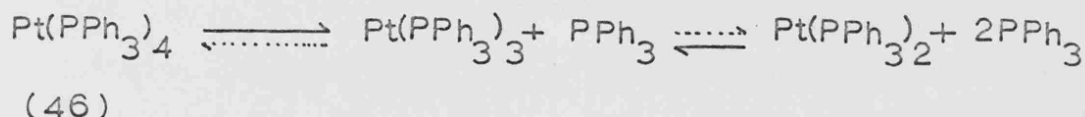
A recent review<sup>90</sup> on transition metal-acetylene chemistry confirms the choice of platinum(0) as one of the most suitable metals to use in this work. There are three general types of acetylene complex involving:

- (i) formation of ring systems, either fused to the transition metal or as hydrocarbons in cyclic or chain polymerisation.
- (ii) polynuclear complexes with bridging alkyne molecules.
- (iii) the alkyne bonded to a single transition metal atom without ring formation  $[M]$ . Some of these complexes are unstable or have only been briefly mentioned in the literature  $[M]$ ; they may require photochemical conditions for preparation (molybdenum and manganese); or only form stable complexes with alkynes bearing very strong electron-withdrawing groups (nickel and palladium).

A benzyne-platinum complex would belong to group (iii) and the diagram illustrates transition metals which show this behaviour.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt

Zerovalent platinum was used exclusively in this work as the transition metal to 'trap' the benzyne intermediate. Tetrakis(triphenylphosphine)platinum(0)<sup>102</sup> (46) which dissociates in solution<sup>135</sup> was used as a source of zerovalent platinum



after preliminary experiments had shown that alkyne complexes could be made from it simply by stirring its benzene solution with the alkyne. Tolanbis(triphenylphosphine)platinum and cyclooctynebis(triphenylphosphine)platinum were each prepared in 70% yield in this way. Their i.r. spectra were interesting to compare. The absorptions attributed to the carbon-carbon triple bond of the alkyne were found at 1765 and 1795 cm.<sup>-1</sup> respectively. The higher stretching frequency for the cyclooctyne complex was thought to be due to the additional strain imposed upon the carbon-carbon triple bond in the eight-membered ring. Attempts were made (see Section Three) to prepare cycloheptyne and cyclohexyne bis(triphenylphosphine) platinum complexes in order to substantiate this hypothesis.

#### Infra-red spectra.

A (triphenylphosphine)platinum fragment in a compound always gave absorptions in the i.r. spectrum at 1440, 1175, 1145, 1100(strong), 1025, 1000 cm.<sup>-1</sup>

cis-Disubstituted bis(triphenylphosphine)platinum complexes have characteristic absorptions in the i.r. spectrum<sup>170</sup> at ca. 1585(strong) and 1570(weak)  $\text{cm}^{-1}$ , in contrast to trans-disubstituted complexes which have similar absorptions with reversed relative intensities, e.g. 1585(weak) and 1570(strong) $\text{cm}^{-1}$ . The position of the absorptions depended upon the complex and the strengths were not related to other absorptions in the i.r. spectrum which might be considerably stronger.

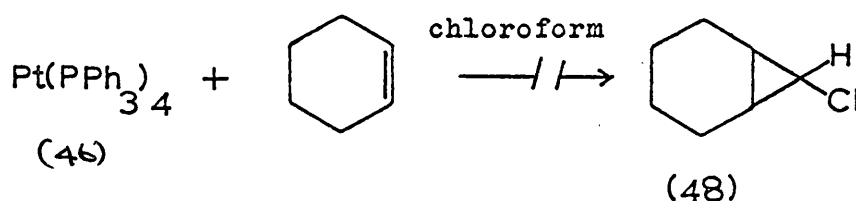
The Discussion is divided into three main sections which describe the work with the benzyne precursors: 1,2,3-benzothiadiazole-1,1-dioxide, benzenediazonium-2-carboxylate, and 1-aminobenzotriazole.

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SECTION ONE. 1,2,3-BENZOTHIADIAZOLE-1,1-DIOXIDE.

A preliminary investigation showed that thermolysis of 1,2,3-benzothiadiazo1e-1,1-dioxide(4a) in the presence of tetrakis(triphenylphosphine)platinum(0) (46) gave triphenylene. However biphenylene and not triphenylene was the normal product obtained from the thermolysis of compound (4a) in solution and the formation of triphenylene was thought to indicate participation of a platinum species in the reaction. The reaction was therefore investigated at low temperature in the hope of isolating the platinum complex which was responsible for triphenylene formation.

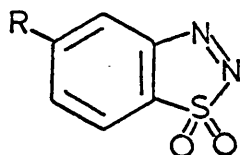
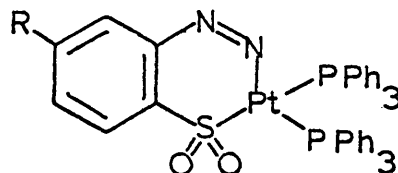
When the reaction was performed at  $-20^{\circ}$  in chloroform it was found that the triphenylphosphine-platinum complex (46) reacted with the solvent and gave cis-dichlorobis(triphenylphosphine)platinum(II) (47). A yellow phosphine-platinum complex (i.r. only) was isolated from the filtrates. A stirred chloroform solution of the triphenylphosphine-platinum complex (46) precipitated the cis-dichloro-platinum complex (47) in 26% yield. The possibility that the triphenylphosphine-platinum complex (46) abstracted two chlorine atoms from chloroform to give monochlorocarbene was eliminated. When the



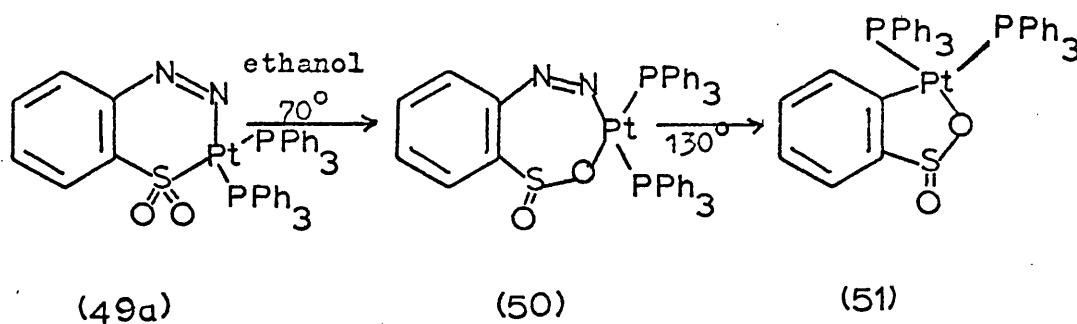
triphenylphosphine-platinum complex (46) and cyclohexene were refluxed overnight in chloroform no 7-chloronorcarane (48) was produced.

In cold benzene the azo complex (49a)<sup>136</sup> was precipitated in high yield as yellow crystals (79%). Its stoichiometry (confirmed by analysis) was suggested originally because there was no gas evolution during the reaction. The retention of sulphur dioxide was indicated in the i.r. spectrum by absorption

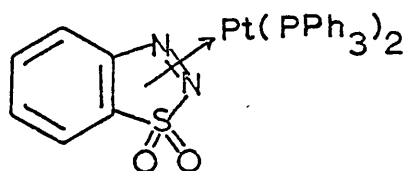
bands at  $1284$  and  $1156\text{ cm}^{-1}$  and retention of nitrogen by thermolysis of the compound in diglyme at  $120^\circ$  when nitrogen was evolved. The incorporation of the entire 1,2,3-benzothiadiazole-1,1-dioxide molecule was confirmed by preparing the 6-methyl derivative (49b) which had the correct NMR spectrum.

(4)(a)  $R = H$ (b)  $R = \text{CH}_3$ (49)(a)  $R = H$ (b)  $R = \text{CH}_3$ 

Independently and simultaneously Cook and Jauhal<sup>103</sup> prepared this complex ( $R = H$ ) using ethylenebis(triphenylphosphine) platinum (118) and had assigned its structure on the basis of their i.r. spectrum. Thus their absorption at  $1446\text{ cm}^{-1}$  was assigned to the nitrogen - nitrogen stretching frequency and those at  $1285$  (asymmetric) and  $1159$  and  $1136\text{ cm}^{-1}$  (symmetric) to the sulphur - oxygen stretching frequencies. They investigated its thermolysis and characterised the products (50) and (51).



We also considered an alternative structure (X) for compound (49) and it still cannot be completely ruled out.



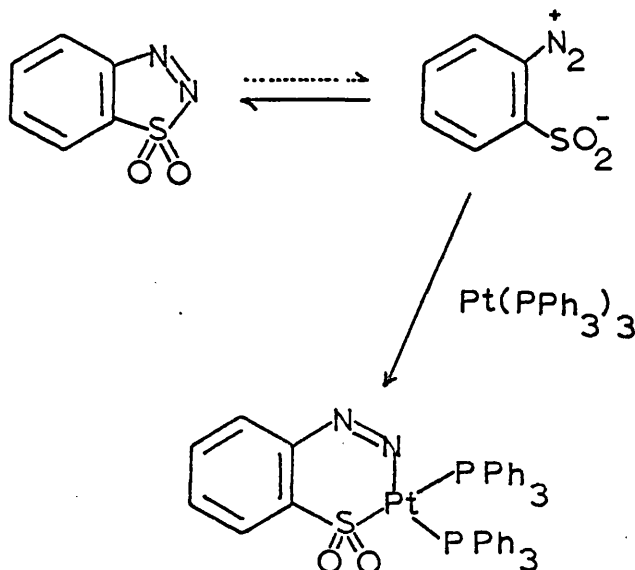
(X)

This structure had an advantage over (49a) as it could easily explain the ability of compound (49) (see later) to behave as a benzyne precursor. The benzothiadiazole ring is coordinated intact to the bis(triphenylphosphine)platinum species and dissociation would regenerate 1,2,3-benzothiadiazole-1,1-dioxide which could then decompose to benzyne as normal.

The structure (X) was considered unlikely because of two considerations:

(i) 1,2,3-benzothiadiazole-1,1-dioxide is thermally very unstable (even at  $0^{\circ}$ ) and it seemed unlikely that its stability would be so dramatically increased (as it was in compound (49)) which had a m.p. of  $177 - 179^{\circ}$ ) when it was coordinated to a bis(triphenylphosphine)platinum species,

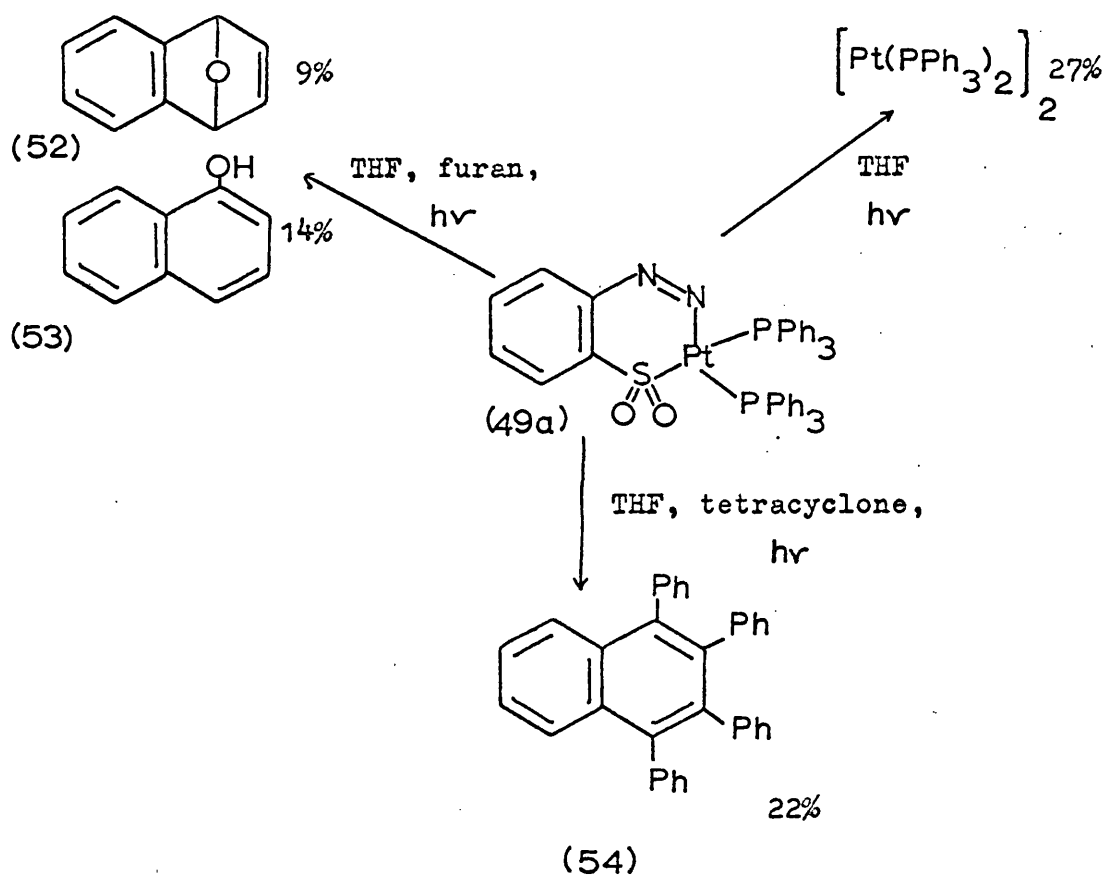
(ii) by analogy with the benzenediazonium-2-carboxylates (Section Two) the mechanism of formation of compound (49) was thought to involve a betaine intermediate (benzenediazonium-2-sulphinite), which was in equilibrium in small concentration, with 1,2,3-benzothiadiazole-1,1-dioxide.



If it was correct this mechanism which involved scission of the benzothiadiazole ring suggested that structure (X) was unlikely. However it cannot be eliminated on the basis of considerations (i) and (ii) alone and it remains a possibility for the structure of compound (49).

It was thought that compound (49) might still be a benzyne precursor if the nitrogen and sulphur dioxide could be extruded; furthermore it might produce benzyne in the proximity of bis-(triphenylphosphine)platinum and hence could possibly lead to the desired benzyne-platinum complex. Its properties were investigated with these considerations in mind.

Thermolysis of compound (49a) in diglyme gave one mole. of a gas (presumed to be nitrogen) between 100 - 120° together with biphenyl. Initial experiments with compound (49a) suspended in furan gave no 1,4-naphthalene endoxide (52) or  $\alpha$ -naphthol (53) but exposure to sunlight of this suspension for three weeks gave trace quantities of (52). This provided a clue to the conditions required for benzynoid decomposition of compound (49). Photolysis of homogeneous solutions using the 'Sunlamp' gave benzyne adducts with tetracyclone and with furan.



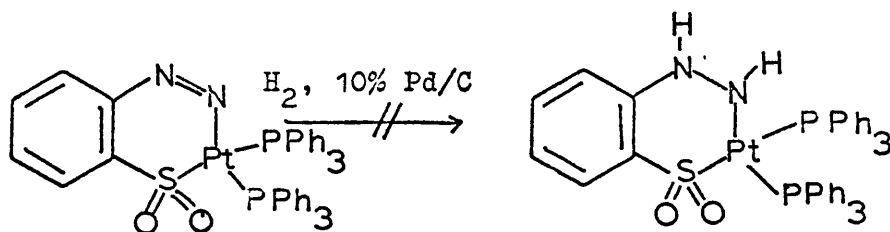


Photolysis of the azo complex (49a) on its own in THF gave a bis(triphenylphosphine)platinum(0) species, dimeric in benzene solution (osmometric molecular weight), which had different physical properties from those of the complex reported by Ugo, Cariati and La Monica<sup>137</sup> or of a phosphine-platinum complex prepared under photolytic conditions from oxalato-bis(triphenylphosphine)platinum(II)<sup>138</sup>.

In two reactions with the azo complex (49a) and the 6-methyl derivative (49b), the triphenylphosphine-platinum complex (46) was used as the benzyne trap. Triphenylene formation was thought to be good evidence for benzyne-platinum intermediates after the preliminary results, but it was not detected in this reaction. Only sulphatobis(triphenylphosphine)platinum(II)<sup>108</sup> and a colourless bis(triphenylphosphine)-platinum species were isolated. The melting points of the two platinum - phosphine complexes from (49a) and (49b) were slightly different but their i.r. spectra were identical and analysis was correct.

Parshall<sup>139</sup> had shown that arylazoplatinum complexes could be converted to arylplatinum complexes by percolation of their benzene solutions down a short column of basic alumina. When the azo complex (49a) was treated in this way, three compounds were formed. Compound (50) was isolated (33%) as violet crystals. A red oil containing a sulphur - oxygen linkage (i.r.) and a phosphine-platinum complex were not characterised.

It was noticed that the azo complex (49a) decomposed on standing in air at room temperature. Hydrogenation of (49a) to (55) was attempted using 10% palladium on charcoal as a catalyst. Compound (55) should be more stable than (49a) as it could not directly lose molecular nitrogen.

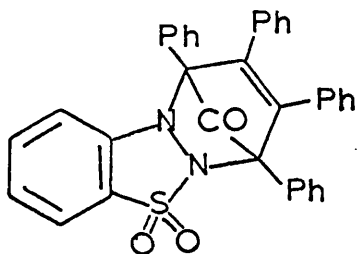


(49a)

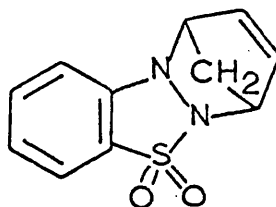
(55)

Reduction did not occur even though hydrogen appeared to be absorbed. Chromatography of the reaction mixture gave the same products as chromatography of the azo complex (49a) on basic alumina.

All the chemical properties of the azo complex (49a) suggested that it could not by itself be responsible for triphenylene formation in the reaction between 1,2,3-benzothiadiazole-1,1-dioxide and the triphenylphosphine-platinum complex (46) in refluxing ether - benzene. 1,2,3-Benzothiadiazole-1,1-dioxide (4a) decomposed and gave benzyne under the conditions that (49a) was prepared as a control experiment showed. Tetraphenylnaphthalene (54) (27%) was produced when tetracyclone was used as the benzyne trap instead of the triphenylphosphine-platinum complex (46). No adducts such as (56) were isolated which were formed when (4a) and cyclopentadiene were reacted in cold benzene (57)<sup>20</sup>.



(56)

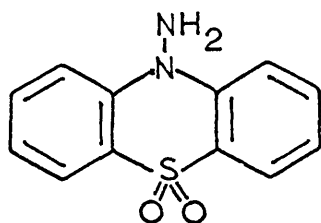


(57)

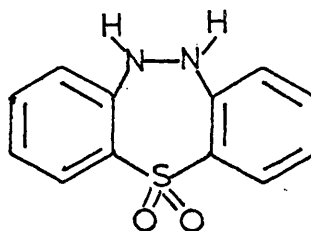
Thus 1,2,3-benzothiadiazole-1,1-dioxide (4a) was trapped by tris(triphenylphosphine)platinum(0) (the main species in solution) before it could decompose.

Reaction of the triphenylphosphine-platinum complex (46) with excess of 1,2,3-benzothiadiazole-1,1-dioxide (4a) did not give a different compound which was capable of decomposing on thermolysis to triphenylene. Thus addition of (4a) (two equivalents) to (46) in cold benzene gave the azo complex (49a) (65%) and products from the reaction between (4a) and triphenylphosphine.

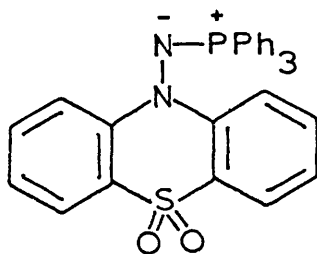
The reaction of 1,2,3-benzothiadiazole-1,1-dioxide (4a) with triphenylphosphine was investigated further. A precipitate formed on addition of (4a) to triphenylphosphine in cold benzene which gave triphenylphosphine oxide and a mixture of two amines when decomposed by chromatography on silica gel. The bright red filtrate contained small quantities of triphenylphosphine sulphide and a red compound  $C_{30}H_{23}N_2O_2PS$ . One of the amines had a parent peak in the mass spectrum at  $m/e$  246 which could be assigned to N-aminophenothiazine-5,5-dioxide (58) although i.r. evidence did not support the hydrazine structure. The alternative, dibenzo-1-thia-4,5-hydrazocyclohepta-2,4,6-triene-1,1-dioxide (59), had to be rejected as its reported properties<sup>140</sup> (i.r. spectrum and m.p.) were different. The other amine had a



(58)



(59)



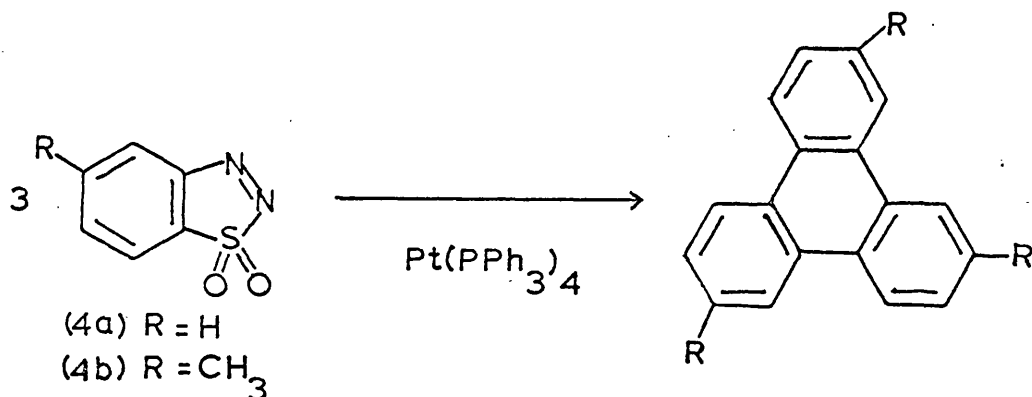
(60)

parent peak at  $m/e$  326 and the i.r. suggested that it was a primary amine, but no structure can be assigned to it.

The formation of these amines together with triphenylphosphine oxide suggested that they were products formed by hydrolysis of iminophosphoranes<sup>141</sup> or betaines. Thus hydrolysis of compound (60) would explain the formation of (58). Compound (60) was a possible structure for the red compound previously described, but it was rejected on the basis of its mass spectrum and iminophosphoranes of this type (see Section Three) were found to be colourless. The red colour suggested an azo linkage in this compound.

Triphenylene formation.

Wittig and Hoffmann<sup>20</sup> have shown that thermolysis of 1,2,3-benzothiadiazole-1,1-dioxide (4a) in warm benzene gave biphenylene (1 - 9%) but no triphenylene. However we found that when (4a) was decomposed in a refluxing ether - benzene solution of the triphenylphosphine-platinum complex (46) it gave triphenylene in 38% yield.



Formation of triphenylene was thought to be due to benzyne-platinum intermediates and the following control experiments support this idea.

(i) Triphenylphosphine was in equilibrium with the triphenylphosphine platinum complex (46), but it was not responsible for triphenylene formation as thermolysis of (4b) under the same conditions, with triphenylphosphine, gave no triphenylene derivative.

(ii) Formation of triphenylene was accompanied by precipitation of the azo complex (49a) which was then assumed not to participate in the reaction any further. The active platinum species was thus gradually removed as an experiment has shown in which a catalytic quantity of (46) in this reaction gave both triphenylene and biphenylene.

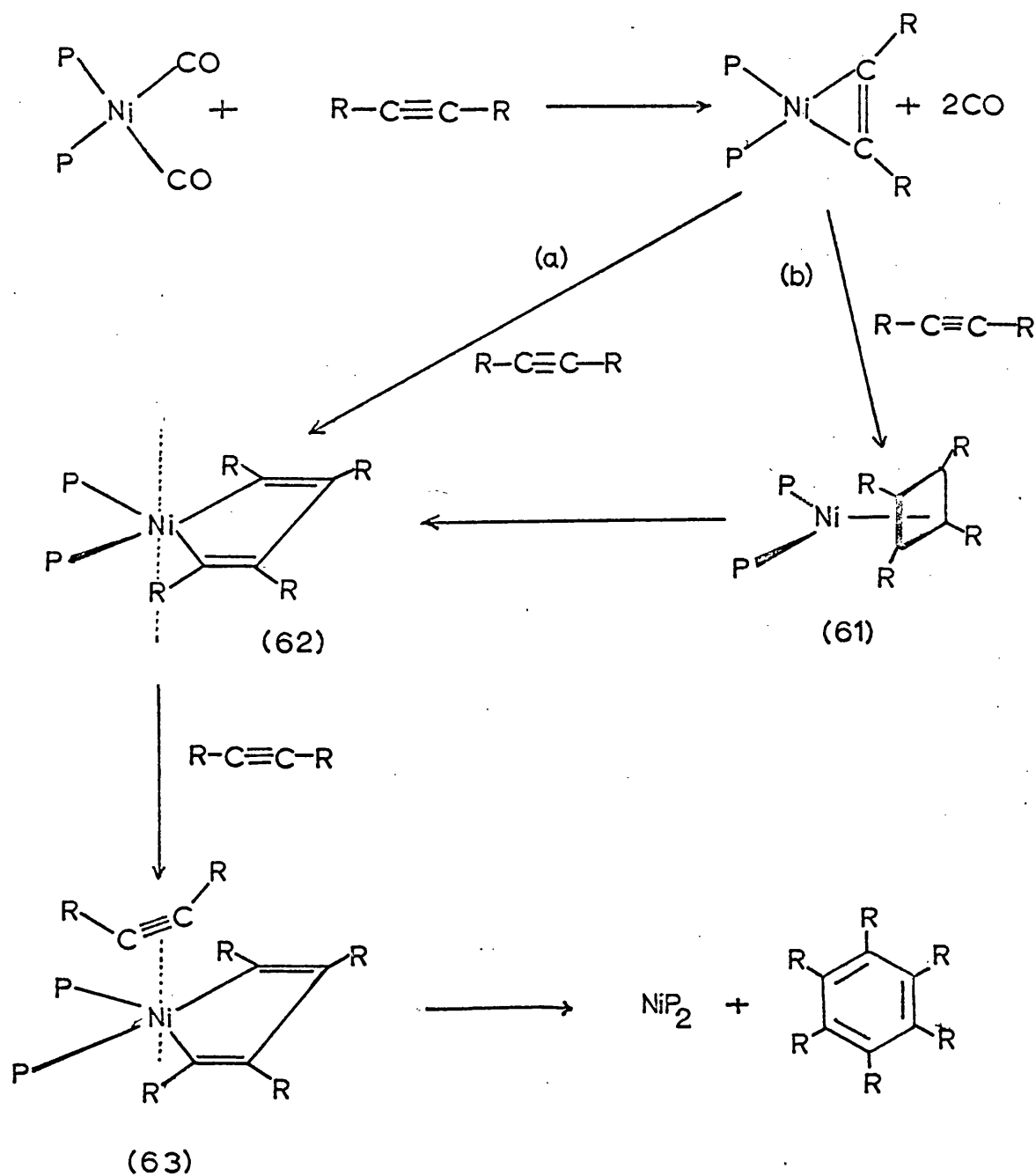
(iii) Compound (49) could contribute to triphenylene formation when in solution. A refluxing THF solution of the azo complex (49a) gave triphenylene (9.3%) on addition of (4a). The low yields of triphenylene may be due to the competing reaction of benzyne with THF. Experiments have shown (see Section Three) that benzyne generated in THF gave a lower yield of the tetracyclone adduct than when generated under identical conditions in benzene.

(iv) Decomposition of (4b) in this reaction gave only 2,6,11-trimethyltriphenylene(35%). The absence of isomers indicated electronic or perhaps steric control in the intermediate responsible for triphenylene formation.

(v) When the reaction was repeated with (4a) in benzene at 50°, lower yields of triphenylene (11.5%) were produced.

(vi) Ethylenebis(triphenylphosphine)platinum(0) also gave triphenylene (20%) when it replaced the triphenylphosphine-platinum complex (46) in this reaction with (4a).

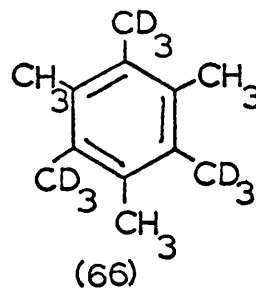
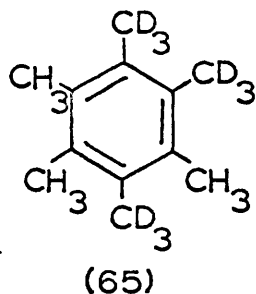
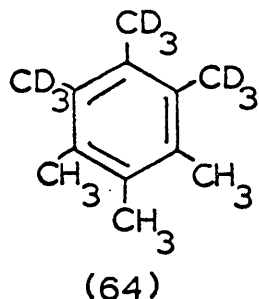
Formation of triphenylene from benzyne in the presence of platinum(0) was thought to be analogous to the cyclic trimerisation of acetylenes by other transition metals<sup>96</sup>. There are two different mechanisms suggested in the literature for cyclic polymerisation of acetylenes. Meriwether *et al.*<sup>142</sup> showed that zerovalent nickel, which has the same number of valence electrons as platinum(0), trimerised acetylenes to benzene derivatives. Monosubstituted acetylenes gave a mixture of 1,2,4- and 1,3,5-trisubstituted benzenes with the former isomer predominating. They described a stepwise process<sup>143</sup> for monosubstituted acetylenes involving oxidative addition of the acetylenic C-H bond to the metal. This mechanism had the advantage of explaining the formation of linear polymers. However they recognized that it would not apply to the cyclic trimerisation of disubstituted acetylenes and proposed a different mechanism which was equally applicable to mono and disubstituted acetylenes.



The role of metallocyclopentadienes (62) in cyclotrimerisation reactions of disubstituted acetylenes has recently been established for iridium and rhodium<sup>144</sup> and metallocyclopentadienes had been suggested before<sup>145</sup> in the trimerisation of tolan to hexaphenylbenzene by bis(benzonitrile)palladium chloride.

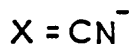
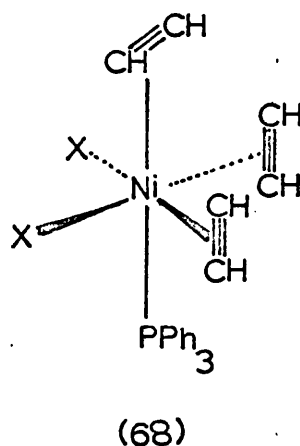
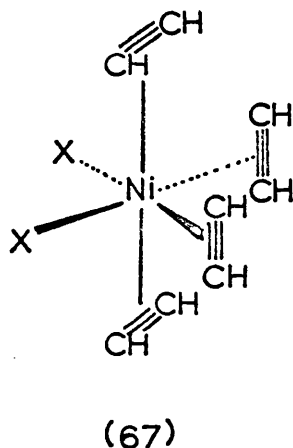
Cyclobutadiene intermediates like (61) have been eliminated by a study<sup>146</sup> of the isomer ratios produced in the cyclic trimerisation of 2-butyne-1,1,1- $d_3$ . A cyclobutadiene intermediate

in this reaction with triphenyltris(tetrahydrofuran)chromium(III) would permit formation of compound (64) as well as (65) and (66). Compound (64) was found only in amounts attributable to impurities (hexadeuterio-2-butyne) in the starting material. Meriwether's



reaction mechanism has only to be modified by direct formation of metalocyclopentadiene (pathway (a)) to take into consideration this new evidence.

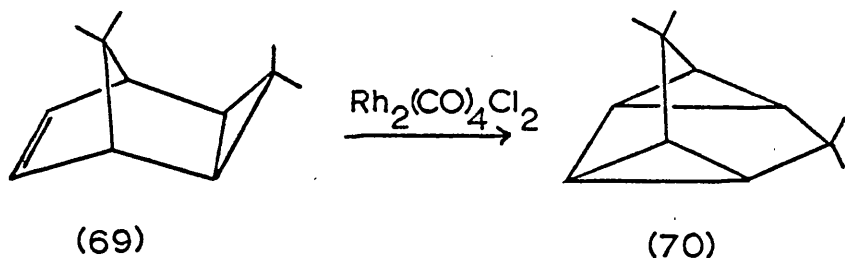
Schrauzer<sup>147</sup> proposed a ' $\pi$  complex multicentre mechanism' in the cyclic tetramerisation and trimerisation of acetylene by nickel(II) complexes. An intermediate (67) was envisaged, which fragmented in a concerted fashion to form the new carbon - carbon  $\sigma$  bonds simultaneously. Formation of cyclooctatetraene was



completely inhibited by addition of triphenylphosphine which blocked one of the octahedral positions (68). Schrauzer had rejected cyclobutadiene intermediates in these reactions before the above experimental evidence<sup>146</sup> became available. He had

argued that in a catalytic reaction only small quantities of cyclobutadiene could be formed and that these highly reactive species would add to the vast excess of acetylene present to give benzene derivatives rather than dimerise selectively to cyclooctatetraene.

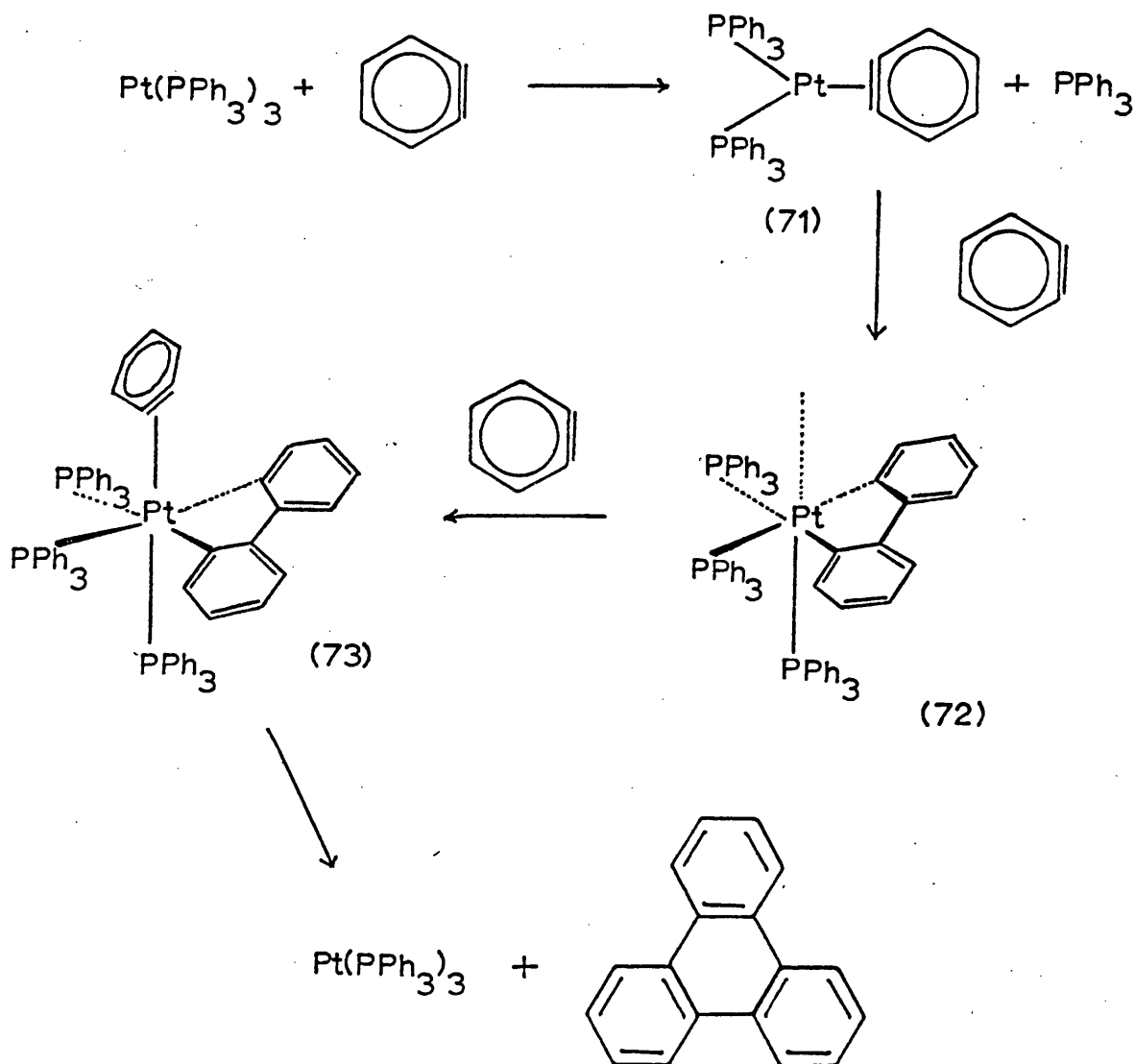
The ' $\pi$  complex multicentre mechanism' has generated considerable interest among theoretical chemists<sup>148</sup>. The concerted thermal uncatalysed cycloaddition of four acetylene molecules is not allowed by the Woodward Hoffmann Rules<sup>43</sup>. That it should occur when the acetylene was complexed to a transition metal suggested a new electronic pathway involving the metal's atomic orbitals. Other reactions<sup>149,150,151</sup> which are strictly forbidden by the Woodward Hoffmann Rules proceeded in the presence of certain transition metals and the authors attributed the catalysis to the transformation of molecular orbital symmetries which made concerted electrocyclic processes allowed. A recent example<sup>150</sup> was the quantitative conversion of exo-tricyclo(3.2.1.0)oct-6-ene (69) to tetracyclo(3.3.0.0.0)octane (70).



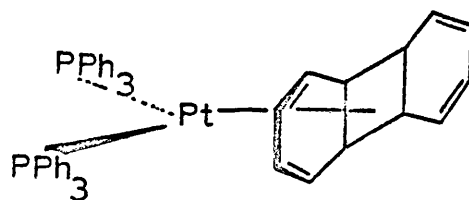
octane (70). However a closer investigation of this reaction<sup>152</sup> using tris(triphenylphosphine)chlororhodium(I) showed that (70) was not the only compound produced and other products could not be formed from concerted electrocyclic reactions. The authors suggested that the role of the transition metal in all of these reactions was now in doubt.



Our suggested reaction scheme for triphenylene formation is analogous to the amended Meriwether pathway for the trimerisation of acetylenes.



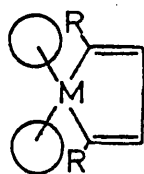
The formation of a transient cyclobutadiene complex, dibenzocyclobutadienebis(triphenylphosphine)platinum (74) was unlikely after cyclobutadiene intermediates had been rejected in acetylene trimerisation. Also complex (74) might be expected to dissociate to some extent to give the very stable biphenylene but the main feature of the decomposition of 1,2,3-benzothiadiazole-1,1-dioxide (4a) in the presence of the triphenylphosphine-platinum complex (46) was the complete suppression of biphenylene formation.



(74)

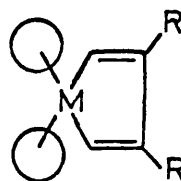
The lower yields of triphenylene when benzene was used as a solvent could be explained on the basis of competition between benzyne and benzene for the sixth octahedral site in (72). The success of ethylenebis(triphenylphosphine)platinum(0) in this reaction implied that the role of triphenylphosphine to block one of the octahedral sites in (72) and (73) was not essential.

Another feature of this reaction was the production of only 2,6,11-trimethyltriphenylene when 5-methyl-1,2,3-benzothiadiazole-1,1-dioxide (4b) was decomposed. This isomer is directly related to the 1,2,4-trisubstituted benzenes formed when unsymmetrical acetylenes were trimerised. The formation of this isomer has a statistical advantage (3:1) over the symmetrical 1,3,5-isomer (viz. 2,6,10-trimethyltriphenylene). The complete absence of 2,6,10-trimethyltriphenylene must indicate steric or electronic control in the transition state. Meriwether<sup>143</sup> explained the predominance of the 1,2,4-isomers on the basis that substituents had a lower steric interaction in the  $\beta$  positions of the metallocyclopentadiene ring (75), (76).



(75)

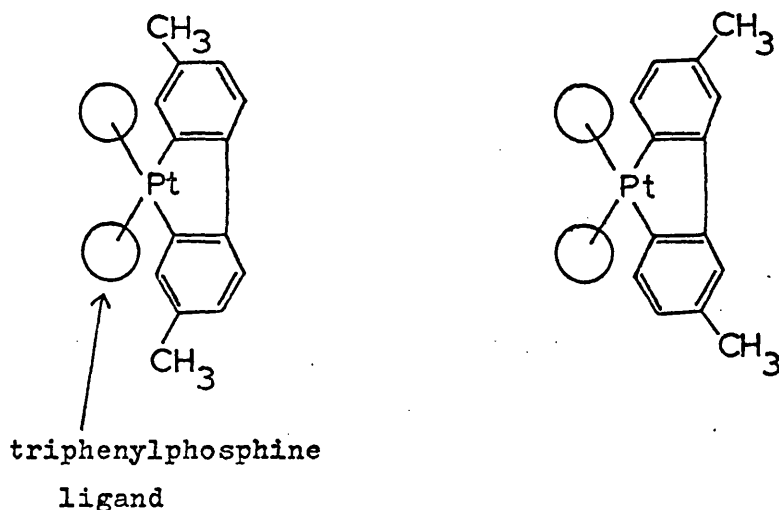
bulky substituted  
phosphine ligands



(76)

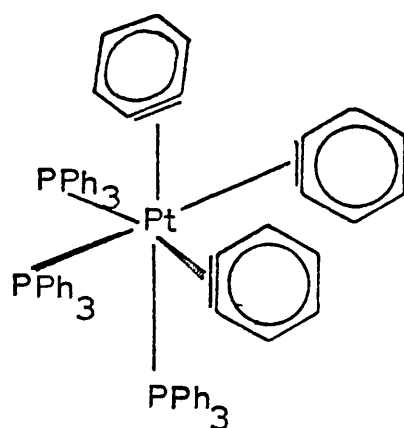
According to Meriwether the predominance (sometimes exclusive) of 1,2,4-trisubstituted benzenes was a serious shortcoming of a ' $\pi$  complex multicentre mechanism' where 1,3,5-trisubstituted benzenes would be expected to predominate on steric grounds.

Steric interaction of the methyl groups with triphenylphosphine in the trimerisation of methyl-substituted benzyne is shown below, but its importance in determining only the formation of 2,6,11-trimethyltriphenylene is uncertain.



The mechanism proposed above suggests a catalytic reaction in which tris(triphenylphosphine)platinum is regenerated. The reaction was complicated by a competing reaction to form the azo complex (49) and the yields of triphenylene based on platinum varied between 47% and 63%. However these yields do not truly reflect the situation as the active platinum species was being siphoned off during the reaction as compound (49).

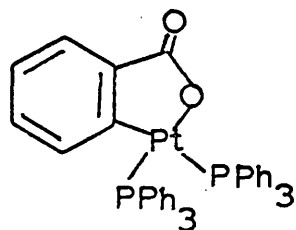
We have avoided the ' $\pi$  complex multicentre mechanism' in an explanation of the formation of triphenylene. The tri-benzyne intermediate (77) which this mechanism implies seemed unlikely when the properties of benzyne were considered.



(77)

This mechanism was even more doubtful now that metalocyclopentadienes have been isolated<sup>144</sup> and shown to be effective catalysts in acetylene cyclic trimerisation.

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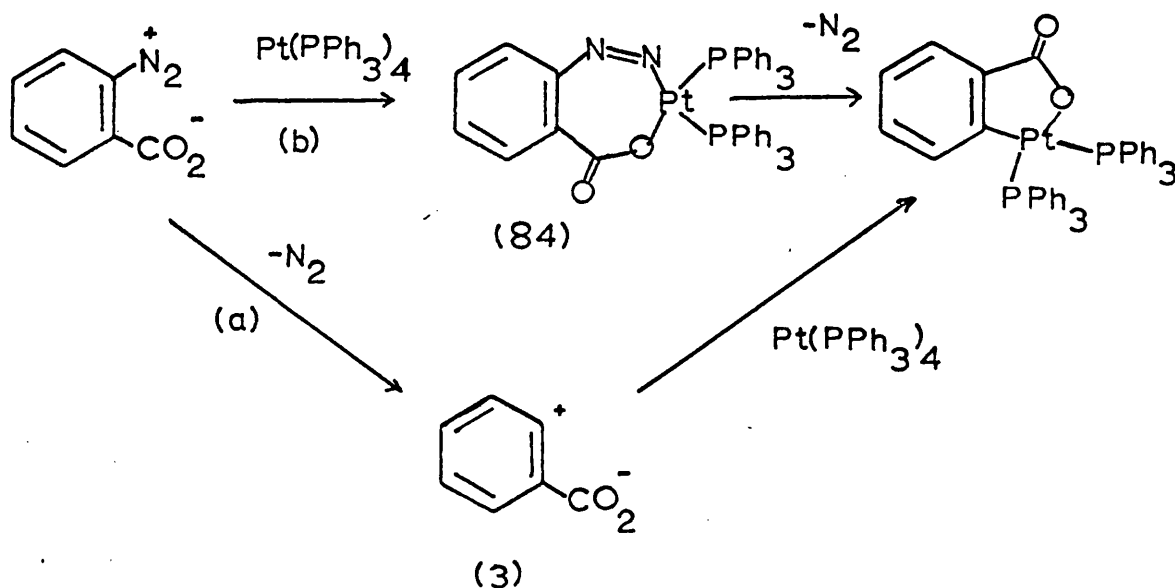
SECTION TWO. BENZENEDIAZONIUM-2-CARBOXYLATE.

(78)

When benzenediazonium-2-carboxylate was decomposed in the presence of the triphenylphosphine-platinum complex (46), a gas was evolved and a white precipitate of the carboxylato-platinum complex (78) separated. The carboxylato group in this compound was indicated in the i.r. spectrum by absorptions at 1655, 1305 and 1295  $\text{cm}^{-1}$ .

Gilchrist<sup>116</sup> reacted the carboxylato complex (78) with bromine. Hydrolysis of the reaction mixture gave *o*-bromobenzoic acid which supported the  $\sigma$  bond to platinum from a position ortho to the carboxylate group. He also showed that compound (78) did not decompose to benzyne on irradiation or by heating at temperatures up to 200°.

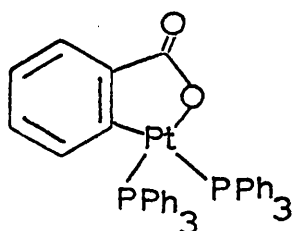
There were two possible reaction mechanisms for the formation of complex (78)



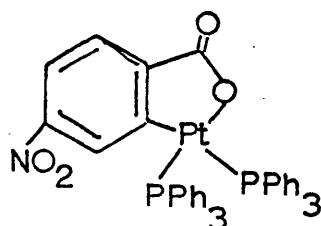
Mechanism (a).

Yaroslavsky<sup>17</sup> in an effort to prove that loss of nitrogen and carbon dioxide from benzenediazonium-2-carboxylate (2) was non concerted had shown that nickel carbonyl reacted with (2) and gave phthalic anhydride. He proposed that formation of phthalic anhydride was due to the reaction of nickel carbonyl with the intermediate (3).

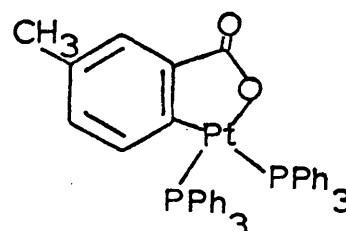
Reaction with the intermediate (3) to form the carboxylato-complex (78) might also occur with the triphenylphosphine-platinum complex (46). Attempts were made to labilize the



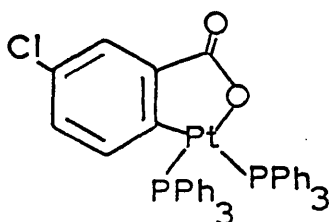
(78)



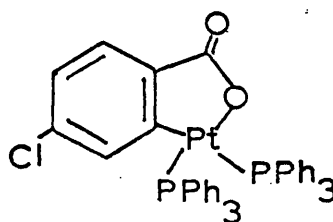
(79)



(80)



(81)

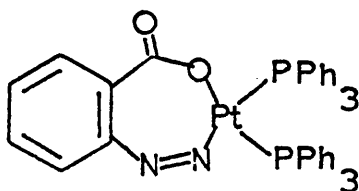


(82)

the carboxylate group in (3) by introducing substituents into the benzene ring<sup>136</sup>. In this way it was hoped to promote the formation of benzyne which might then be trapped (instead of (3)) by the triphenylphosphine-platinum complex (46). Electron withdrawing groups in a position para to the carboxylate group or the diazonium group should encourage loss of carbon dioxide or inhibit loss of nitrogen but this expectation was not reflected in the yields of (78) to (82). If benzyne was generated in the reaction then formation of biphenylene or triphenylene might have been expected, but they were not detected.

Mechanism (b).

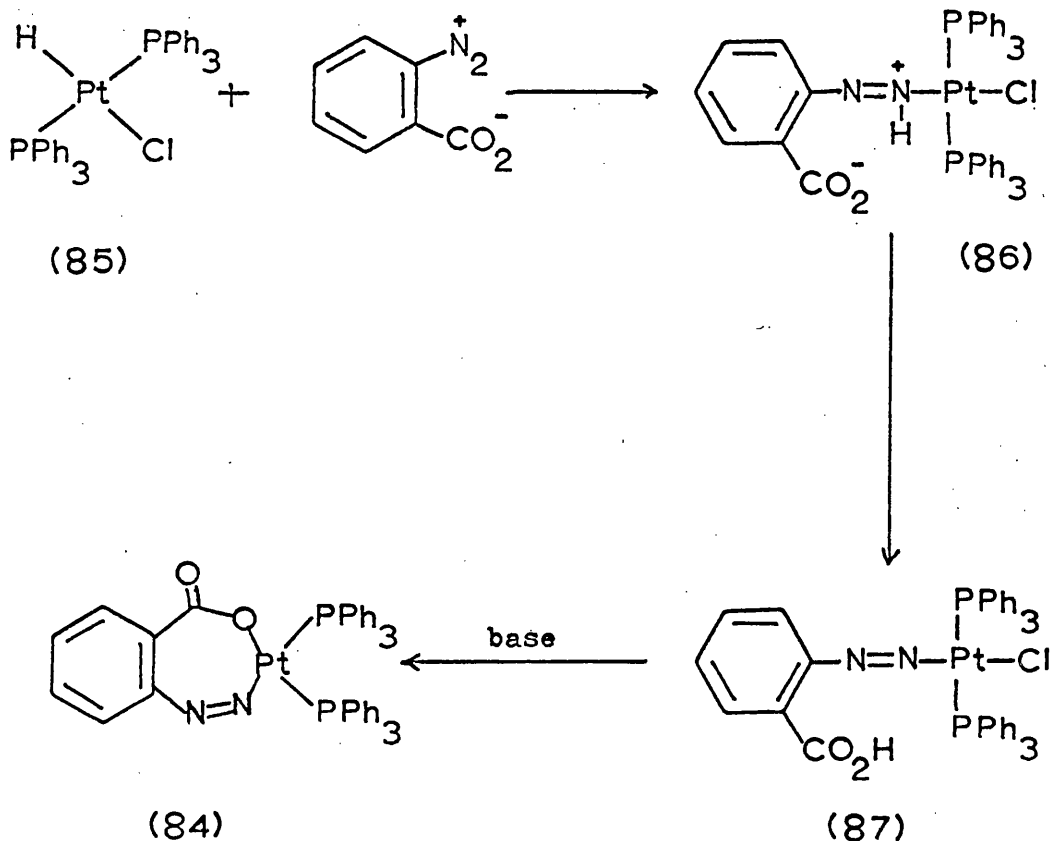
A transient red colouration in the reaction between benzenediazonium-2-carboxylate and the triphenylphosphine-platinum complex (46) suggested that an azo complex (84) was an intermediate. When the reaction was performed in cold



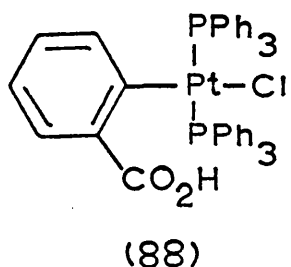
(84)

benzene in an attempt to isolate the intermediate (84) slightly higher yields of the carboxylato-platinum complex (78) were achieved and no intermediate (84) could be isolated. However Cook and Jauhal<sup>103</sup> prepared this complex using ethylene-bis(triphenylphosphine)platinum(0) and showed that it was thermally stable at temperatures upto 130°, when it lost nitrogen to form compound (78). Its i.r. spectrum showed the carboxylate function at 1630 and 1314 cm.<sup>-1</sup>. This result suggested that (84) could have been an intermediate in the reaction between benzenediazonium-2-carboxylate and the triphenylphosphine-platinum complex (46) but, that it was unstable in a system which contained free triphenylphosphine. This hypothesis was not investigated.

When we were involved in this work the results of Cook and Jauhal had not been published and we attempted to synthesize compound (84) to investigate its properties in order to find evidence to support our hypothesis that it was an intermediate in the reaction between benzenediazonium-2-carboxylate and the triphenylphosphine-platinum complex (46). trans-Hydrido-chlorobis(triphenylphosphine)platinum(II)<sup>105</sup> was treated with benzenediazonium-2-carboxylate to try to prepare the azocarboxylic acid derivative (87). A pink colouration developed when (2) was added to the trans-hydrido-chloro-platinum complex (85) but simultaneously a gas was evolved and the products isolated from

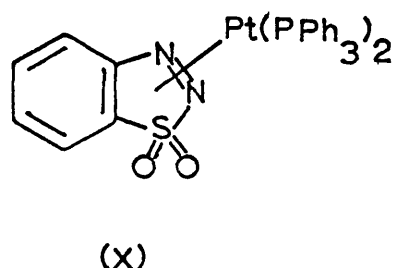
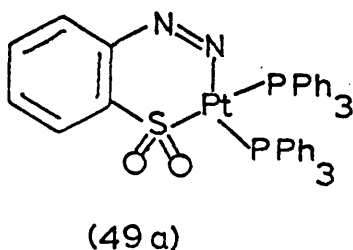
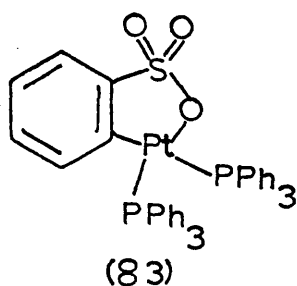


the reaction contained no nitrogen. Three compounds were formed which were partially separated by fractional crystallisation. A hydrido-platinum complex which appeared as an impurity was not characterised. The other two compounds both contained chlorine and a carboxylate group. A structure (88) was assigned to one of them, although the analysis was poor, on the basis of an hydroxyl stretching frequency in the i.r. spectrum at  $3300\text{ cm}^{-1}$ .





The reaction of the triphenylphosphine-platinum complex (46) with ortho-substituted benzenediazonium betaines to give platinum heterocyclic systems was thought to be a general reaction. This reaction was employed to prepare a compound which might support the assignment of structure (49a) to the azo complex formed by the reaction of 1,2,3-benzothiadiaazole-1,1-dioxide with the triphenylphosphine-platinum complex (46). Benzenediazonium-2-sulphonate was decomposed with (46) and gave the sulphato complex (83). Its i.r. spectrum had absorptions at



1274, 1160, 1128 and 1095  $\text{cm}^{-1}$  which were similar to those observed in the azo complex (49). However these similarities in the S=O stretching frequencies still do not eliminate the alternative structure (X) which might also have similar spectral characteristics to (83).

#### Decomposition of benzenediazonium-2-carboxylate in 1,2-dichloroethane.

Friedman<sup>153</sup> reported that refluxing 1,2-dichloroethane was the best system for benzynoid decomposition of benzenediazonium-2-carboxylate (2). Although Gompper<sup>16</sup> had shown that (2) decomposed in a non concerted fashion the reaction between (2) and the triphenylphosphine-platinum complex (46) was investigated in refluxing dichloroethane. Compound (78) (89%) was isolated but the yield of the methyl derivative (80) was not improved in this way. If refluxing dichloroethane did improve the decomposition of (2) to benzyne then the formation of biphenylene or triphenylene (from the reaction of benzyne with (46)) might have been expected, but they were not detected.

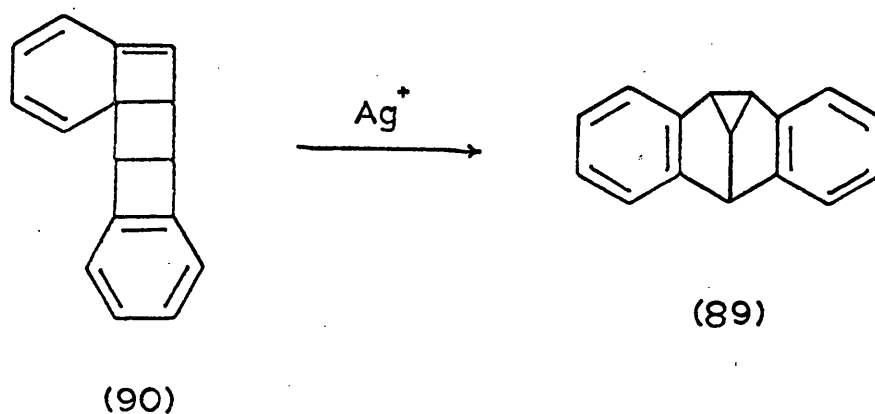
Under these conditions (2) on its own decomposed and gave biphenylene(5.5%).

The triphenylphosphine-platinum complex (46) and benzenediazonium-2-carboxylate (2) had to be added almost simultaneously to refluxing 1,2-dichloroethane if side reactions were to be avoided. Thus compound (46) reacted with dichloroethane and gave cis-dichlorobis(triphenylphosphine)platinum(II), and compound (78) could only be recovered in 68% yield from dichloroethane after 5 hr..

If the triphenylphosphine-platinum complex (46) was left in contact with dichloroethane for 5 min. before (2) was added, then the yield of the carboxylato complex (78) was reduced (48%) and was accompanied by the formation of a different carboxylato-platinum complex. This compound decomposed on recrystallisation to a compound that absorbed in the i.r. spectrum at 1640, 1630 and 1330  $\text{cm}^{-1}$ . The structure of this compound has not been elucidated but similarities to (84) in the i.r. spectrum indicated that the carboxylate function might form part of a six or seven-membered ring. There was no evidence from the mass spectrum that the solvent had been incorporated and no fragments contained chlorine.

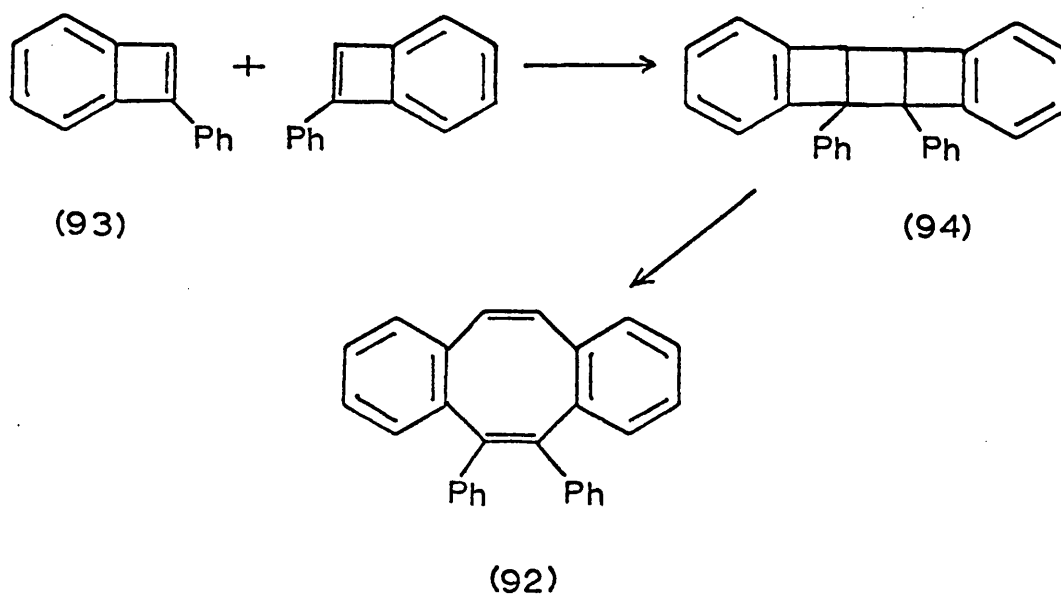
Friedman<sup>115</sup> demonstrated that thermal decomposition in benzene of benzenediazonium-2-carboxylate (2) contaminated with silver ions gave a different product distribution to a silver free reaction. He postulated a benzyne-silver complex to explain his results.

Silver ions have been shown to affect the course of other reactions. Pettit had explained the formation of the dimer (89)<sup>7</sup> from benzocyclobutadiene by a reaction in which cyclobutene ring opening in the intermediate (90) became thermally allowed<sup>151</sup> because of the presence of silver ions.



We investigated the reaction between benzyne and phenylacetylene<sup>51</sup> to see if there was any dramatic change in the product distribution in the presence of silver ions. The ratio of phenanthrene (91) to 5,6-diphenyldibenzocyclooctatetraene (92) did change from a silver free environment (1:1.64) to one contaminated with silver ions (1:3.8).

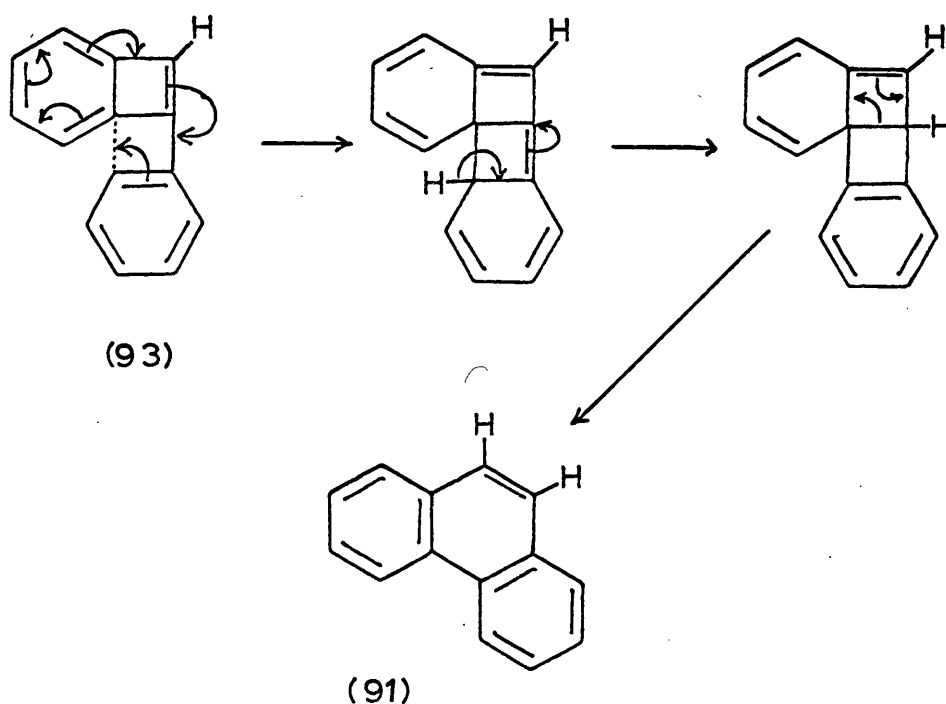
The formation of (92) was envisaged as a (2 + 2) cycloaddition of 1-phenylbenzocyclobutadiene (93) to itself in a dimerisation reaction. The proportion of this compound increased



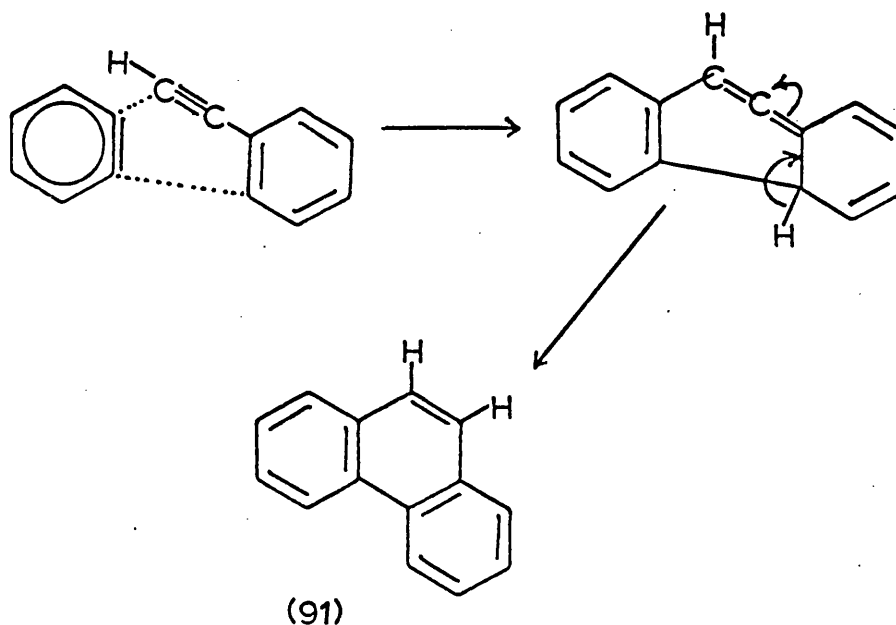
in the presence of silver ions. A concerted thermal (2 + 2) cycloaddition was not allowed by the Woodward Hoffmann Rules<sup>43</sup> but it may become an allowed process in the presence of silver ions which could transform the symmetry of the molecular orbitals involved.

There were two possible ways that phenanthrene could have been produced:

(i) rearrangement of (93) by an internal Diels Alder reaction,

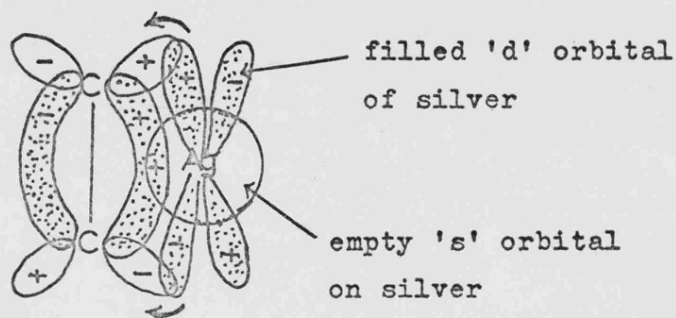


or (ii) Diels Alder (2 + 4) cycloaddition of benzyne to phenylacetylene.



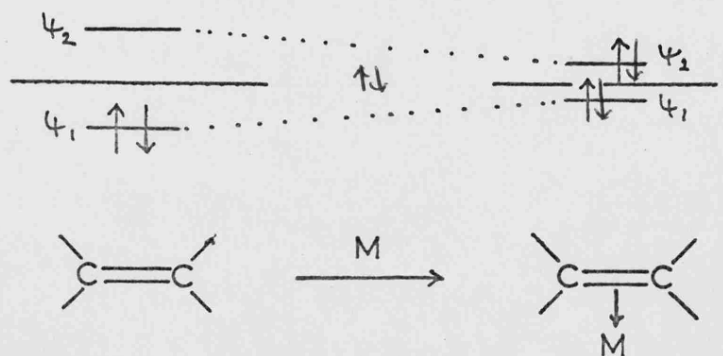
The proportion of phenanthrene decreased in the presence of silver ions. This would be expected as the highest occupied molecular orbital of benzyne in a benzyne-silver complex would not have the correct symmetry to participate in a concerted electrocyclic reaction with a diene.

Transformation of molecular orbital symmetries in these reactions could be explained by formation of  $\sigma\pi$  complexes in which electron density was transferred to  $\pi$  antibonding orbitals. The mechanism of this transfer is indicated in the diagram (95).

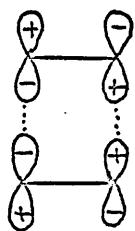


(95)

Silver (or any transition metal capable of forming  $\sigma\pi$  bonds) would therefore effect occupation of both  $\psi_1$  ( $\pi$  bonding) and  $\psi_2$  ( $\pi$  antibonding) orbitals. The complexed carbon - carbon



double bond should therefore be able to undergo concerted thermal cycloaddition reactions with external olefins to form cyclobutanes as this is now a symmetry allowed process (see diagram below). Stereospecific cycloaddition reactions of



Highest (partially) occupied orbital of the olefin complexed to the transition metal.

Lowest unoccupied orbital of the external olefin.

olefins to form four-membered rings have been observed<sup>43,154</sup> when u.v. light is responsible for excitation of electrons into  $\psi_2$ .

A similar argument could be used to explain the inhibition of Diels Alder addition in the formation of phenanthrene, as the highest occupied orbital of the dienophile (benzyne) would be antisymmetric.

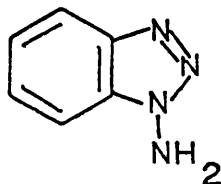
The high yields of biphenylene produced by the LTA oxidation of 1-aminobenzotriazole (5) have been explained by the formation of a high standing concentration of benzyne which dimerised stepwise to biphenylene. An interesting alternative explanation would be that a concerted (2 + 2) cycloaddition reaction proceeded due to the formation of a benzyne-lead(IV) complex. However Klanderman and Criswell<sup>39</sup> demonstrated that benzyne generated by oxidation of (5) had a reactivity and selectivity comparable to that of benzyne generated from other sources in a Diels Alder reaction with 1,4-dimethoxyanthracene.

The investigation of the reaction between benzyne and phenylacetylene gave an opportunity to compare methods of preparing benzenediazonium-2-carboxylate (2). Friedman's method<sup>115</sup> of preparing (2) free from silver ions by precipitation from tetrahydrofuran was extremely hazardous and was the most dangerous method to use. Compound (2) could be generated in situ safely and rapidly from benzenediazonium chloride and 1,2-epoxypropene. Preparation of (2) by Stiles' method<sup>15</sup> took about 3 hr. but it was isolated in a form which was safe to handle provided that it was kept damp with ether.

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### SECTION THREE. 1-AMINOBENZOTRIAZOLE.

Benzenediazonium-2-carboxylate and 1,2,3-benzothiadiazole-1,1-dioxide had been chosen as the benzyne precursors in the work described in Section One and Section Two because they fragmented to benzyne under mild conditions without the aid of external reagents. Benzyne precursors which needed fierce reaction conditions to generate benzyne (e.g. thermolysis, strong base) were not used as it was thought that these conditions would probably, either cause decomposition of the platinum complex (46), or destroy any benzyne-platinum complex formed.

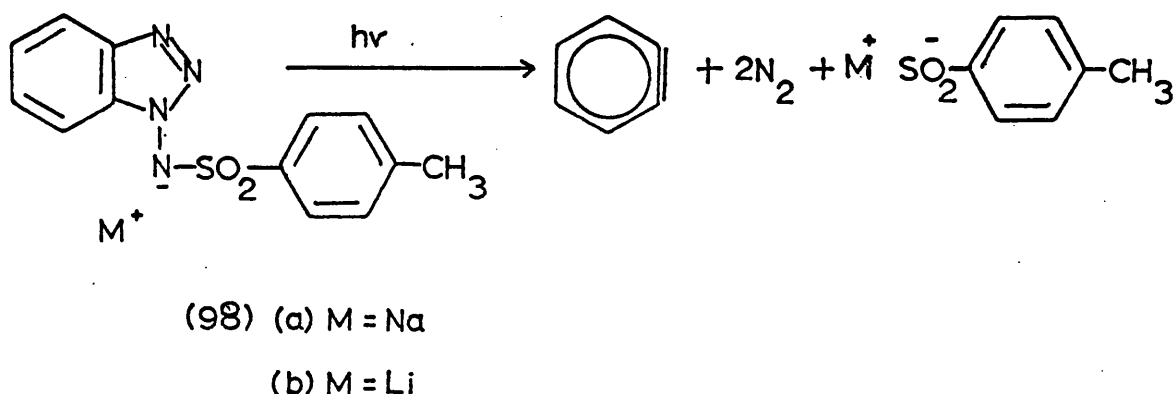
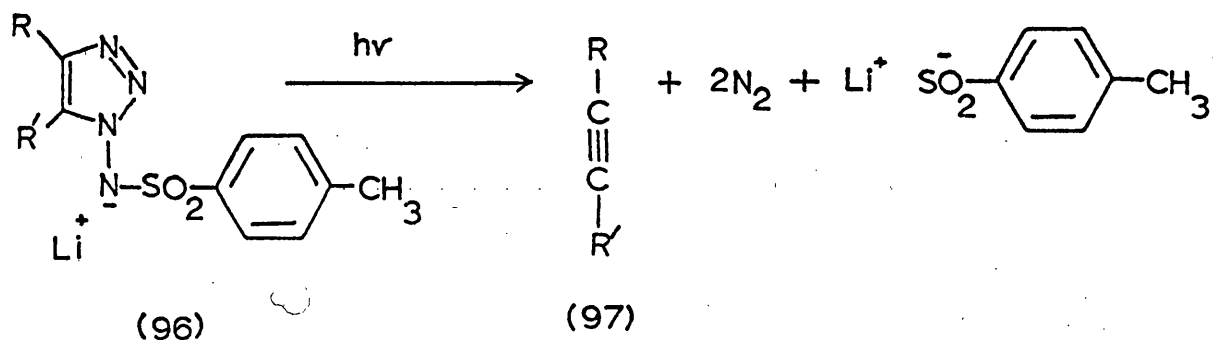


(5)

1-Aminobenzotriazole (5) was not an ideal benzyne precursor to use in this work as it required oxidising conditions to generate benzyne. These conditions might also oxidise the zerovalent platinum complex (46). Two new systems based on the 1-aminobenzotriazole nucleus were designed which fragmented to benzyne without the use of oxidising conditions. They were employed in an effort to prepare a benzyne-platinum complex from the triphenylphosphine-platinum complex (46).

#### 1. Alkali metal salts of (toluene-p-sulphonamido)benzotriazole.

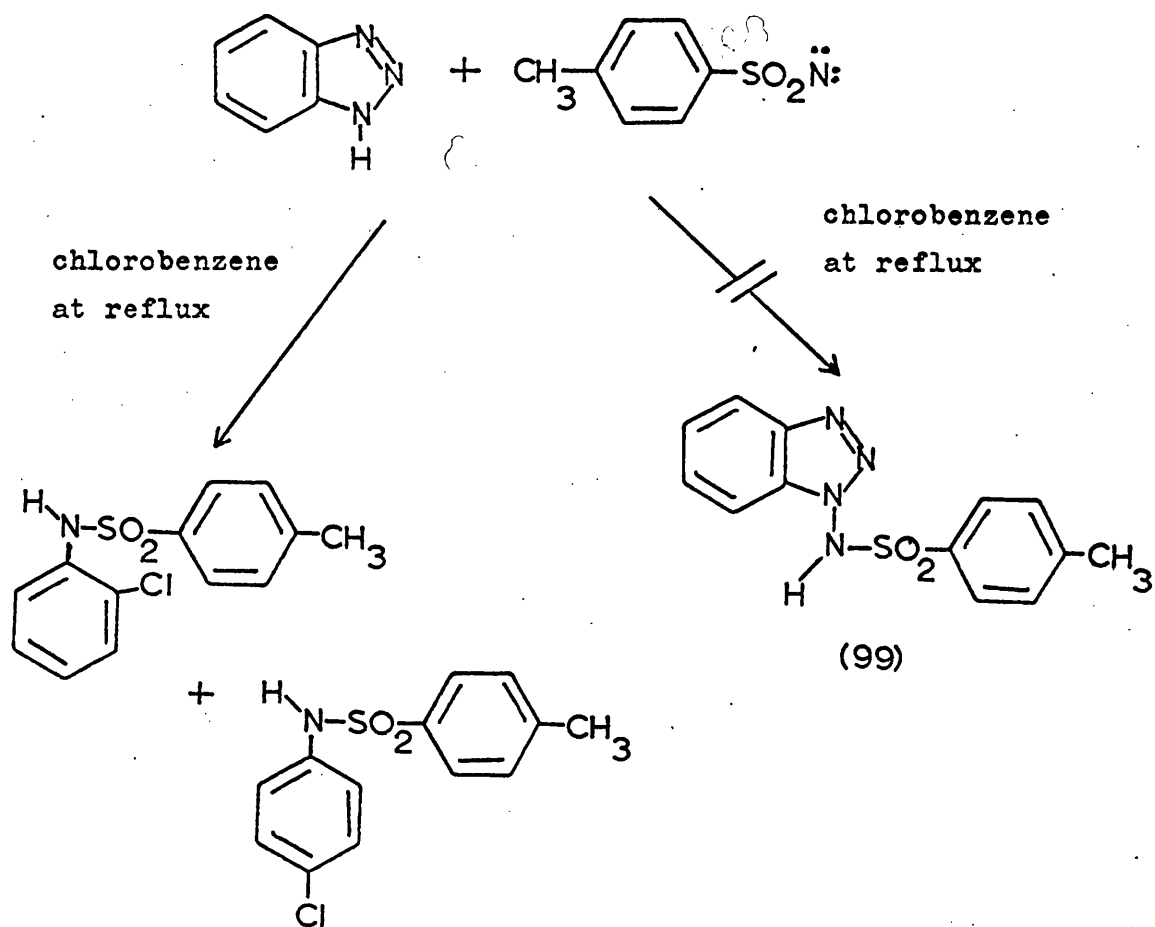
Willey<sup>73</sup> had shown that photolysis of the lithium salts (96) gave acetylenes (97) and by analogy it was thought that compound (98) would fragment to benzyne.



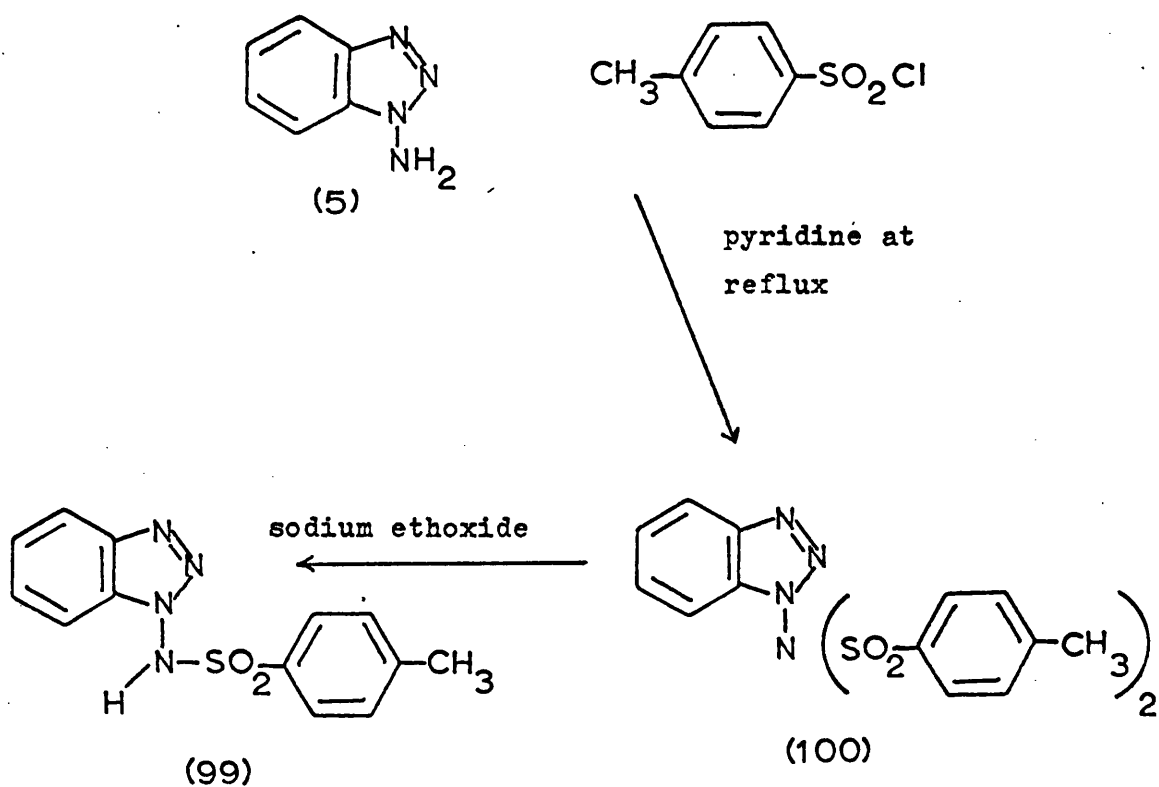
The lithium and sodium salts (98) were prepared by reaction of 1-(toluene-p-sulphonamido)benzotriazole (99) with butyllithium and sodium ethoxide. The salts were deliquescent and absorbed water from the atmosphere even during the short time required to take i.r. spectra.

We hoped to prepare the sulphonamide (99) from benzotriazole which was readily available. Attempted insertion of toluene-p-sulphonyl nitrene into the N-H bond of benzotriazole failed, giving products formed by insertion of the nitrene into the aromatic C-H bond of the solvent. They were identical to authentic specimens prepared from toluene-p-sulphonyl chloride and ortho- and para-chloroaniline.





The sulphonamide (99) was prepared from 1-aminobenzotriazole.



1-Aminobenzotriazole (5) was treated with two equivalents of toluene-*p*-sulphonyl chloride in pyridine and gave 1-(N,N-di(toluene-*p*-sulphonyl)amino)benzotriazole (100), which was hydrolysed to (99) by sodium ethoxide in ethanol. Treatment of the amine (5) with one equivalent of toluene-*p*-sulphonyl chloride gave a mixture of (99) and (100).

Photolysis of the salts (98a) and (98b) gave benzyne which was trapped by furan and tetracyclone (Table I).

Table I.

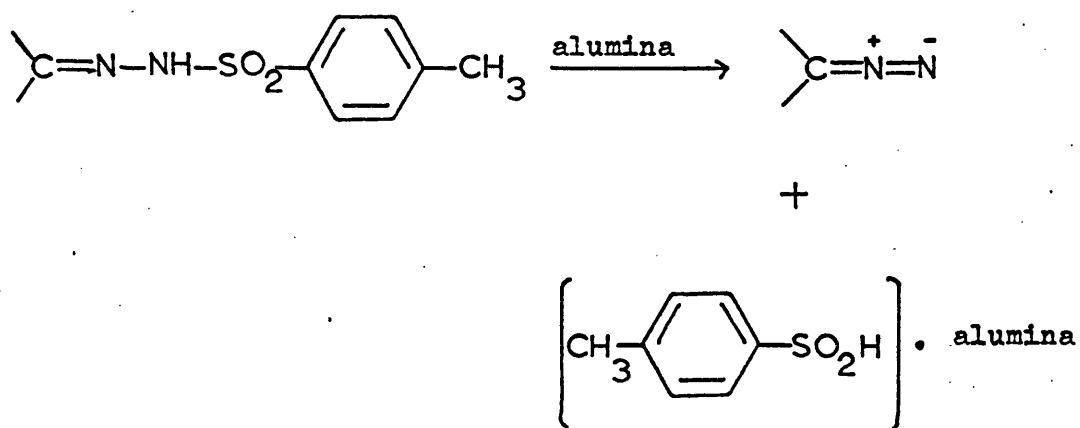
Method	Solvent	Time (hr.)	Trap	Adduct	Yield
(98a) ' <u>Rayonet</u> '	Dimethyl- sulphoxide	15	furan	$\alpha$ naphthol	18%*
' <u>Rayonet</u> '	Suspension in benzene	15	furan	no $\alpha$ naphthol	
(98b) ' <u>Rayonet</u> '	THF	20	furan	$\alpha$ naphthol	52%
' <u>Hanovia</u> '	THF	20	tetracyclone	tetraphenyl- naphthalene	22%
' <u>Hanovia</u> '	THF	20	furan	1,4-naphthalene - endoxide	17%

\* Compound (99) (20 - 30%) was recovered in this reaction.

It was essential that the reaction was homogeneous. Photolysis of a suspension of (98a) in benzene gave no benzyne-furan adduct. Photolysis of (98b) by the 'Rayonet' method in THF gave the best yield of a benzyne adduct. The isolation of  $\alpha$  naphthol (53) rather than 1,4-naphthalene endoxide (52)

in these reactions was due to the work up procedure in which the endoxide (52) in the crude reaction mixture was hydrolysed to (53) by hydrochloric acid. The endoxide (52) was isolated in one reaction to prove that it was the initial product formed.

Meinwald and Crandale<sup>155</sup> have shown that tosylhydrazones can be decomposed to diazoalkanes when they are eluted down a short column of basic alumina. The sulphonamide (99) was



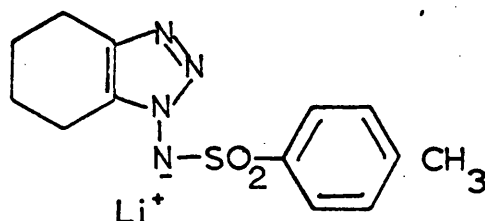
was treated in this way in the hope that it would fragment to benzyne, but no benzyne adduct with tetracyclone was detected and (99) was too strongly adsorbed onto the alumina to be recovered.

Decomposition of the lithium salt (98b) in the presence of tetrakis(triphenylphosphine)platinum(0) (46).

Compound (98b) was irradiated by the 'Rayonet' method in the presence of the triphenylphosphine-platinum complex (46) which was added to trap benzyne as a benzyne-platinum complex. When the reaction mixture was evaporated an oil was obtained which could not be crystallised. Chromatography gave a platinum complex which only showed absorptions in the i.r. spectrum due to triphenylphosphine ligands.

The suitability of these reaction conditions for isolating

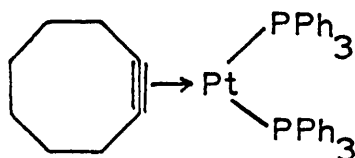
a benzyne-platinum complex was examined by generating cyclohexyne from compound (101) in a similar manner<sup>73</sup>. It was thought that



(101)

a cyclohexyne-platinum complex would have a similar reactivity to a benzyne-platinum complex and would have an absorption in the i.r. spectrum in the region  $2000 - 1600 \text{ cm}^{-1}$  to help in its identification. No complex was isolated which had an absorption in this region of the i.r. spectrum. A scanty, flocculent, yellow precipitate separated when ether was added to an ethanol solution of the reaction mixture, but its i.r. spectrum was poorly resolved and it was not characterised.

It was recognized that cyclohexyne in a cyclohexyne-platinum complex might have reacted with ethanol. Ethanol had proved to be a good solvent to promote the crystallisation of cyclooctynebis(triphenylphosphine)platinum<sup>136</sup> (102) and it was used in the reaction with the cyclohexyne precursor (101) for the same purpose after the original solvent (dioxan) had been removed.

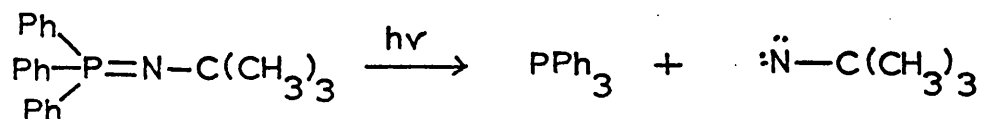


(102)

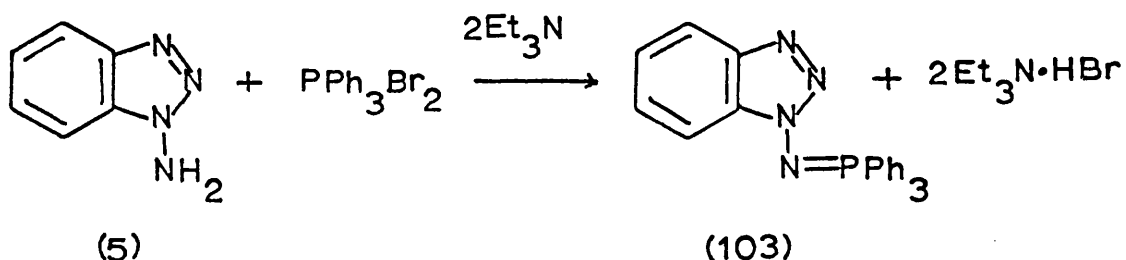
A cyclohexyne-platinum complex could not be isolated when compound (101) was irradiated in the presence of the triphenylphosphine-platinum complex (46) and it was therefore unlikely that a benzyne-platinum complex would be isolated by the photolysis of (98) under the same conditions also in the presence of compound (46). The preliminary experiment to prepare a benzyne-platinum complex in this way had failed to show any evidence at all of this complex and therefore this approach with (98) was not pursued further.

Iminophosphorane of 1-aminobenzotriazole.

Zimmer *et al*<sup>156</sup> had shown that photolysis of an iminophosphorane gave a nitrene and triphenylphosphine.



The iminophosphorane of 1-aminobenzotriazole (103) was prepared by the general method of Bestmann<sup>157</sup>. This involved treating 1-aminobenzotriazole (5) with triphenylphosphine dibromide (prepared *in situ*) in the presence of triethylamine to remove liberated hydrogen bromide. The osmometric molecular weight



decreased as the concentration increased which indicated that the iminophosphorane (103) was associated in solution. The mass spectrum showed the parent peak *m/e* 394 and a very strong peak at *m/e* 366 due to loss of nitrogen. The u.v. spectrum had absorptions at 312 nm. and 267.5 nm. which suggested that both the Sunlamp and medium pressure mercury lamps would emit radiation capable of being absorbed by this compound. Photolysis of other

1-substituted triazoles proceeded by loss of nitrogen<sup>158</sup> and the mass spectrum suggested that this might occur with the iminophosphorane (103), but there was no conclusive evidence for this and photolysis by the 'Sunlamp', 'Rayonet' and 'Hanovia' methods all gave benzyne adducts with tetracyclone and furan (Table II).

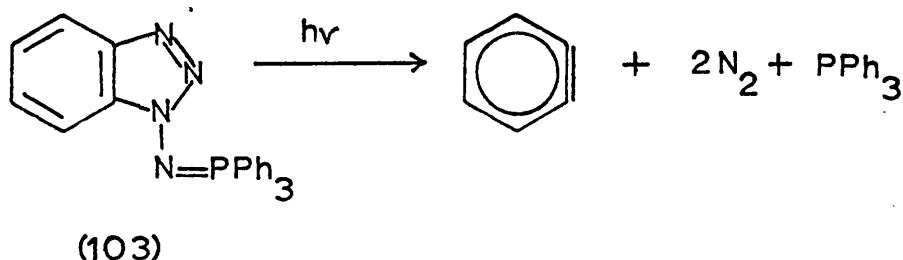


Table II.

Method	Solvent	Time (hr.)	Trap	Adduct	Yield
'Rayonet'	THF	20	furan	Mixture of 1,4-naphthalene endoxide and naphthol	9%
	Benzene	20	tetracyclone	tetraphenyl-naphthalene*	10%
'Sunlamp'	Benzene	20	tetracyclone	tetraphenyl-naphthalene	23%
'Hanovia'	THF	12	tetracyclone	tetraphenyl-naphthalene	13.6%
	Benzene	12	tetracyclone	tetraphenyl-naphthalene**	25%
	Benzene	20	furan	1,4-naphthalene endoxide	16.5%

\* Compound (103) (20%) was recovered.

\*\* Biphenyl (3%) was also formed.

In all experiments triphenylphosphine, triphenylphosphine oxide and recovered tetracyclone were isolated.

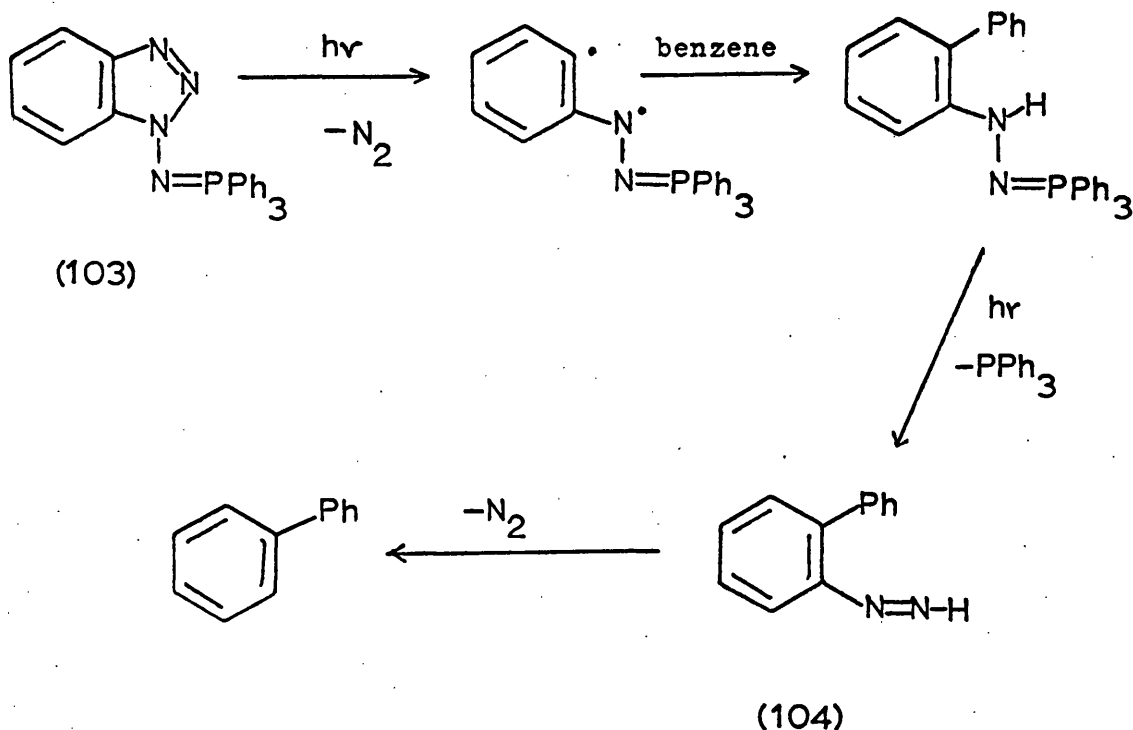
Tryptcene was not formed when anthracene was used as the benzyne trap. Anthracene was dimerised under the conditions of the reaction to dianthracene (67%). The 'Hanovia' method, although it gave the best yields of benzyne adducts, also promoted side reactions. In two experiments, when anthracene and tetracyclone were used as benzyne traps, biphenyl (11%, 3%) was formed. Tetracyclone was also decomposed and in one experiment a reduction product, 2,3,4,5-tetraphenylcyclopentenone (9.5%) was isolated. Table II also indicated the superiority of benzene over THF as a solvent in these reactions.

#### The origin of biphenyl from the photolysis of the iminophosphorane(103)

The appearance of biphenyl, even in the presence of a benzyne trap, led to an investigation of the photolysis of the iminophosphorane (103) on its own. Irradiation of (103) in benzene by the 'Sunlamp' and 'Hanovia' methods gave biphenyl in 13% and 18.5% yield respectively. In toluene however, biphenyl was not isolated; the solvent had been incorporated into the new hydrocarbon as was shown by an absorption in the NMR spectrum at  $\tau$ 7.62 (assigned to benzyl protons). The yield of biphenyl in these reactions was calculated on the basis that only one phenyl ring originated from the iminophosphorane (103).

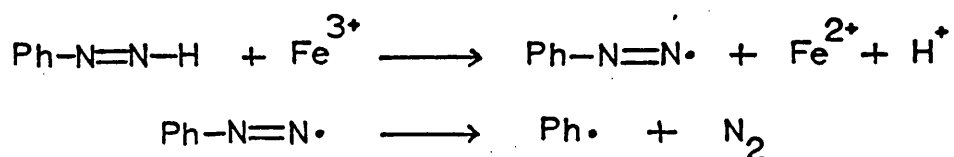
Biphenyl could have been formed by three possible reaction pathways:

1. The work of Burgess et al<sup>158</sup> suggested that biphenyl could be produced in a process which involved initial loss of nitrogen from the iminophosphorane (103).

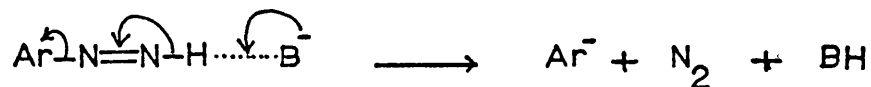


The last stage involves loss of nitrogen from the diimide (104) without formation of a biphenyl radical which would have reacted with the solvent to give terphenyl derivatives.

Substituted diimides decomposed by a radical mechanism<sup>159</sup> when they were generated under oxidising conditions -

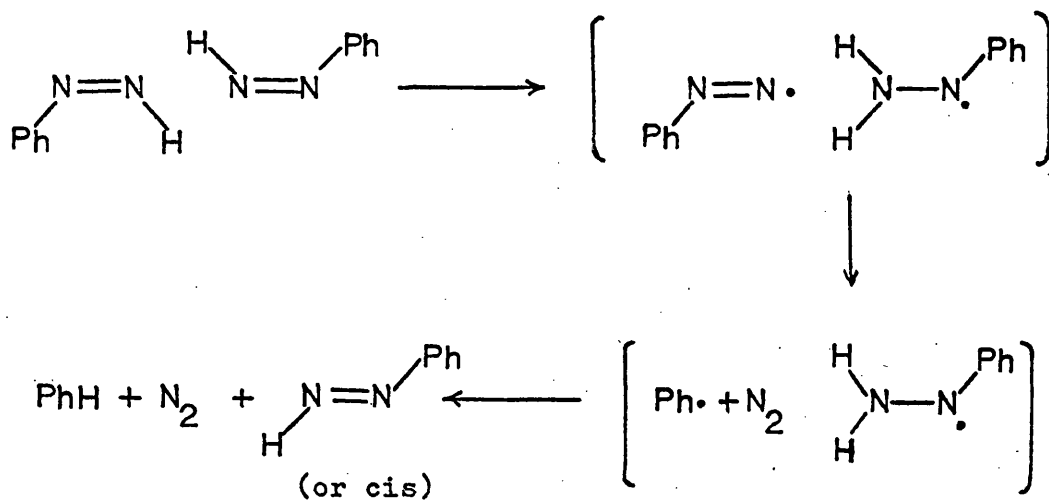


- and under basic conditions they decomposed via a carbanion<sup>160</sup>.



These modes of decomposition were not applicable to the decomposition of the diimide (104) under the conditions that it was generated. Huang and Kosower<sup>161</sup> suggested a bimolecular reaction of phenyldiimide with itself in a solvent cage as a mechanism for the decomposition of phenyldiimide.



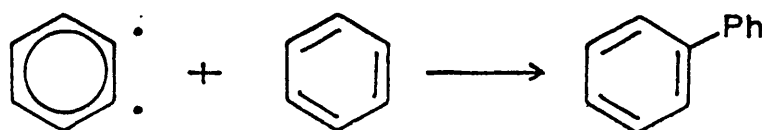


This mechanism could be employed to explain the decomposition of the diimide (104) to biphenyl.

2. Triphenylphosphine could be a source of phenyl radicals under these reaction conditions<sup>162,163</sup> and therefore offered an alternative explanation for the formation of biphenyl.

Triphenylphosphine gave biphenyl in only 4% yield when it was irradiated by the 'Hanovia' method and therefore its photolysis cannot explain the much higher yields of biphenyl (18%) isolated when the iminophosphorane (103) was irradiated. It is possible, however, that the triphenylphosphine residue in the iminophosphorane (103) might provide a better source of phenyl radicals (and hence a higher yield of biphenyl) than free triphenylphosphine.

3. The formation of biphenyl (45%) from the photolysis of the benzyne precursor, 2-iodophenylmercuric iodide<sup>26</sup> had been explained by Hoffmann<sup>13</sup> as a reaction of the benzyne diradical (105) with the solvent. The spectrum obtained during the



(105)

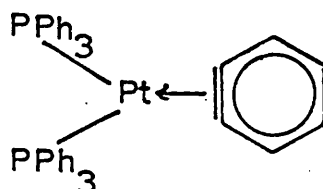
flash photolysis of benzenediazonium-2-carboxylate<sup>50</sup> was explained on the basis that a transient excited state of benzyne (e.g. a diradical) was formed.

The generation or excitation of benzyne to (105) when the iminophosphorane (103) was photolysed might offer another explanation for the formation of biphenyl in this reaction.

Photolysis of the iminophosphorane (103) in the presence of tetrakis(triphenylphosphine)platinum(0) (46).

The photolysis of the iminophosphorane (103) in the presence of furan and tetracyclone had shown that it was a benzyne precursor. No triphenylene was found when the iminophosphorane (103) was irradiated in the presence of the triphenylphosphine-platinum complex (46) which suggested that: either 1. No benzyne-platinum intermediates were formed.

or 2. Benzyne was generated slowly from the iminophosphorane (103). The benzyne-platinum complex initially formed (71) had little opportunity therefore, to react with



(71)

additional molecules of benzyne to give triphenylene, before it decomposed under the reaction conditions.

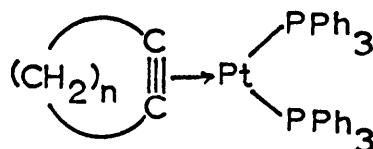
Photolysis by the 'Rayonet' method (20 hr.) gave a red coloured solution which gave no crystalline compounds when it was reduced in volume. A platinum complex precipitated when the solvent was exchanged for ethanol but it only showed absorptions in the i.r. spectrum due to triphenylphosphine ligands.

Photolysis by the 'Sunlamp' method (20 hr.) followed by evaporation to small bulk gave triphenylphosphine oxide, probably due to the reaction of adventitious oxygen with triphenylphosphine. The filtrates did not contain any compound which absorbed in the i.r. spectrum between 2000 - 1600  $\text{cm}^{-1}$ .

Tetracyclone was decomposed when the 'Hanovia' method was used and the stability of a benzyne-platinum complex to these conditions was doubtful especially as there was no evidence for its formation when the 'Rayonet' and 'Sunlamp' methods were used. Tolanbis(triphenylphosphine)platinum (36) was recovered in only 50% yield when it was irradiated for 12 hr. by the 'Hanovia' method which reinforced the doubts about the stability of a benzyne-platinum complex to photolysis.

In view of these doubts it was decided to test this approach to a benzyne-platinum complex by attempting to prepare cyclohexyne and cycloheptyne-platinum complexes using a similar method. These cycloalkynes were very reactive and had properties which were similar to benzyne and therefore their platinum complexes might also show similarities in reactivity to a benzyne complex.

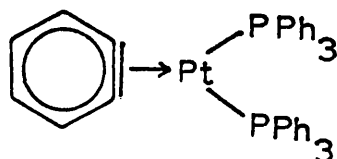
It was also anticipated that experimental results with these cycloalkynes would be easier to interpret. It was reasonable to expect that cycloalkyne-platinum complexes (106) would have absorptions in the i.r. spectrum in the region 2000 - 1600  $\text{cm}^{-1}$  as they still had isolated and strained carbon - carbon double bonds. This idea was substantiated by



(106)

the i.r. spectrum of the cyclooctyne complex (102) which did have an absorption in this region. The presence of characteristic absorptions in the i.r. spectrum would have made identification

of cycloalkyne-platinum complexes much easier than a benzyne-platinum complex (71) whose spectral characteristics were uncertain.

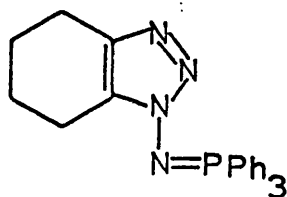


(71)

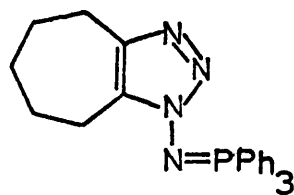
A benzyne-platinum complex (71) would not necessarily have an absorption in the i.r. spectrum in the region 2000 - 1600  $\text{cm}^{-1}$  as the carbon - carbon double bond in this complex is part of an aromatic system. The absence of such an absorption in the i.r. spectrum when benzyne was generated in the presence of the triphenylphosphine-platinum complex (46) was therefore not conclusive evidence for the absence of a benzyne-platinum complex. It was therefore possible that some complexes, which have been dismissed as phosphine-platinum complexes, were in fact benzyne-platinum complexes. The only argument that can be brought forward to support the idea that a benzyne-platinum complex would have a characteristic absorption in the i.r. spectrum was a suggestion by Coulson<sup>72</sup> that benzyne would be stabilized by partial bond fixation in the aromatic system.

If cyclohexyne- and cycloheptyne-platinum complexes could be isolated then the same experimental conditions might achieve the isolation of a benzyne-platinum complex.

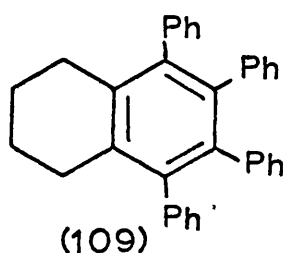
The iminophosphoranes (107) and (108) were prepared in the same way as the iminophosphorane of 1-aminobenzotriazole. When they were photolysed they gave cyclohexyne and cycloheptyne which were trapped with tetracyclone as 1,2-tetramethylene-3,4,5,6-tetraphenylbenzene (109) and 1,2-pentamethylene-3,4,5,6-tetraphenylbenzene (110).



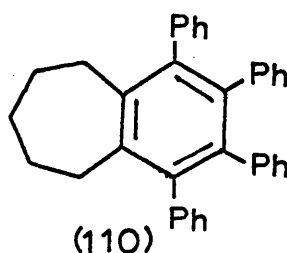
(107)



(108)



(109)



(110)

Table III.

Compound	Method	Solvent	Time (hr.)	Cycloalkyne adduct	Yield
(107)	' <u>Sunlamp</u> '	THF	24	(109)	7%
	' <u>Hanovia</u> ' with pyrex filter	THF	48	(109)*	3%
	' <u>Hanovia</u> '	THF	12	(109)	11.5%
(108)	' <u>Hanovia</u> '	Benzene	20	(110)**	36%

\* Starting material (36%) was recovered.

\*\* Biphenyl (7.7%) was isolated.

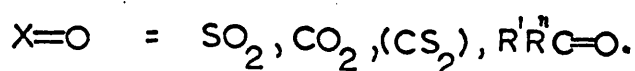
The pyrex filter was used with the 'Hanovia' method in an effort to prevent decomposition of tetracyclone and to see if good yields of cycloalkyne adduct (109) were formed. Tetracyclone (80%) was recovered, but the yield of cycloalkyne adduct (109) was poor even after irradiation for 48 hr.. The high energy radiation had been cut off by the pyrex filter and if this modified 'Hanovia' method had worked well, it would have been employed when the triphenylphosphine-platinum complex (46) was used as the cycloalkyne trap. In this way it was hoped that decomposition of the alkyne-platinum complex would have been avoided.

The low yields of the cycloalkyne adducts with tetracyclone and the instability of the tolan-platinum complex (36) to photolysis did not promise that a cycloalkyne-platinum complex would be isolated. Photolysis of the cyclohexyne precursor (107) in the presence of the platinum complex (46), followed by evaporation to dryness of the reaction mixture, gave no compounds which absorbed in the i.r. spectrum in the region 2000 - 1600 cm.<sup>-1</sup>. The failure to detect a cyclohexyne-platinum complex in this experiment suggested that photolysis conditions were not suitable for the preparation of a benzyne-platinum complex.

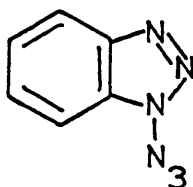
One other significant result in the photolysis of these cycloalkyne precursors was the formation of biphenyl when the iminophosphorane (108) was irradiated in benzene. This supported the hypothesis, mentioned before, that biphenyl formation in the photolysis of the iminophosphorane (103) was a consequence of the decomposition of triphenylphosphine or the triphenylphosphine residue in the iminophosphorane. However the yield of biphenyl (7.7%) in the reaction with (108) could not account for the much higher yields of biphenyl (18%), when the iminophosphorane (103) was photolysed, especially if the same mechanism of formation accounted for the yields in both reactions. The two other mechanisms for biphenyl formation in the photolysis of (103) might contribute therefore to the overall yield of biphenyl in this reaction.

Other experiments with the iminophosphorane of 1-aminobenzotriazole.

It was decided to make use of the properties of iminophosphoranes<sup>164</sup> to attempt the synthesis of other derivatives of 1-aminobenzotriazole which might decompose to benzyne on photolysis in an even better yield than the iminophosphorane (103).



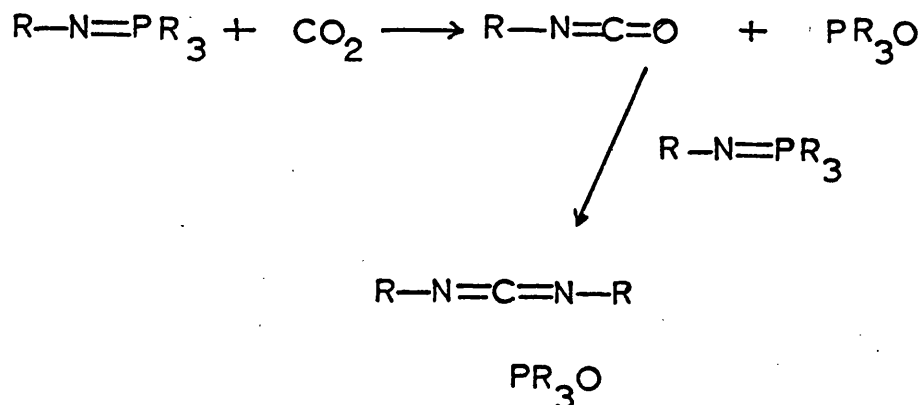
There was no record in the literature that nitrous oxide ( $X=O = N_2O$ ) reacted with iminophosphoranes to give azides, but compound (103) was treated with nitrous oxide in an attempt to prepare 1-azidobenzotriazole (111).



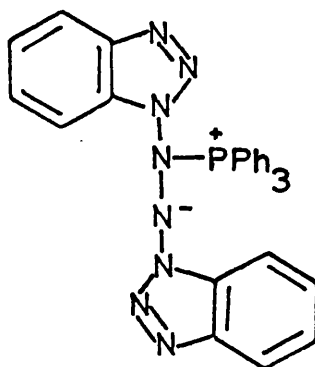
(111)

The reaction was followed by solution i.r. spectroscopy but there was no change in the i.r. spectrum except for that due to the absorption of nitrous oxide in the solvent, and the iminophosphorane (103) was recovered (82%). If 1-azidobenzotriazole (111) had been formed in the reaction, it was reasonable to assume that on photolysis it would decompose readily to benzyne. Photolysis of a solution of the iminophosphorane (103), as nitrous oxide was bubbled through it, gave lower yields of the benzyne-tetracyclone adduct than photolysis of a solution of (103) without nitrous oxide. It was therefore unlikely that 1-azidobenzotriazole was formed in the reaction.

The formation of isocyanates from iminophosphoranes is a well known reaction<sup>165</sup> but is complicated by formation of carbodiimides which result from the reaction of the initially formed isocyanate with iminophosphorane.



In the reaction with the iminophosphorane (103), carbon dioxide was passed through a chloroform solution of (103) so that the reaction could be followed by solution i.r. spectroscopy. Any subsequent reaction to carbodiimide would then be seen. No absorptions in the i.r. spectrum due to the isocyanate group developed and *p*-toluidine which normally forms insoluble ureas with isocyanates gave no insoluble material when it was added to the reaction mixture. However a new compound (112) was formed. There are doubts about the structure of this compound but it was assigned structure (112) because this structure fitted best the available evidence.



(112)

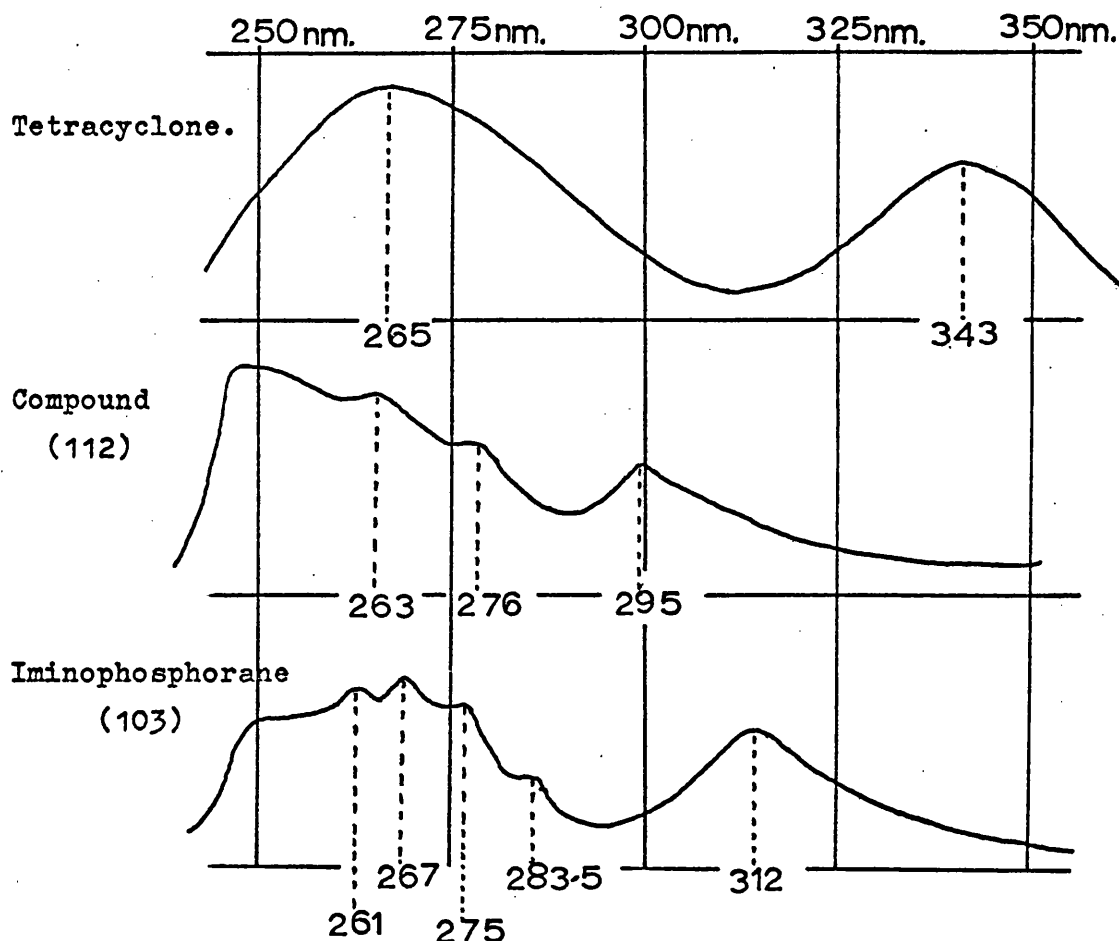


The absorption of the P=N bond<sup>141</sup> in the u.v. spectrum of compound (103) occurred at 261, 267 and 275 nm. and there were similarities to this absorption pattern in the spectrum of compound (112) which suggested that there was a similar but not identical chromophore in this compound. The i.r. spectrum confirmed the presence of triphenylphosphine (1440 and 1100 cm.<sup>-1</sup>) but the appearance of strong absorptions at 1600 and 1585 cm.<sup>-1</sup> could not be accounted for on the basis of structure (112). Compound (112) had a mass spectrum very similar to that of the iminophosphorane (103), but its parent peak was at m/e 366 instead of m/e 394 which suggested that it was a compound derived by loss of nitrogen from (103). This was not supported by analysis which showed a very high nitrogen content (25%) and indicated a stoichiometry consisting of two 1-aminobenzotriazole nuclei and one triphenylphosphine species. Osmometric molecular weight in chloroform (590  $\pm$  30) on two different concentrations was in agreement with this stoichiometry (M 526).

Compound (112) was prepared in better yield when a solution of the iminophosphorane (103) and tetracyclone, saturated with carbon dioxide, was irradiated by the 'Hanovia' method for 4 hr..

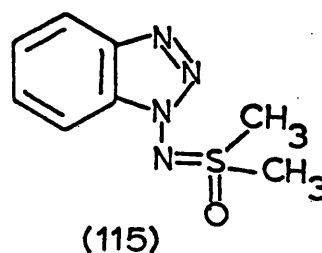
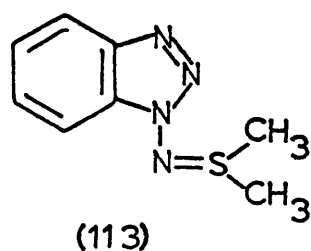
These conditions were found quite accidentally. It had been argued that if 1-isocyanatobenzotriazole was formed in the reaction it should decompose to benzyne on photolysis. The conditions which gave good yields of compound (112) were designed originally to examine the yield of the benzyne-tetracyclone adduct formed during the photolysis of the iminophosphorane (103) in the presence of carbon dioxide. The yield of tetraphenyl-naphthalene (8%) was the same as that which would have been expected if carbon dioxide had been omitted (Table II). The sides of the reaction vessel were encrusted with colourless needle-like crystals of compound (112).

The u.v. spectra of the iminophosphorane (103), compound (112) and tetracyclone.



This compound was not formed without tetracyclone, but tetracyclone was not incorporated into the compound. Compound (112) reacted further after prolonged irradiation so that, although tetracyclone was behaving as a radiation filter, it had a 'window' in its absorption spectrum which allowed radiation capable of being absorbed by compound (112) to penetrate into the solution.

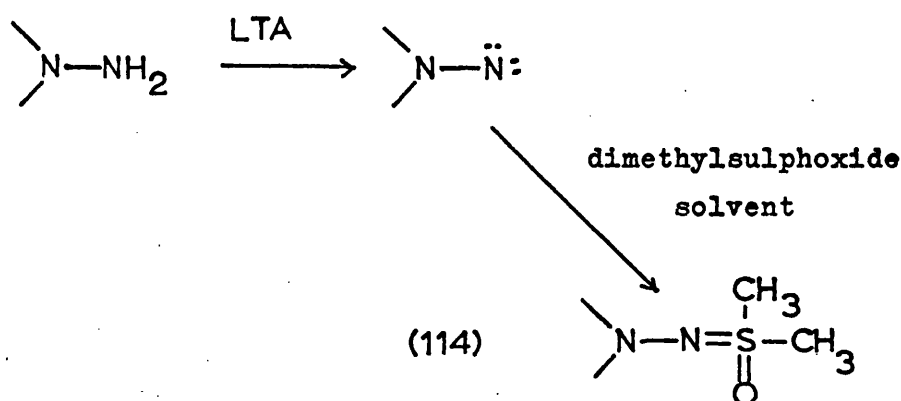
Two other reactions of the iminophosphorane (103) were investigated briefly. Thermal decomposition of (103) in dimethylsulphoxide at 180° in an effort to prepare the sulphimine of 1-aminobenzotriazole (113) gave an oil from which (103) (50%) was recovered and no other compound was isolated.



An attempt to decompose the iminophosphorane (103) to benzyne by pyrolysis failed. A melt of (103) and tetracyclone was heated at  $240^{\circ}$  for 30 min., but no tetraphenylnaphthalene was detected in the products.

Another possible route to the sulphimine (113) was explored. 1-Aminobenzotriazole (5) was treated with dimethylsulphur dibromide in the presence of triethylamine which by analogy with the preparation of the iminophosphorane (103) was expected to give (113), but the amine (5) (42%) was recovered.

Rees *et al*<sup>166</sup> have shown that oxidation of N-amino compounds in dimethylsulphoxide gave 1:1-nitrene-dimethylsulphoxide adducts (sulphoximines) (114). No similar adducts



were isolated<sup>116</sup> when 1-aminobenzotriazole was oxidised in dimethylsulphoxide, presumably because its nitrene fragmented to benzyne too quickly to react intermolecularly. Another route to the sulphoximine (115) similar to the one tried for the sulphimine (113) was attempted. Dimethylsulphoxide was treated with bromine and gave the unreported dimethylsulphoxide

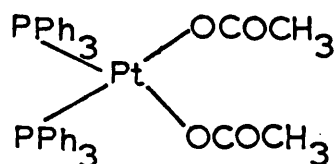
dibromide as a red oil. Addition of triethylamine and the 1-aminobenzotriazole (5) gave no compound which could have been the sulphoximine (115). Chlorine was known to oxidise sulphoxides to sulphones, but when chlorine replaced bromine in this reaction, 1-aminobenzotriazole was recovered in 72% yield. This might have been due to the rapid hydrolysis of dimethylsulphoxide dichloride by adventitious moisture, leaving the amine (5) unreacted.

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Oxidation of 1-aminobenzotriazole.

Difficulty was foreseen in the use of 1-aminobenzotriazole as a benzyne precursor in the preparation of benzyne-platinum complexes from zerovalent platinum because of the possibility of a competing oxidation of the platinum. However, compound (5) was such a good benzyne precursor, especially when it was oxidised by LTA, that its use was thoroughly investigated.

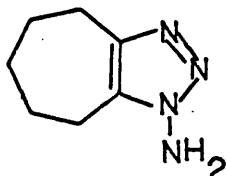
Oxidation of 1-aminobenzotriazole (5) by lead tetraacetate, LTA, in the presence of the triphenylphosphine-platinum complex (46), gave cis-diacetatobis(triphenylphosphine)platinum(II) (116).



(116)

No triphenylene was isolated. The high standing concentration of benzyne, generated by the oxidation of the amine (5), should have resulted in triphenylene formation if any benzyne-platinum complex (71) was present. Biphenylene, which was detected in this reaction, was a normal product from the oxidation of compound (5) and therefore it was thought that the ability of the platinum(0) complex (46) to form triphenylene was destroyed when it was oxidised to the diacetato-platinum(II) complex (116).

This hypothesis was checked by an experiment in which cycloheptyne was generated by the oxidation of 1-amino-4,5-pentamethylenetriazole (27) with LTA in methylene chloride at  $-78^{\circ}$ . Experiments had shown that cycloheptyne had a lifetime



(27)

of 2 min. at this temperature<sup>73</sup> and so the triphenylphosphine-platinum complex (46) was added immediately after gas evolution had ceased in an effort to avoid any reaction of LTA with compound (46). A yellow platinum complex, which only showed absorptions in the i.r. spectrum due to triphenylphosphine ligands, was precipitated when the solvent was exchanged for benzene. Cis-diacetatobis(triphenylphosphine)platinum(II) (116) separated when the filtrate was reduced in volume. The triphenylphosphine-platinum complex (46) might have reacted with acetic acid generated from LTA during the oxidation and therefore was prevented from forming a cycloheptyne complex.

There was an alternative reason why a cycloheptyne-platinum complex had not been found and why no triphenylene was produced in the oxidation of 1-aminobenzotriazole. The isolation of both compounds depended upon the stability of  $\sigma$  bonds under the reaction conditions. Acetic acid formed during the reaction could have destroyed these bonds<sup>167</sup>. When the oxidation of 1-aminobenzotriazole was repeated in the presence of potassium carbonate to remove acetic acid, triphenylene was still not isolated and in this case, failure must be due to the inability of the platinum complexes involved in triphenylene formation to withstand some other conditions of the reaction.

From these initial results it was apparent that either a different oxidant or a different platinum complex would have to be used if a benzyne-platinum complex was to be prepared from 1-aminobenzotriazole.

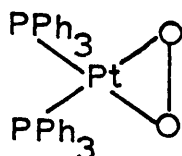
Different oxidants for 1-aminobenzotriazole.

The use of a different oxidant, with the triphenylphosphine-platinum complex (46) as the benzyne trap, was investigated first. A metal oxide would have to be used as the oxidant since an organic compound (e.g. peroxide) would almost certainly have reacted with the platinum complex (46).

When silver(II) oxide was used to oxidise 1-aminobenzotriazole (5) it gave biphenyl in 6% yield and biphenyl was still isolated (7%) in the presence of the platinum complex (46). Friedmann<sup>115</sup> had noticed that benzyne, liberated in the presence of silver ions, gave biphenyl. He had postulated a benzyne-silver complex which reacted with the benzene solvent to explain the formation of biphenyl. In the oxidation experiments described above, the silver residues (which might have contained a benzyne-silver complex), were filtered off and treated with nitric acid in the hope that an organic residue which could be ascribed to the reaction of benzyne with aqueous nitric acid would be isolated. Only a trace of a brown oil was extracted, however, and the origin of biphenyl in these experiments was not investigated further.

The use of insoluble metal oxides in this oxidation was necessarily slow and inefficient as the oxidation could only occur on the surface of the oxide. These conditions might allow the triphenylphosphine-platinum complex (46), which was also susceptible to oxidation, to decompose and therefore a different type of oxidant was tried.

The reactivity of oxygenbis(triphenylphosphine)platinum (117)



(117)

as an oxidant<sup>168</sup> are well known and it was tried as an oxidant for 1-aminobenzotriazole (5) in the hope that its reduced form would then be able to trap the benzyne which had been liberated. The oxygen-platinum complex (117) was made by passing oxygen through a solution of the triphenylphosphine-platinum complex (46). Oxygen was passed through a solution of (46) and the amine(5) in order to prepare the oxygen complex (117) in situ. After three hours a scanty precipitate of carbonatobis(triphenylphosphine) platinum(II) separated due to the reaction of adventitious carbon dioxide with the oxygen complex (117). This material was filtered off and a dark brown solid precipitated by the addition of ethylacetate. It only had absorptions in the i.r. spectrum due to triphenylphosphine ligands and was rejected; chromatography of the filtrates gave no hydrocarbons.

When 1-aminobenzotriazole (5) was heated with the oxygen complex (117), which had been prepared separately, there was again no evidence for benzyne-platinum intermediates and no biphenylene, triphenylene or biphenyl were detected.

It was decided to stop attempts to isolate a benzyne-platinum complex from a system in which new oxidants were used as their ability to oxidise 1-aminobenzotriazole was in doubt.

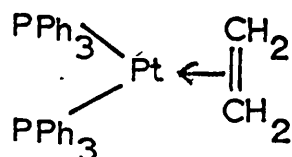
#### Different platinum complexes as benzyne traps.

Platinum complexes which contained a  $\sigma$ -bond might be more stable to oxidation. The platinum 'd' electrons had been used to make the  $\sigma$  bond and were therefore not available in an oxidation reaction, thus tolanbis(triphenylphosphine)platinum (36) might be more stable to oxidation than the triphenylphosphine platinum complex (46).

When the tolan complex was used as a benzyne trap in the oxidation of 1-aminobenzotriazole (5), it was recovered in 33% yield, which supported the hypothesis that  $\sigma$  complexes were more resistant to oxidation than the triphenylphosphine-platinum complex (46) which had not been recovered in a similar experiment. No triphenylene was recovered however, but potassium carbonate had not been used in this reaction to remove acetic acid which

could have destroyed any benzyne-platinum complexes formed.

Ethylenebis(triphenylphosphine)platinum (118) was another complex which had been prepared before in this work and found to trimerise benzyne to triphenylene under suitable conditions (Section One). It was now used in the oxidation of 1-amino-benzotriazole (5) as a benzyne trap. The amine (5) was oxidised by a deficiency of LTA in the presence of the ethylene complex (118). There was a vigorous gas evolution which probably



(118)

indicated that benzyne was being generated, but no triphenylene or biphenylene was detected. The complete absence of both these compounds suggested that a stable benzyne-platinum complex might have been formed, and an attempt was made to isolate it by chromatography on alumina.

It had been found by trial and error that chromatography of platinum complexes was more effective if they were absorbed onto the support by placing a concentrated solution of the mixture to be separated onto the top of the column (Method B). Irreversible adsorption or decomposition occurred when the solution was adsorbed by evaporation onto the support with a rotary evaporator.

When the reaction with the ethylene complex (118) was chromatographed (Method B), carbonatobis(triphenylphosphine) platinum was isolated. It was thought that this might be evidence that a platinum(0) species had survived the reaction conditions. The carbonate complex could have been formed by reaction of a platinum(0) species with atmospheric carbon dioxide and oxygen during column chromatography. If platinum(0) had really survived the reaction conditions and the carbonate complex



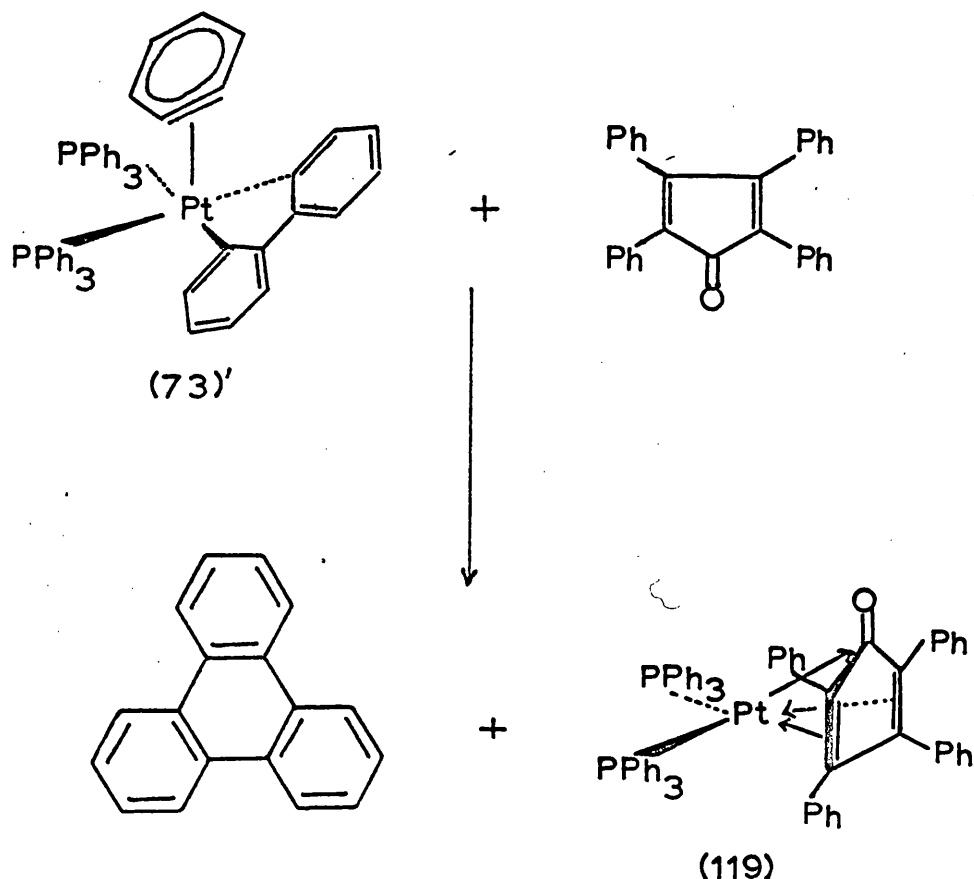
was not formed by some other reaction, then a benzyne-platinum complex could have been formed by reaction of benzyne with platinum(0). No triphenylene was formed which suggested that the benzyne-platinum complex had been decomposed under the reaction conditions to give unrecognized products.

Potassium carbonate had been omitted from this initial reaction but when it was present, traces of biphenylene and triphenylene (3.5%) were found in the products. This was the first indication that a benzyne-platinum complex had been formed in the reaction. A phosphine-platinum complex (15 mg.) which only showed absorptions in the i.r. spectrum due to triphenylphosphine ligands was also isolated by chromatography.

In another experiment, tetracyclone was added after gas evolution had ceased (10 min.), in an effort to trap the benzyne in the benzyne-platinum complex, as the benzyne-tetracyclone adduct. The adduct was not detected but the yield of triphenylene increased dramatically to 26%. Similarly 2,6,11-trimethyltriphenylene was prepared (13%) from 5-methyl-1-aminobenzotriazole, but here it was accompanied by the benzyne-tetracyclone adduct, 6-methyl-1,2,3,4-tetraphenylnaphthalene (2%). It was attractive to consider that the tetracyclone adduct was derived from a benzyne-platinum complex but an alternative origin was possible. Potassium carbonate, which had been added to react with liberated acetic acid, coagulated during the addition of LTA. It was possible therefore that the benzyne-tetracyclone adduct was formed due to the reaction of free benzyne liberated slowly by LTA imprisoned in the coagulated mass of potassium carbonate.

The role of tetracyclone had to be examined more carefully as its presence apparently increased the yield of triphenylene. A tetracyclonebis(triphenylphosphine)platinum complex (119) was isolated from both of the reactions described above. It was made (43%) unambiguously by the reaction of tetracyclone with the ethylene complex (118).

One explanation of its role was that it competed for coordination sites in the benzyne-platinum complex (73)'. The benzyne-platinum complex (73)' was formed in the same way as described in Section One. It was likely that a four-electron



donor was necessary as the displacing ligand because when triphenylphosphine was used in place of tetracyclone it failed to increase the yields of triphenylene. In this experiment, triphenylene was detected (t.l.c.) before the addition of triphenylphosphine and so there must be some tendency for the benzyne-platinum complex (73)' to decompose spontaneously to triphenylene even in cold benzene. The benzyne-platinum complex (73) had been assumed to decompose in this way when it was generated from 1,2,3-benzothiadiazole-1,1-dioxide and the triphenylphosphine-platinum complex (46) in refluxing ether - benzene. However the poor yields of triphenylene which were isolated when tetracyclone was omitted from the reaction indicated that the benzyne-platinum complex (73)' could decompose in other ways to give products which went unrecognized.

These experiments indicated that the benzyne-platinum complex (73)' was stable for at least 10 min. in solution. In one experiment therefore, bromine was added instead of tetracyclone in order to substantiate the structure of the complex. This treatment should have given o-dibromobenzene and 2,2'-dibromobiphenyl if the structure of the complex was correct.

o-Dibromobenzene was isolated from the reaction mixture but it could have originated by a reaction of bromine with the excess 1-aminobenzotriazole (5) in the reaction mixture. A control experiment showed that the amine (5) was oxidised by bromine to dibromobenzene (45%). The yield of dibromobenzene based on the unoxidised amine (5) in the solution of the benzyne complex (73)' was 88% but it was dangerous to assign the greater yield of the bromo compound here to a reaction of bromine with the benzyne complex (73)'. The activity of the LTA used in this reaction was uncertain and therefore the actual excess of amine (5) was unknown. (It is the general practice in this Laboratory to add a slight excess (10%) of LTA in order to effect complete oxidation of an N-amino compound)

As well as o-dibromobenzene, a mixture of other compounds was formed which was not isolated when the amine (5) was oxidised by bromine. This mixture (13 mg., approx. 4%) was shown to contain four compounds when it was examined by t.l.c.. No attempt was made to separate the mixture as a mass spectrum would identify any bromine containing compound. A very strong peak in the mass spectrum at  $m/e$  232 indicated the presence of a monobromobiphenyl compound (M 232), a peak at  $m/e$  310 indicated a dibromobiphenyl compound (M 310) and a peak at  $m/e$  387 indicated a tribromobiphenyl fragment. This was a very significant result as it supported the reaction mechanism for triphenylene formation and the structure of the benzyne complex (73)'.

This experiment supported the existence of the benzyne complex (73)' in solution and attempts were made to investigate its spectral characteristics with a view to confirming or disproving the idea that a benzyne-platinum complex would have a characteristic absorption in the i.r. spectrum.

The reaction was repeated using methylene chloride as a solvent so that samples of the solution could be taken and their i.r. spectrum examined. The solution i.r. spectrum showed an absorption at  $1710\text{ cm.}^{-1}$  (shoulder  $1755\text{ cm.}^{-1}$ ) due to free acetic acid, but there were no other absorptions in the  $2000 - 1600\text{ cm.}^{-1}$  region. One of the criteria for the presence of a benzyne-platinum complex, which had been used in the earlier work, was therefore in doubt and a benzyne-platinum complex might have been overlooked or perhaps dismissed as a triphenylphosphine-platinum complex.

After 15 min., when the solution had been examined in this way, tetracyclone was added and the reaction mixture chromatographed (Method B) on basic alumina. A small quantity of tetraphenylnaphthalene was isolated. The formation of free benzyne in the way described before was unlikely because the oxidation in methylene chloride had been very rapid and the potassium carbonate had not coagulated. It was therefore possible that tetraphenylnaphthalene had been produced by the reaction of tetracyclone with benzyne in the platinum-benzyne complex (73)'.

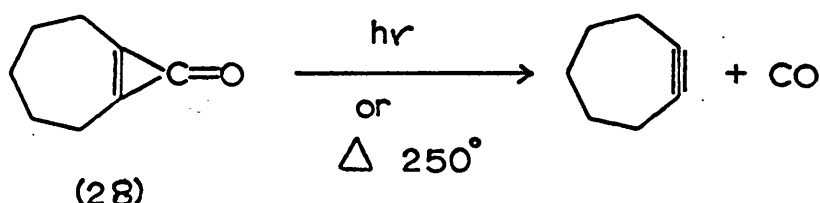
Several attempts were made to isolate the benzyne complex (73)' by fractional crystallisation as it did not survive chromatography. None of these attempts were successful and lower yields of triphenylene (6%) were isolated when the solution was eventually treated with tetracyclone.

The reaction conditions which had given good yields of triphenylene from the 1-aminobenzotriazole were used in an experiment in which the triphenylphosphine-platinum complex (46) replaced the ethylene complex (118). No triphenylene was detected which indicated that there was a significant difference in the ability of the two complexes to survive the conditions of the reaction.

These reaction conditions and the ethylene complex (118) were used in an attempt to prepare cycloheptynebis(triphenylphosphine)platinum from the oxidation of 1-amino-4,5-pentamethylenetriazole (27). No crystals precipitated from the

filtrate after the lead and potassium salts had been removed and as a last resort ethanol was added to the solution to encourage crystallisation. It was hoped that a cycloheptyne complex would be stable to ethanol like the cyclooctyne complex (102). A brown solid which only showed absorptions in the i.r. spectrum due to triphenylphosphine ligands was isolated. It was unlikely that this compound was a cycloheptyne complex as it would be expected to show a characteristic absorption in the i.r. spectrum.

Cycloheptenocyclopropenone (28) gave cycloheptyne when it was thermolysed at  $250^{\circ}$  <sup>127</sup>. It was found that the cyclopropenone (28) also gave cycloheptyne when it was photolysed by the 'Hanovia' method at room temperature. No attempt was made



to prepare a cycloheptyne-platinum complex by irradiating (28) in the presence of the triphenylphosphine-platinum complex (46), as the experiments with the iminophosphorane (107) indicated that alkyne-platinum complexes were unstable to photolysis.

Tris(triphenylphosphine)chlororhodium(I) <sup>128</sup> was used to decarbonylate the cyclopropenone (28). The decarbonylation was performed in the presence of the platinum complex (46) which was added to trap the liberated cycloheptyne. trans-Bis(triphenylphosphine)carbonylchlororhodium(I) was precipitated and proved that decarbonylation had occurred. A compound which could have been a cycloheptyne complex ( $\nu_{\max} 1655 \text{ cm}^{-1}$ ) was isolated from the filtrates but it decomposed when attempts were made to purify it by recrystallisation. A brown solid which showed absorptions in the i.r. spectrum due to triphenylphosphine ligands was also isolated.

Conclusion.

The cyclooctyne-platinum complex (102) has been made by the addition of cyclooctyne to tetrakis(triphenylphosphine) platinum(0). The conditions under which cyclohexyne, cycloheptyne and benzyne were prepared either destroyed the platinum complex which had been added to complex with them or destroyed the alkyne-platinum complexes which were formed.

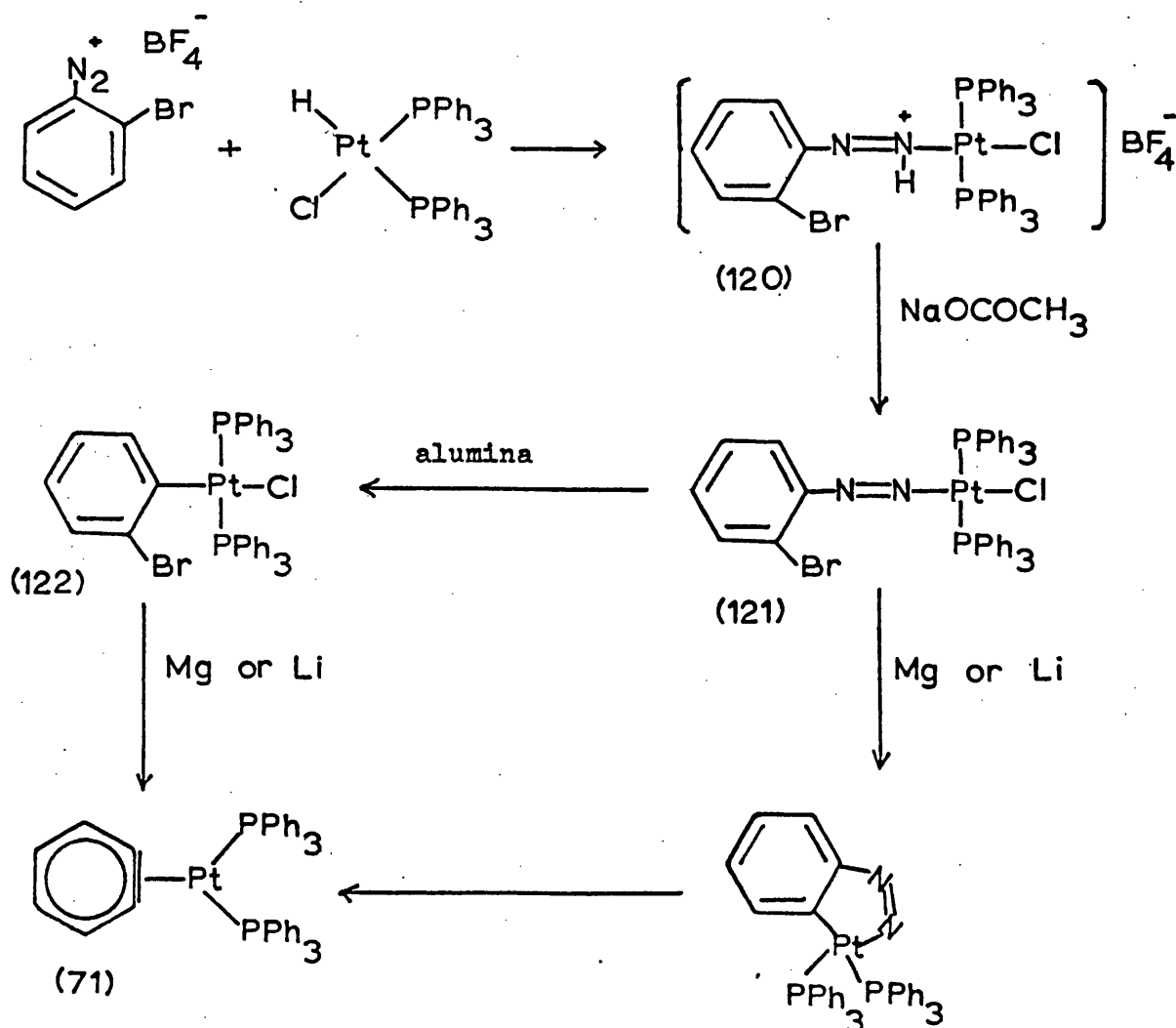
A benzyne-platinum complex (73)' was not isolated although it existed for a short time in solution.

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SECTION FOUR. MISCELLANEOUS.1. Other routes to a benzyne-platinum complex.

The Grignard reagent prepared from *o*-fluorobromobenzene and magnesium was used as a benzyne precursor. The triphenylphosphine-platinum complex (46) was added to a solution of the Grignard at 0°. A phosphine-platinum complex was isolated. This complex only showed triphenylphosphine ligands in the i.r. spectrum, but because the spectral properties of a benzyne-platinum complex were in doubt, it too might be a benzyne-platinum complex. However when this complex was recombined with the filtrate and refluxed with furan no benzyne adduct was detected. The absence of any benzyne adduct suggested that there was no benzyne-platinum complex in solution.

An attempt was made to synthesize a benzyne-platinum complex by the scheme proposed below.

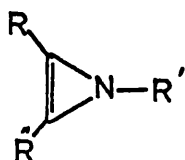
Proposed route to a benzyne-platinum complex.

The complexes (120), (121) and (122) were prepared in exactly the same way that Parshall<sup>139</sup> had made other arylazo and arylplatinum complexes. Only small quantities of the arylplatinum complex (122) were isolated when the arylazo-platinum complex (121) was treated on an alumina column. The behaviour of this compound with magnesium and lithium was not investigated because of insufficient material.

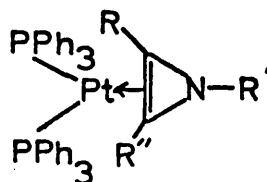
The arylazoplatinum complex (121) was recovered unchanged when it was treated with magnesium in THF, however a gas was evolved with lithium after the reaction had been initiated with a small piece of potassium. A precipitate, which was contaminated with excess of lithium, appeared. Ethanol was added to destroy the excess of lithium. The yellow precipitate which remained was filtered off and consisted of lithium salts and a platinum complex which only showed absorptions in the i.r. spectrum due to triphenylphosphine ligands. No crystalline compounds could be isolated from the filtrate.

## 2. An attempt to stabilize an antiaromatic compound.

Rees *et al.*<sup>169</sup> have shown that nitrenes reacted with acetylenes and gave 1(H)azirines (123). It was thought that these antiaromatic systems might be stabilized if the carbon-carbon double bond in the azirine ring was complexed to platinum by a  $\sigma\pi$  bond. In this way the antiaromatic ( $4n$ ,  $n=1$ ) azirine ring would be converted in the complex (124) to the more stable aziridine ring system.



(123)



(124)

The acetylene molecule in the reaction was complexed to platinum so that a  $\sigma\pi$  bond was already made. Tolanbis-(triphenylphosphine)platinum was used as a source of acetylene



(tolan) and the nitrene generated in its presence by the LTA oxidation of N-aminophthalimide. The reaction mixture was filtered to remove lead diacetate and hexane was added to the filtrate until precipitation occurred. Three different compounds were isolated but in such small amounts that analysis was not possible. All three compounds had absorptions in the i.r. spectrum due to a carbonyl group and triphenylphosphine ligands.

The reaction had given a number of products and not as had been hoped a major compound which was a stabilized azirine. The reaction was therefore not investigated further. The use of potassium carbonate in these LTA oxidation reactions was not appreciated at this time and its presence might have given more encouraging results.

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## Reactions of Some Benzyne Precursors and Cyclo-octyne with a Zerovalent Platinum Complex

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COOK and JAUHAL have reported attempts to stabilize benzyne by co-ordination to platinum.<sup>1</sup> In their conditions, the benzyne precursors, 1,2,3-benzothiadiazole 1,1-dioxide (Ia)<sup>2</sup> and benzenediazonium-2-carboxylate (IIIa),<sup>3</sup> were trapped by the zerovalent platinum species, bis(triphenylphosphine)(ethylene)platinum(0), before they could decompose. Our similar experiments with tetrakis(triphenylphosphine)platinum(0)<sup>4</sup> confirm and extend their observations and show that the reactions of benzyne, generated in the presence of the latter complex, are greatly altered.

Compound (Ia) and its 5-methyl derivative (Ib)<sup>5</sup> react readily with  $(\text{Ph}_3\text{P})_4\text{Pt}$  in benzene at 5° to give complexes (IIa), m.p. 177–179° (79%) and (IIb), m.p. 177–181° (71%). The spectral data for (IIa) are the same as those reported;<sup>1</sup> additional evidence for structure (IIb) is provided by the <sup>1</sup>H n.m.r. spectrum which integrated correctly and showed a singlet at  $\tau$  8.3.

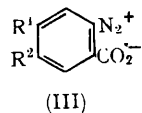
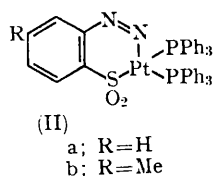
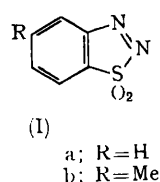
Unlike Cook and Jauhal,<sup>1</sup> we find that complex

(IIa) does generate benzyne on photolysis. When (IIa) was irradiated (300 w sunlamp for 24 hr.) in a mixture of furan and tetrahydrofuran the benzyne adduct, 1,4-dihydronaphthalene endoxide, m.p. 53–54° (9%) and its rearrangement product, 1-naphthol (14%) were isolated. Complex (IIa) is thus a new, stable, benzyne precursor, requiring only irradiation for its decomposition. However, no adduct could be obtained by the thermolysis of (IIa) in furan.

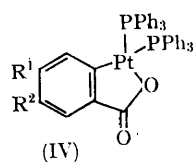
When the reaction between complex (Ia) or (Ib) (3 mmol.) and  $(\text{Ph}_3\text{P})_4\text{Pt}$  (1 mmol.) was carried out in a mixture of ether and benzene at 35°, the reaction took a different course. Triphenylene, m.p. 192–196° [38% based on (Ia)] or 2,6,11-trimethyltriphenylene,<sup>6</sup> m.p. 132–133° [(35% based on (Ib)] was isolated by chromatography on alumina. Complex (Ia) usually gives small yields of biphenylene, and no triphenylene, when decomposed thermally in solution.<sup>2</sup>

No triphenylene was formed when (Ia) was

similarly decomposed in the absence of the platinum complex but in the presence of triphenylphosphine.



a; R<sup>1</sup> = H, R<sup>2</sup> = H  
b; R<sup>1</sup> = H, R<sup>2</sup> = NO<sub>2</sub>  
c; R<sup>1</sup> = H, R<sup>2</sup> = Me  
d; R<sup>1</sup> = H, R<sup>2</sup> = Cl  
e; R<sup>1</sup> = Cl, R<sup>2</sup> = H

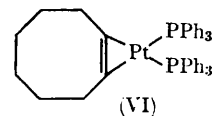
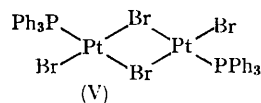


a; R<sup>1</sup> = H, R<sup>2</sup> = H, m.p. 260–264°  
b; R<sup>1</sup> = H, R<sup>2</sup> = NO<sub>2</sub>, m.p. 285–287°  
c; R<sup>1</sup> = H, R<sup>2</sup> = Me, m.p. 261–262°  
d; R<sup>1</sup> = H, R<sup>2</sup> = Cl, m.p. 268–270°  
e; R<sup>1</sup> = Cl, R<sup>2</sup> = H, m.p. 270–272°

Benzenediazonium-2-carboxylate (IIIa) decomposes in 1,2-dichloroethane under reflux to give benzyne;<sup>7</sup> in the presence of (Ph<sub>3</sub>P)<sub>4</sub>Pt, however, complex (IVa) was obtained (80%). The structure (IVa) was assigned on the basis of the i.r. spectrum which was identical to that reported,<sup>1</sup>

and its reaction with bromine in chloroform; with an aqueous work-up this gave *o*-bromobenzoic acid and a platinum complex, m.p. 320°, assigned structure (V). An attempt to labilize the carboxylate function in the diazonium-carboxylate by introducing suitable substituents was unsuccessful; the zwitterions (IIIb–e) gave good yields of the complexes (IVb–e) as the only products. Complex (IVa) is unchanged by irradiation or by heating at temperatures up to 200°; it is not, therefore, a benzyne precursor.

Thus all attempts to isolate a benzyne-platinum complex analogous to acetylene-platinum complexes<sup>8</sup> have failed at the stage of generation of benzyne. We are encouraged in this general approach, however, by the isolation in high yield (70%) of a stable cyclo-octyne-platinum complex, m.p. 180–182°, by the addition of cyclo-octyne<sup>9</sup> to (Ph<sub>3</sub>P)<sub>4</sub>Pt in benzene. Structure (VI) is supported by the n.m.r. and i.r. spectra and, like all other new compounds reported, by correct analytical data.



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