PART I

BIS-ANNELATION OF ARENES VIA BIS-ARYNE EQUIVALENTS; MECHANISM AND SYNTHETIC APPLICATIONS

PART II

METALLACYCLOPENTANES AS CATALYSTS FOR THE LINEAR AND CYCLODIMERIZATION OF OLEFINS

By

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ABSTRACT

PART I

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PART II

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In the first part of this thesis bis-annelation of arenes via bis-aryne equivalents was studied. Tetrahalo arenes such as tetrabromo-p-xylene (25) act as bis-aryne equivalents upon treatment with n-butyllithium. The aryne intermediate formed from this reaction was intercepted with 2,5-dimethylfuran (28) to give 9,10-dimethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-endoxide (29)

as a mixture of syn and anti isomers. The mechanistic routes to this bis-adduct were explored. The stepwise process involves the mono-metalation of 25. Elimination of LiBr generates the aryne which can be trapped with diene 28 to form a mono-adduct. This mono-adduct can subsequently go through the same process (metalation, elimination of LiBr, and cycloaddition) to form 29 (Path A). The other possibility is bis-metalation of 25 which could directly eliminate two moles of LiBr to give a bis-aryne intermediate which would be intercepted by diene (Path B). Several experiments designed to distinguish between Paths A and B were performed. From the results of our experimental data we have concluded that this bis-annelation reaction proceeds stepwise (Path A) and an aryne, not an organolithium compound, is involved in the product-determining step.

The choice of solvent is important in this bis-annelation reaction. Use of toluene as solvent made it possible to control the reaction by the amount of n-butyllithium used to synthesize the mono-adducts such as 1,4-dimethyl-1,4-dihydronaphthalene-1,4-endoxide (31), whereas ether or tetrahydrofuran as solvents always gave 29 no matter how much n-butyllithium was used. Mono-adducts of this type were used to synthesize unsymmetric bis-adducts.

Cyclopentadiene and its derivatives such as fulvenes and spirocyclopentadienes gave very good yields of the corresponding bis-adducts with novel structures. Several experiments were performed to show that cyclopentadiene, and not its anion, is required for this bis-annelation reaction.

A simple one-step synthesis of triptycene analogs prepared by the reaction of a bis-aryne equivalent with anthracene is described. For example, **25**, anthracene and n-butyllithium gave 6,13-dimethyl-5,7,12,14-tetrahydro-5,14[1',2']: 7,12[1",2"]-dibenzenopentacene **86** (trivially called a para-pentiptycene).

Several analogs of **86** were also prepared to show the generality of the method. 4,5-Dibromo-3,6-diiodo-o-xylene (**97**) functioned as an ortho bis-aryne equivalent to give, for example, with anthracene 6,7-dimethyl-5,8,13,14-tetrahydro-5,14[1',2']: 8,13-[1",2"]dibenzenopentaphene (**87**) (trivially called an ortho-pentiptycene). The synthesis of heptiptycene (5,6,11,12,13,18-hexahydro-5-8[1',2']: 6,11[1",2"]12,17[1‴ ,2‴]tribenzenotrinaphthylene) (**88**) has been improved and the intermediate cycloalkyne (9,10-dihydro-9,10-ethynoanthracene) has been trapped with various dienes.

The technique of o-bis-annelation was extended to a new and simple synthesis of phenanthrenes, particularly

applicable to hindered phenanthrenes. For example, the reaction of 97 with N-(dimethylamino)tetramethylpyrrole and n-butyllithium gave the corresponding bis-adduct which upon pyrolysis resulted in the previously unknown decamethylphenanthrene (138). 1,4,5,8,9,10-Hexamethylphenanthrene and 9,10-dimethylphenanthrene were prepared in a similar manner.

The application of this bis-annelation technique to the synthesis of polyphenylarenes was explored. Bis-adducts of 2,5-diphenylfuran or 3,6-diphenylisobenzofuran with bis-aryne equivalents could be aromatized to give compounds with groups sandwiched between phenyl rings. For example, 6,13-Dimethoxy-5,7,12,14-tetraphenylpentacene was synthesized in this way.

In Part II of this thesis it is demonstrated that metallacycles can play the role of catalyst for linear or cyclodimerization of olefins. Cyclodimerization of acrylonitrile to 1,2-dicyanocyclobutane using bis(triphenylphosphine)tetramethylene Ni(II) as the catalyst is described.

This thesis is dedicated to the memory of my father

Mosheh Shamouilian

ACKNOWLEDGMENTS

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Appreciation is extended to Michigan State University, National Science Foundation, and National Institutes of Health for financial support in the form of teaching and research assistantships.

Finally I would like to thank my brother Yousef and my friend Sue for their continued help and encouragement in the past few years.

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BIS-ANNELATION OF ARENES VIA BIS-ARYNE EQUIVALENTS; MECHANISM AND SYNTHETIC APPLICATIONS

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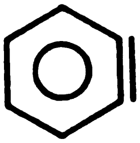
INTRODUCTION

Benzyne (1)[1] and activated alkynes (2) have very similar reactions. Both exhibit the same tendency towards polar addition and cycloaddition, but benzyne (1) is by far the more reactive. This reactivity must be attributed to the ring strain which results from lateral bending of the bonds at the formal triple bond from the normal 180° found in alkynes to be an angle close to 120° in benzyne. The ground state energy of dehydrobenzene is thereby raised relative to that of 2. Moreover, relief of angular strain during any reaction of benzyne will make the reaction more exothermic and promote earlier attainment of the transition state by the reactants. The combination of these factors accounts for increased reactivity of benzyne relative to 2.



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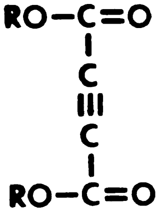

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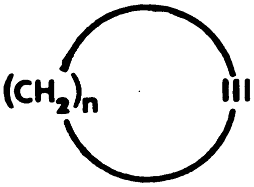
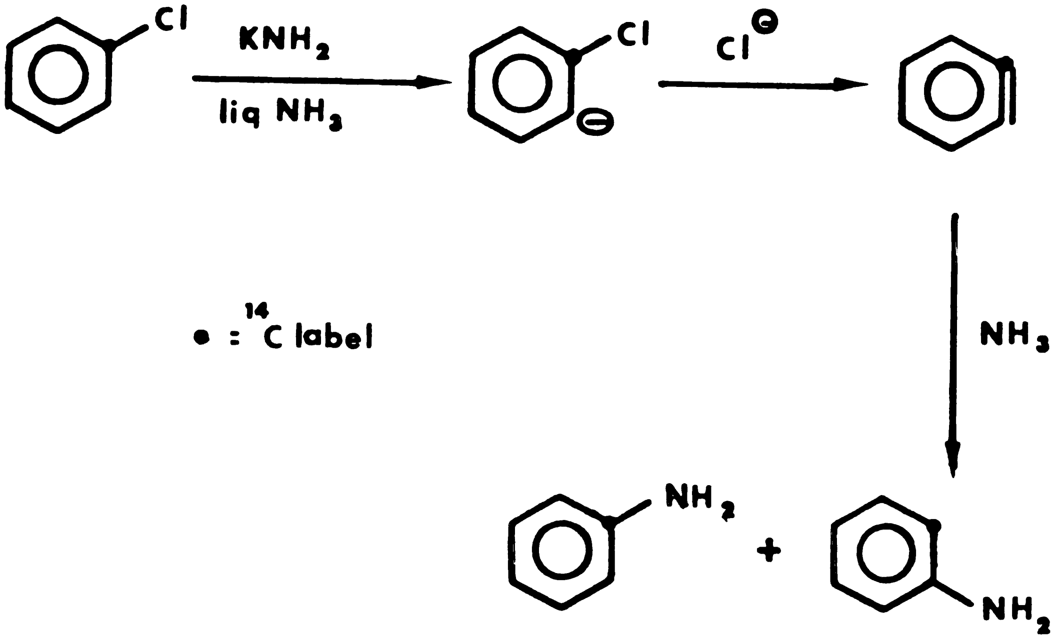


3

Such an increase in reactivity with the introduction of strain is readily recognized in a series of cycloalkynes (**3**). When $n > 7$ cycloalkynes are stable. Cyclooctyne ($n = 6$) can be isolated but it polymerizes readily.[2] Cycloheptyne has a lifetime of only a few minutes at -20°C,[3] whereas cycloalkynes with n equal to 4 or 3 are capable only of transient existence and are very reactive intermediates.[4]

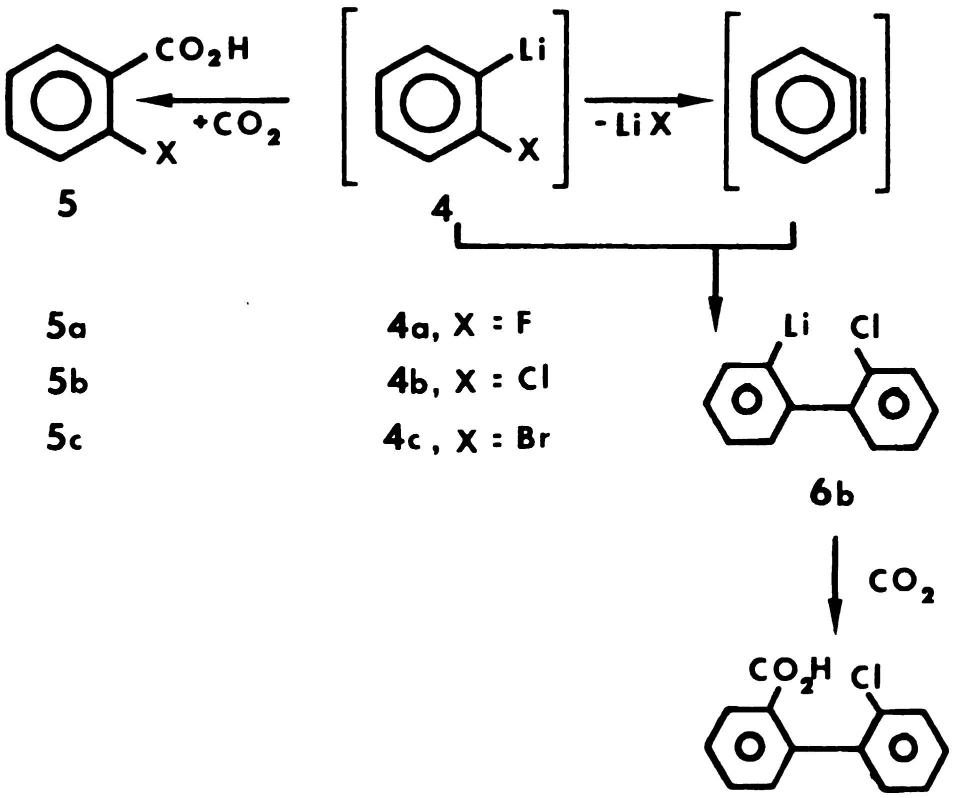
In 1953, Roberts[5] carried out decisive experiments to test the participation of benzyne in the amination of haloarenes. It was realized that if the amination of chlorobenzene with potassium amide in liquid ammonia did proceed via benzyne as an intermediate, then the amination of [1-^{14}C]-chlorobenzene should lead to equal amounts of [1-^{14}C]-aniline and [2-^{14}C]-aniline. This result was in fact obtained.



Soon after, a new period in benzyne chemistry started. Benzynes were trapped with different dienes in Diels-Alder reactions.[6] In a short time benzyne chemistry was pursued in many laboratories. It received a great boost one decade later when methods were found to generate benzyne in the absence of organometallic agents.

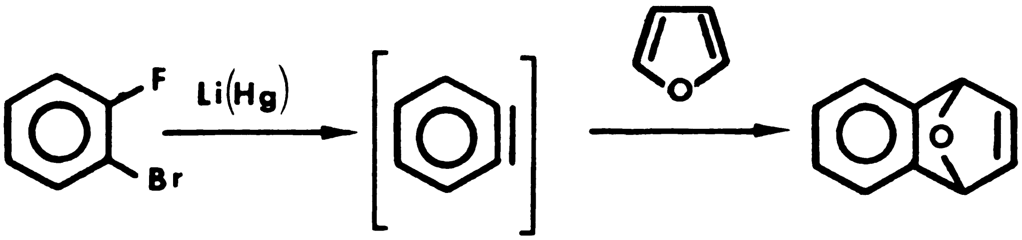
The most widely used procedures for generating benzyne from o-halogenophenyl anions are metalation of aryl halides and metal-halogen exchange reactions on o-dihalogeno aromatic compounds. Metal amides have been widely used as metalating agents for aryl halides. Metalation of aryl halides with organometallic compounds is a protophilic substitution; thus the rate of this reaction in general will increase with basicity of the metalating agent. This rate for organolithium compounds decreases in the order of t-butyllithium > isopropyllithium > n-butyllithium > phenyllithium > methyllithium, while naphthyllithium or anisyllithium are much weaker metalating agents.[7]

Generation of benzyne from o-halogenophenyl anions depends on the nature of the halogen, because a carbon halogen bond is broken in the loss of halide ion from **4**. **4a** can be prepared at -70°C by metal-halogen exchange between 1,2-fluorobromobenzene and butyllithium, and may be intercepted at temperatures below -60°C with carbon dioxide, to give **5a** in 88% yield.[8] To effect the same reaction with **4b** the temperature must be lowered to -90°C. At that temperature a 93% yield of acid **5b** was



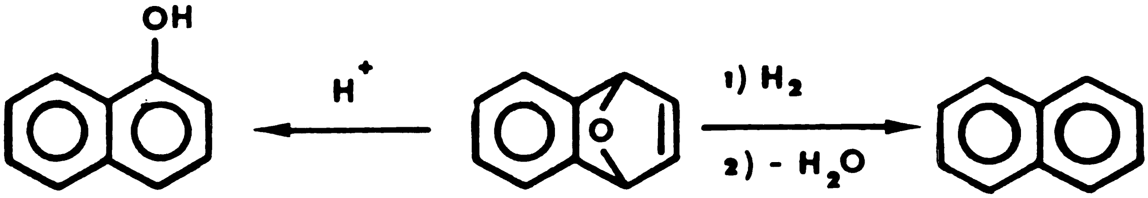
obtained, but if the solution was warmed to -60°C prior to carboxylation 6b was formed and trapped as the acid in 17% yield.[8] If similar reactions are tried with 2-bromophenyllithium 4c, even a temperature of -100°C is not low enough to stabilize the anion. Immediate carboxylation after preparation of 2-bromophenyllithium by metal halogen exchange at -100°C gave only 23% of 5c; after 45 minutes none could be obtained at all.[8] At -130°C, however, 2-bromophenyllithium has been trapped in reasonable yield with chlorodiethylphosphine.[9]

Wittig,[6] in 1955, was the first to trap benzyne in a Diels-Alder reaction. The benzyne was generated from o-fluorobromobenzene and lithium amalgam in the presence of furan as a trap. This reaction became so characteristic that it now serves as a diagnostic test for the formation of benzyne from various precursors. Because of their thermal stability, anthracene and tetracyclone have become standard reagents for trapping benzynes generated at elevated temperatures.[10]



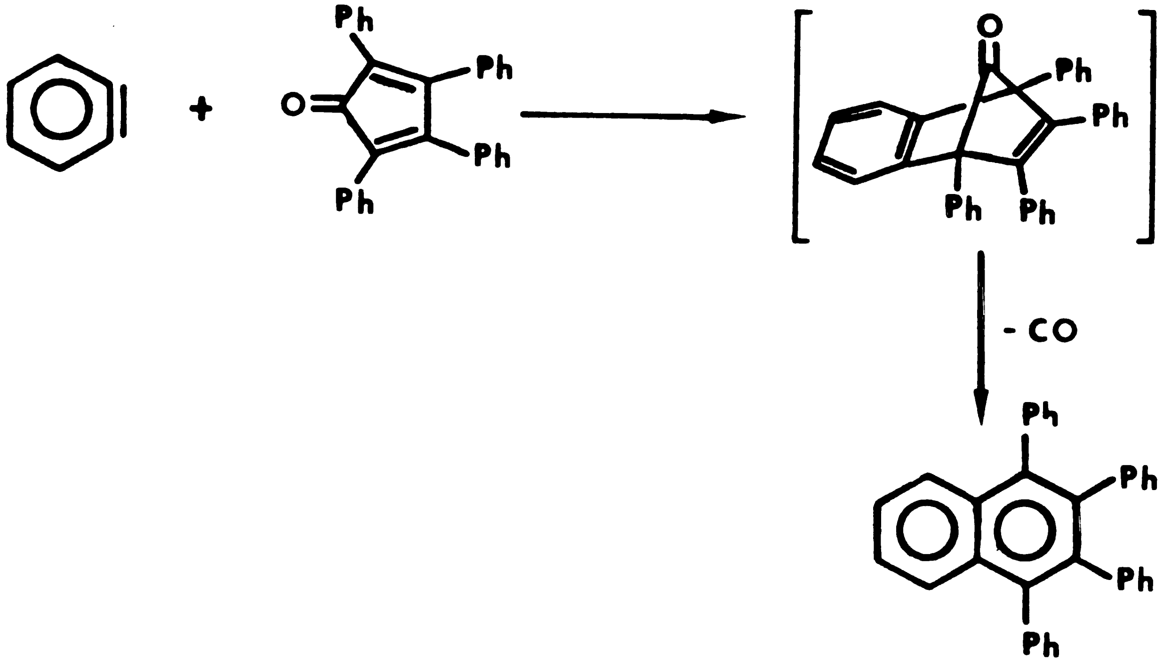
7

Many of these reactions have considerable preparative value. For example, 1,4-dihydronaphthalene-1,4-endoxide 7 is readily converted into α-naphthol 8 or naphthalene 9.[11] Decarbonylation occurs during the reaction of



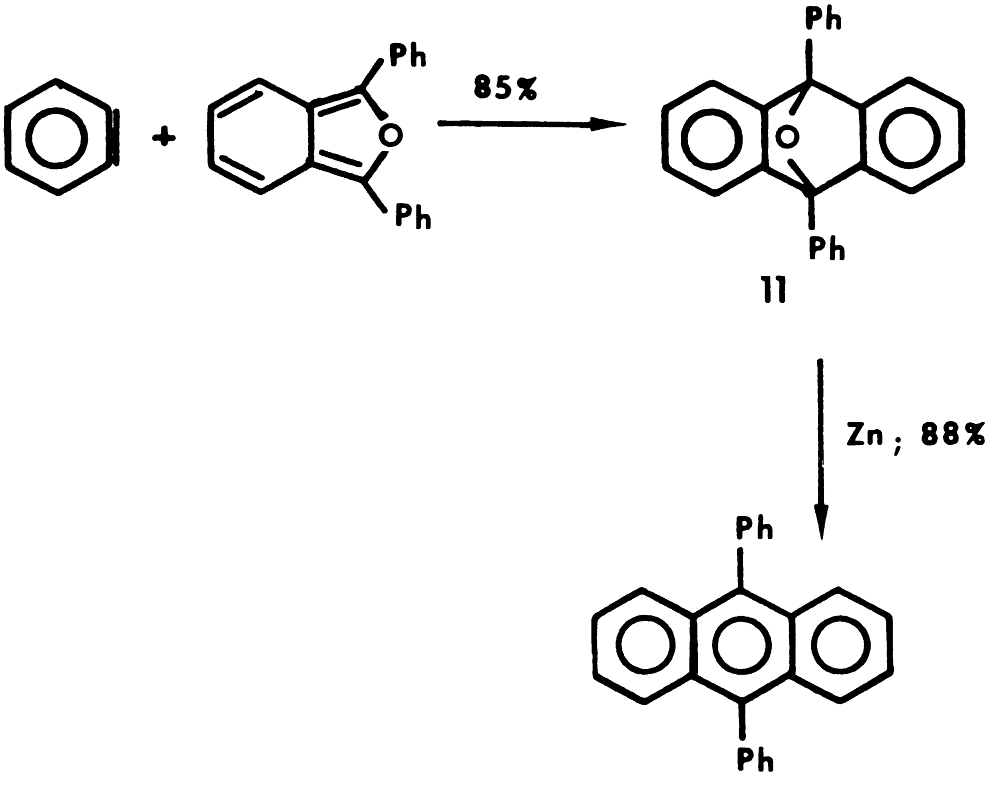
8 7 9

benzyne with tetracyclone, giving rise directly to tetraphenylnaphthalene **10**.[12] Annelation of two aromatic rings can be achieved by cycloaddition of diphenylisobenzofuran



10

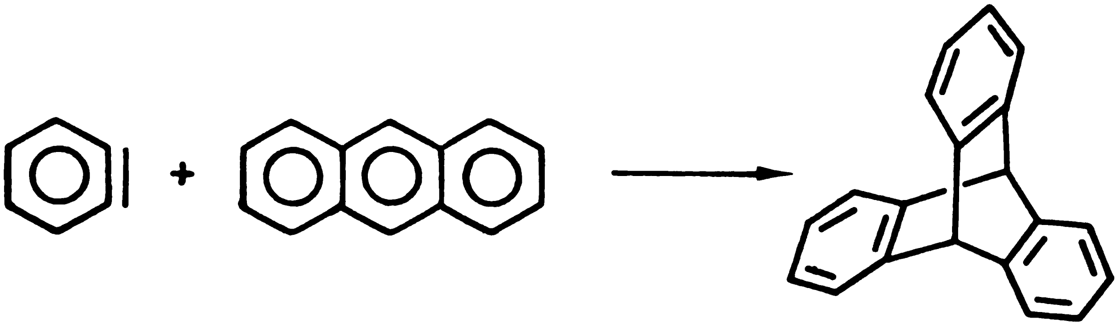
to benzyne, since the resulting adduct **11** can be deoxygenated either thermally or with metallic zinc to give 9,10-diphenylanthracene **12**.[13]



11

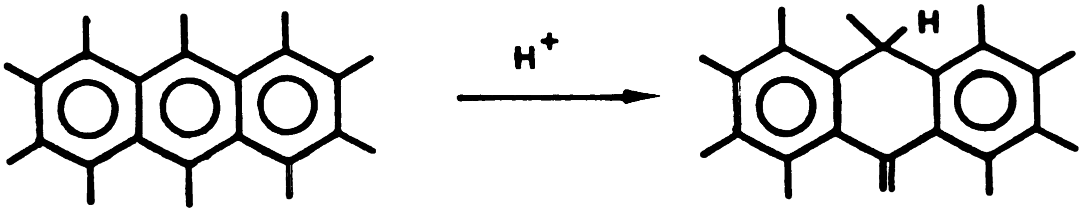
12

A simple synthesis of triptycene 13 was achieved by Wittig[14] through the cycloaddition of benzyne to anthracene. A large variety of dienes, such as cyclopentadiene,[15] dimethylfulvene[16] and N-substituted pyrroles[17] have been used in similar processes.



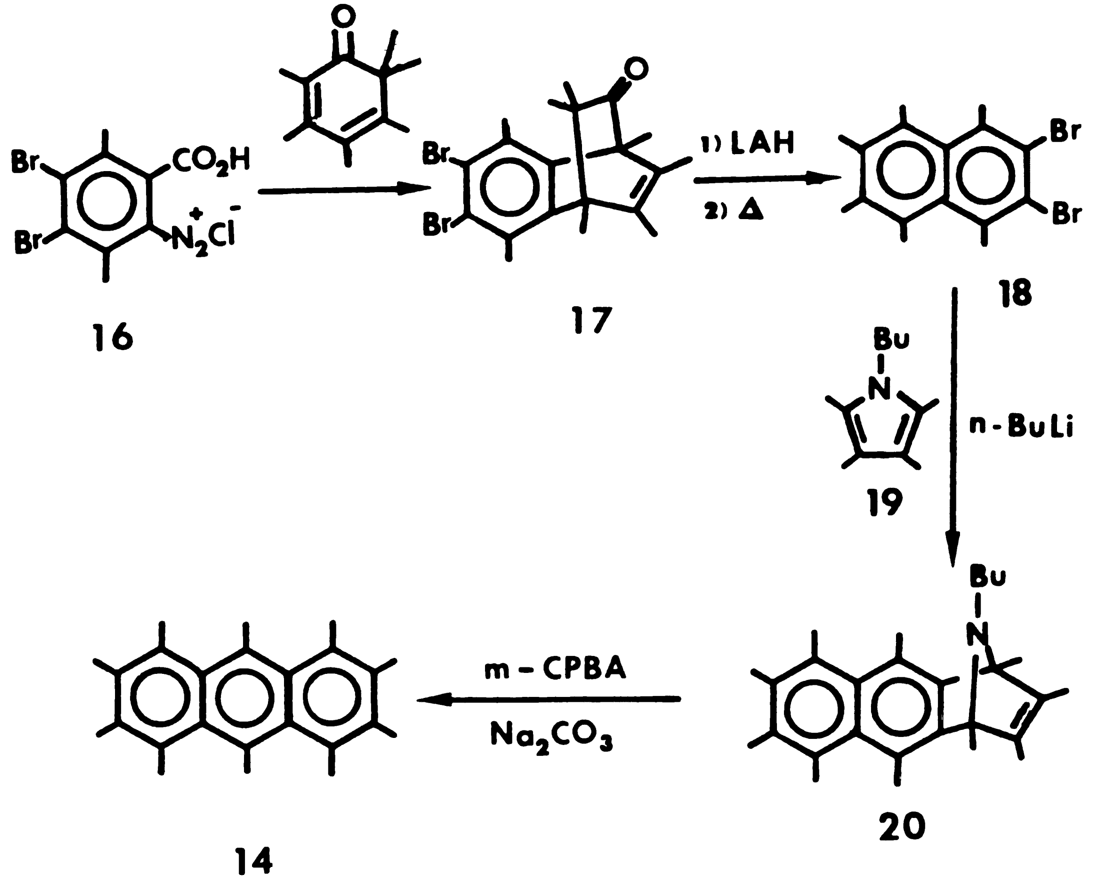
13

Arynes have been used in the synthesis of polymethylarenes such as decamethylanthracene[18] and octamethylnaphthalene.[19] The synthetic challenge arises from the need to introduce peri-interacting groups, such as the methyls, at the 1,8 positions in naphthalene or at the 1,4,5,8, 9,10 positions in anthracene. Substituents located at these positions are in much closer proximity than similar substituents located at ortho positions. Octamethylnaphthalene contains two peri methyl interactions and decamethylanthracene contains four such interactions. Therefore these molecules are strained relative to the nonsubstituted ones. This strain induced special reactivity in these compounds. For example decamethylanthracene (**14**) is unstable in acidic or basic media and it will rearrange (1,5-hydrogen shift) to the hydrocarbon tautomer **15** in which the central ring is not aromatic, to relieve this strain.[18]



14 **15**

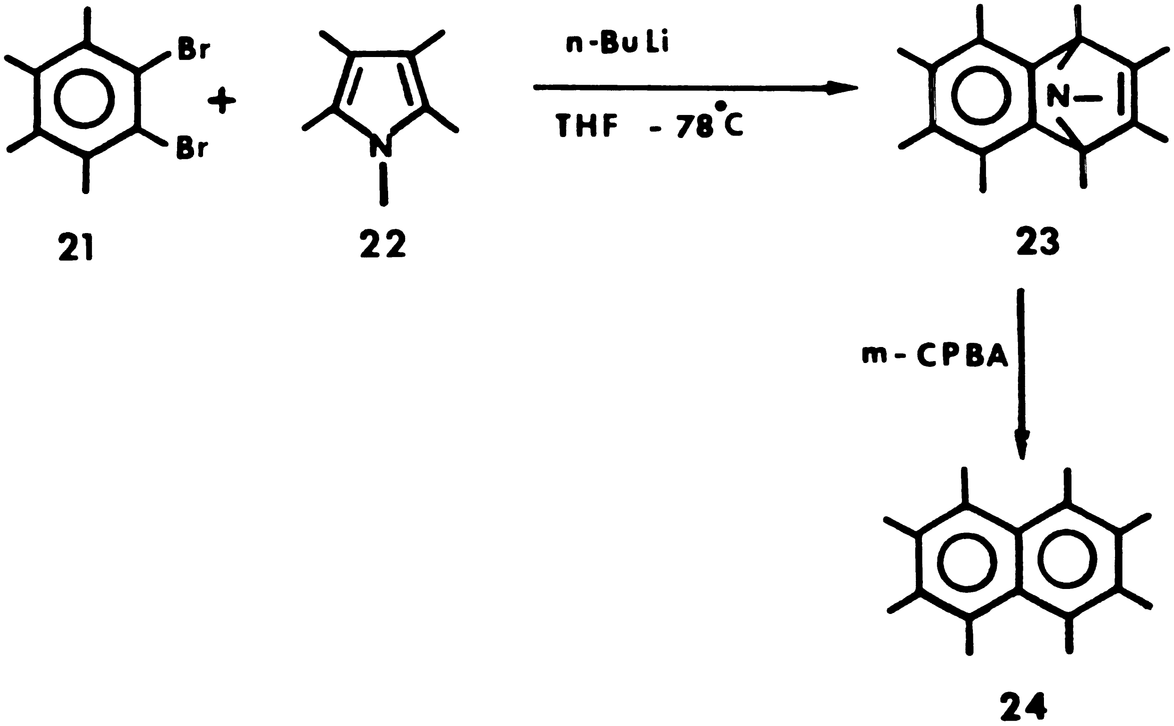
Decamethylanthracene was first synthesized in our laboratory as follows:[18]



Diazoniumcarboxylate 16 was used as the aryne precursor in the first step. Reduction of adduct 17 and pyrolysis of the reduced product gave dibromonaphthalene 18, which was used as a second aryne precursor in the next step. Treatment of 18 with n-butyllithium in the presence of pyrrole 19 formed cycloadduct 20. Removal of the nitrogen bridge was achieved by oxidation with meta-chloroperbenzoic acid (*m*-CPBA) to give 14. This synthesis was designed to gradually introduce the peri-interactions and also to compensate for some of the resulting strain energy by other energy-releasing processes (i.e., aromatization).

Both cycloaddition steps are exothermic because arynes are high energy intermediates. The bridge removal steps, which introduce the peri-strain, are accompanied by the formation of an aromatic ring. This aromatization energy compensates for some of the energy introduced in the molecule because of the peri-interacting groups. Also note that the last step in this sequence occurs under essentially neutral conditions which prevents rearrangement of the decamethylanthracene.

This strategy also was used to synthesize octamethylnaphthalene in excellent yield.[19]



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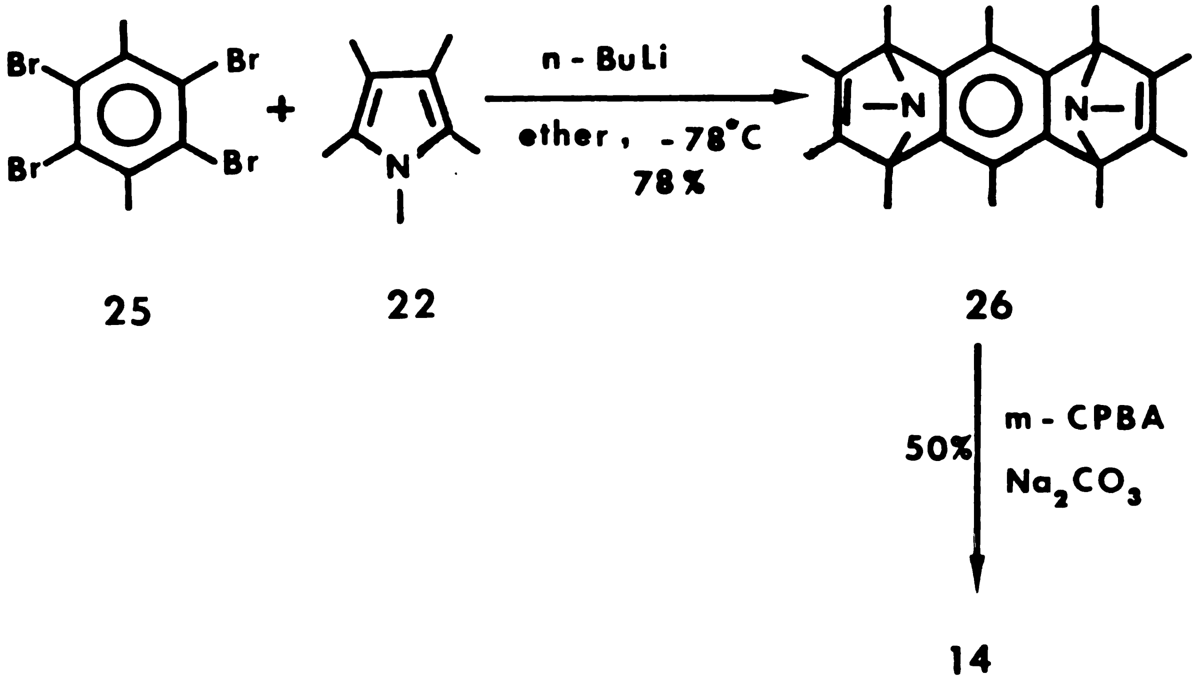
Looking back at the synthesis of decamethylanthracene, the strategy was to start with one of the benzene rings and construct the other two in separate steps from cycloaddition of the arynes to the proper dienes. It was thought that this synthesis could be shortened to two steps by constructing the two benzene rings simultaneously; therefore a properly functionalized benzene was sought.

It seemed that tetrabromo-p-xylene could function as a bis-benzyne precursor or its equivalent upon its reaction with n-butyllithium. Thus, when a mixture of tetrabromo-p-xylene (**25**) and pentamethyl pyrrole (**22**) was reacted with n-butyllithium at -78°C under argon, a 78% yield of the expected bis-adduct **26** was obtained. Subsequent excision of the nitrogen bridges gave decamethylanthracene in good yield (Scheme 1). Successful accomplishment of this idea substantially increased the overall yield of **14**.

Several possible mechanistic routes can be considered for the formation of bis-adduct **26**. Several experiments designed to determine the mechanisms whereby bis-aryne equivalents such as **25** function were performed. Discovery of toluene as an appropriate solvent for this reaction permitted synthesis of the corresponding mono-adducts. Use of these mono-adducts as benzyne precursors in reactions similar to that shown for **25** gave cross bis-adducts in which the two new annelated rings need not be identical.

Scheme 1



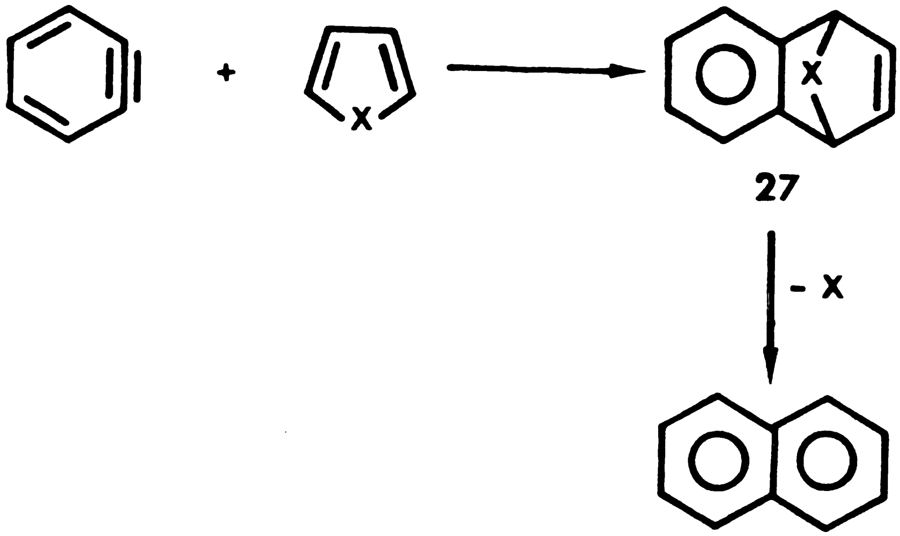
Subsequent bridge removal from these cross bis-adducts would result in unsymmetrically substituted anthracenes.

In our further attempt to explore the scope of this bis-annelation technique, a variety of dienes were used. Cyclopentadiene, fulvenes and spirocyclopentadienes all gave bis-adducts with novel structures in good yields. Use of 2,5-diphenylfuran or 3,6-diphenylisobenzofuran in this bis-annelation reaction was explored, and could be considered as a simple entry to polyphenyl substituted arenes such as anthracene or pentacenes. Bis-annelation of bis-aryne equivalents with anthracene gave a very simple entry to a whole new class of compounds for which the name "iptycenes" is proposed.

This bis-annelation technique was also extended to angular rather than horizontal bis-annelation by using the properly substituted tetrahalo arene. Application of this angular bis-annelation led to a new and simple synthesis of phenanthrenes. Dienes such as dipyrroles have also been used in this bis-annelation reaction in an attempt to synthesize N-N bridged bis-adducts (basket type compounds). The main part of this thesis describes mechanistic and synthetic studies on bis-aryne equivalents.

RESULTS AND DISCUSSION

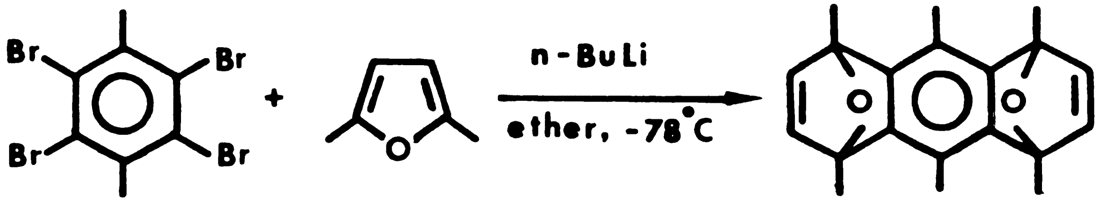
The reactions between benzyne and selected dienes have been used to annelate benzenes. For example,



The first step is a [2+4] cycloaddition to give the adduct 27; in the second step the X-bridge is eliminated in some way, thus producing a second aromatic ring fused to the benzene ring of the benzyne precursor.

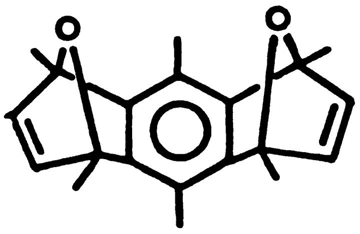
Some time ago we thought that mono-annelation of benzyne with dienes could be extended to bis-annelation simply by using a properly functionalized benzene which in effect would function as a bis-aryne precursor. The first experiments, which were carried out by Dr. Chana Zlotogorski,[20] showed that this idea was feasible, and the application of this idea to the synthesis of decamethylanthracene has already been described (Scheme 1, p. 13).

We have also used 2,5-dimethylfuran as a diene in a similar bis-annelation reaction. When a suspension of tetrabromo-p-xylene (25) and 2,5-dimethylfuran (28) in ether at -78°C was treated with n-butyllithium under argon, a 78% yield of bis-adduct 29 was obtained.



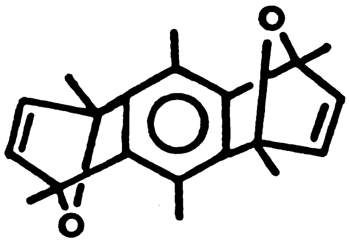
25 28 29

This bis-annelation reaction was expected to produce two isomers of bis-adduct 29, the syn isomer, in which the two oxygen-bridges are both on the same side of the plane of the benzene ring (29a), and the anti isomer, in which one oxygen-bridge is above and the other is below the plane of the benzene ring (29b).



Syn

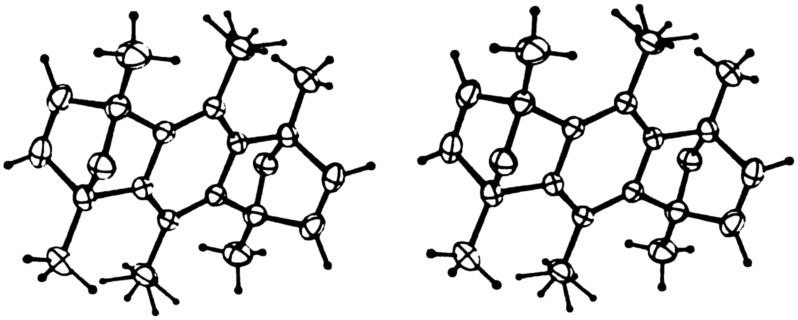
29a



Anti

29b

Figure 1



The proton NMR spectrum of bis-adduct **29** clearly showed the presence of these two isomers. The major isomer showed singlets at δ 1.93 (12 H, bridgehead methyls), 2.28 (6 H, aromatic methyls), and 6.78 (4 H, the vinyl hydrogens), whereas those of the minor isomer were at δ 1.95, 2.34 and 6.75. In order to determine the ratio of these isomers in the reaction product, the area ratio in the ^{1}HNMR spectrum signals at 180 MHz of the crude reaction product were measured. A ratio of 57:43 was obtained. Spectroscopic data such as NMR, mass, IR and UV were not able to distinguish which isomer was which; thus, we used X-ray crystallography. A pure sample of the major isomer was obtained by repeated washing of the crude product mixture with ether, and crystallization from acetonitrile. The X-ray crystal structure of the isomer determined that the oxygen bridges were anti. Figure 1 shows the stereo drawing of this anti isomer. In Appendix 1, tables of the bond distances and the bond angles are given.

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1. Mechanistic Studies of the Bis-Annelation of Arenes via Bis-Aryne Equivalents.

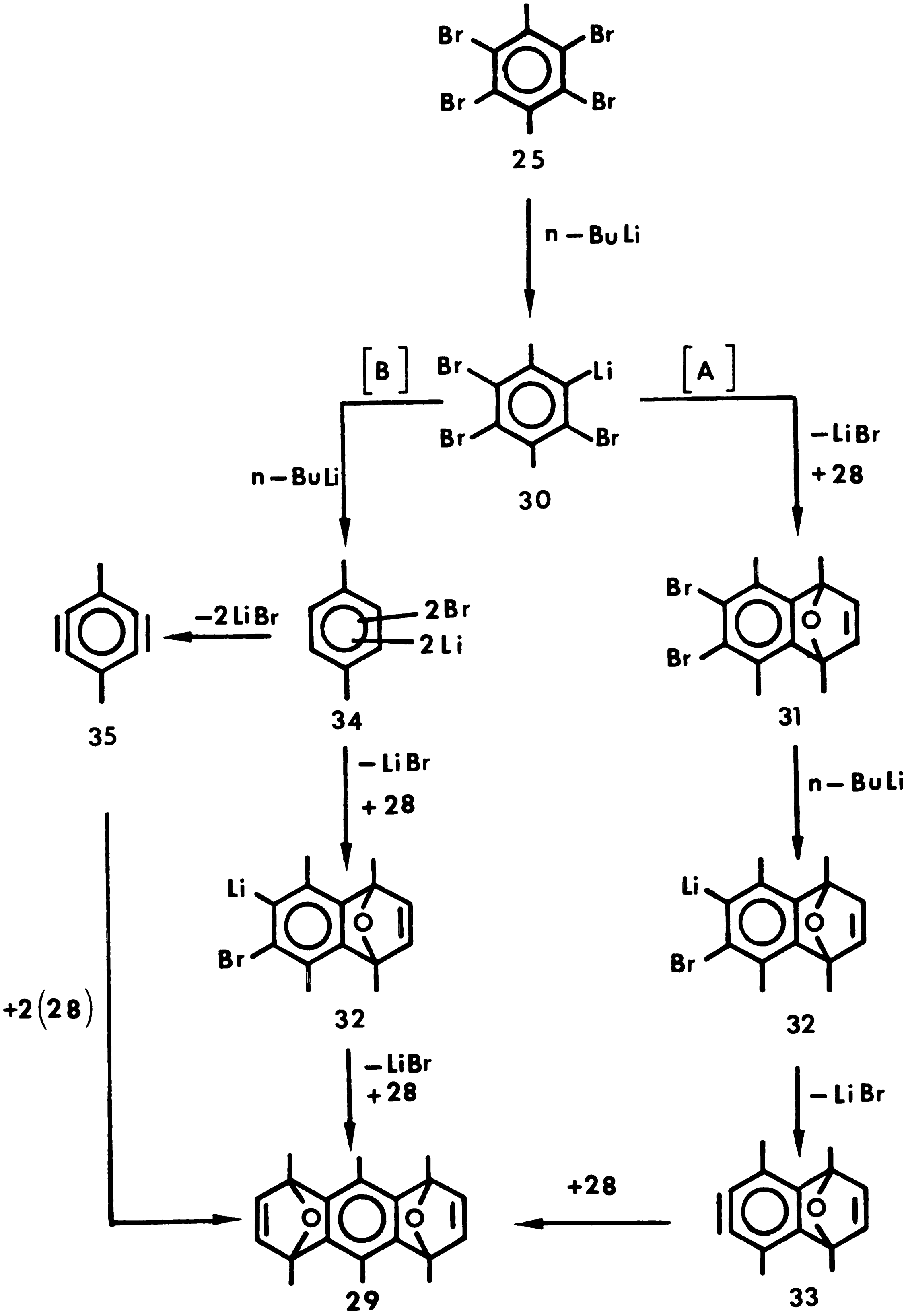
Several pathways can be considered to explain the formation of the bis-adduct **29**, and several experiments were performed in order to explore these possibilities. Scheme 2 shows some of these possible paths.

Path [A] is a stepwise process involving monometalation of **25**. Elimination of lithium bromide generates the aryne which can be trapped with diene **28** to form the mono-adduct **31**. This mono-adduct can subsequently go through a similar process (metalation, elimination of LiBr, cycloaddition) to form the bis-adduct **29**. On the other hand, bis-metalation of **25** would result in intermediate **34**. This intermediate might either lose two moles of LiBr simultaneously to generate the bis-aryne **35**, which could be trapped with 2,5-dimethylfuran to give the bis-adduct **29**, or the two equivalents of LiBr could be eliminated stepwise to first give **32** and then give **29**.

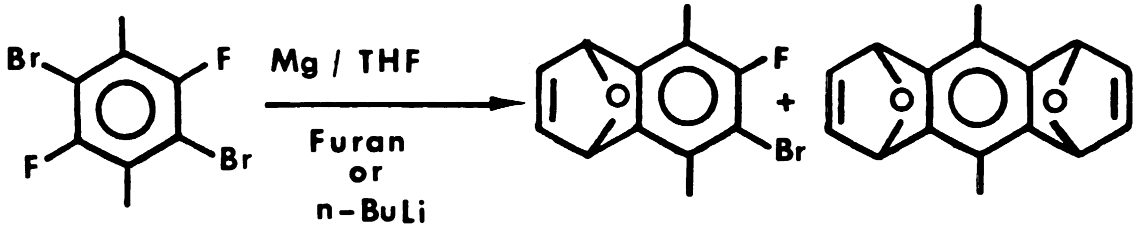
One of the other possibilities is that this reaction may not proceed through aryne intermediates, but rather via organo lithium compounds such as **32** or **34**, which react directly with the furan.

The first experiment performed in order to distinguish between Path A or B was to react 1 equivalent of tetrabromo-p-xylene (**25**) with only 1 equivalent of n-butyllithium. If this reaction proceded stepwise, we would expect to obtain only the mono-adduct **31**. The result showed that

Scheme 2


Br
Br
Br
Br
25
n – Bu Li
[B]
Br
Li
Br
Br
30
[A]
n – BuLi
– LiBr
+ 28
– 2 LiBr
2 Br
2 Li
35
34
Br
Br
31
– LiBr
+ 28
n – Bu Li
Li
Br
32
Li
Br
32
+2 (28)
– LiBr
+ 28
– Li Br
+28
29
33

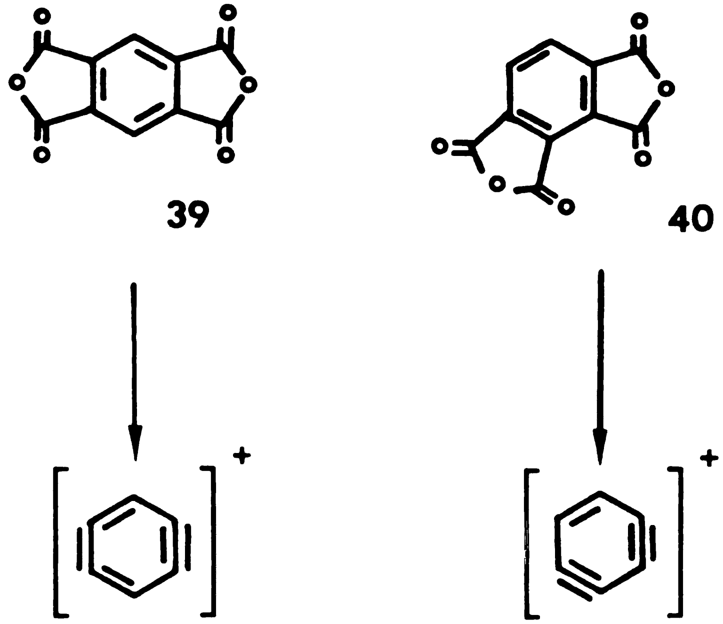
bis-adduct 29 was the only reaction product, plus some unreacted 25. No trace of mono-adduct 31 was observed. This result is somewhat similar to Wittig's,[21] who found that whereas the reaction of dibromodifluoro-p-xylene (36) with furan and magnesium in refluxing THF gave mainly the mono-adduct 37 (34%) and 5% of the bis-adduct 38, n-butyllithium gave only the bis-adduct 38 in 15% yield. Wittig concluded, because he isolated mono-adduct



	36	37	38
Mg ;		35%	5%
n-BuLi;		0%	15%

37 in the magnesium reaction, that the reaction is stepwise. But formation only of bis-adduct 29 when n-butyllithium was used is also consistent with Path B, which involves bis-metalation.

Bis-arynes have been postulated as intermediates in the mass spectral fragmentation of pyromellitic (39) or mellophanic (40) dianhydrides. Both 39 and 40 showed an intense peak at *m/e* 74 (about 60%) which was explained by formation of the corresponding bis-aryne fragments 41 and 42 respectively.[22]

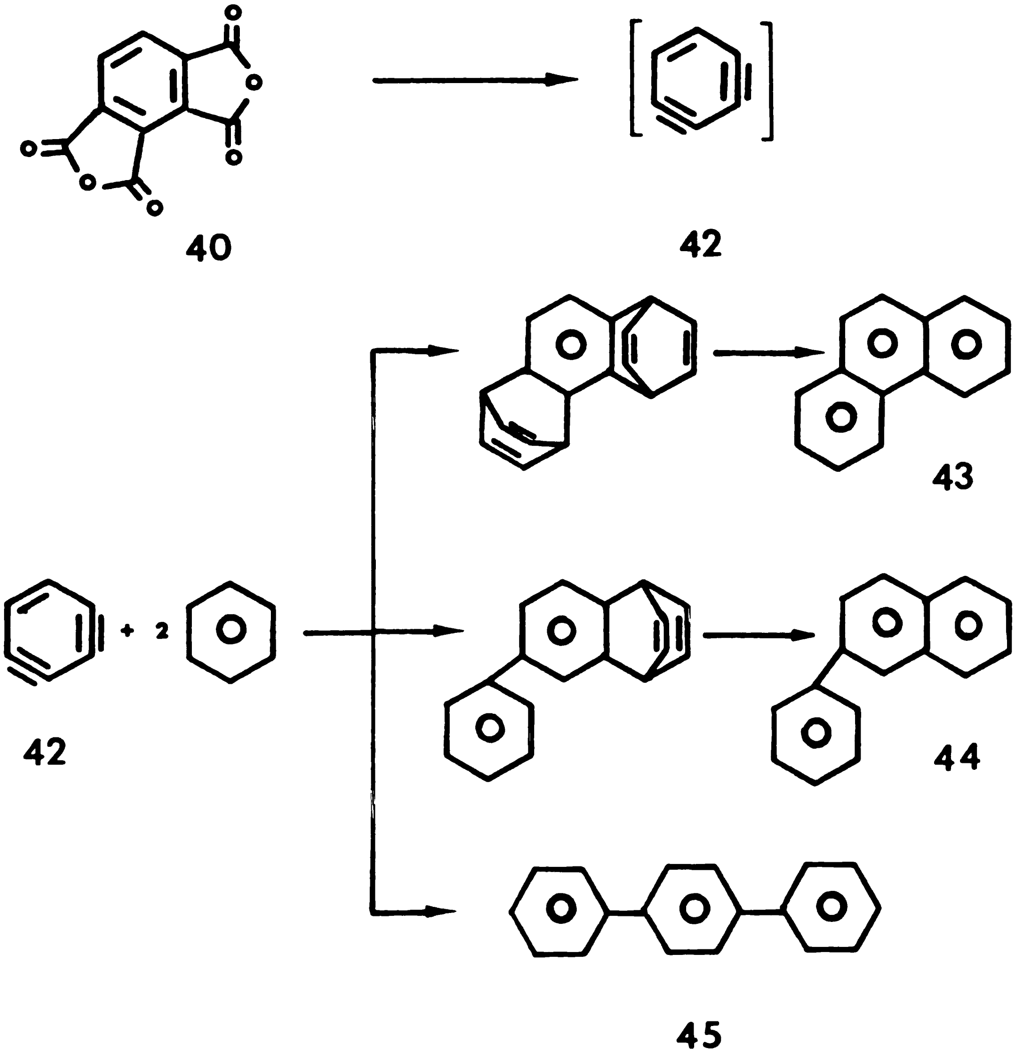


39 **40**

41 **42**

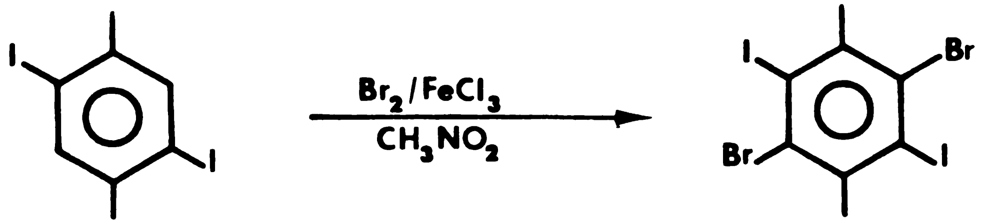
The cyclic structure of these fragments was not proven. Bis-arynes were also used to rationalize the products formed from the copyrolysis of benzene with **39** or **40**.[22] Scheme 3 shows the products derived from the pyrolysis of **40**. Phenanthrene (**43**) may be formed by two 1,4-additions of bis-benzyne to benzene; phenylnaphthalene (**44**) can result from an addition and an insertion; and terphenyl (**45**) may be formed from two insertions. Although bis-benzyne **42** as an intermediate would account for the formation of these products, other explanations, such as stepwise formation of these products, are possible.

Scheme 3



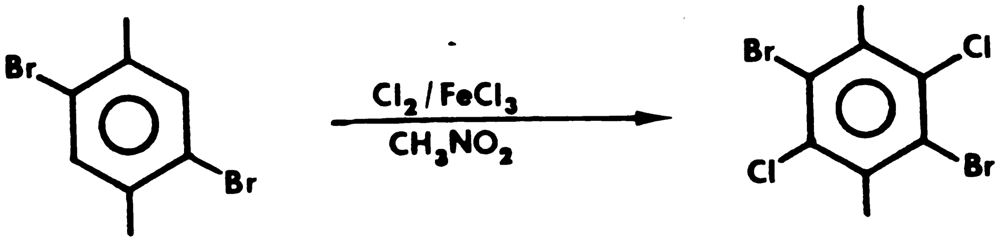
In our effort to investigate the reaction mechanism of the bis-annelation of arenes, we designed experiments to distinguish between Paths A and B, as follows:

a) In order to determine whether arynes or organolithium compounds are involved in the product-determining step, a variety of arenes such as dibromodiiodo (46), dibromodichloro (47) and tetraiodo (48)-p-xylenes were synthesized. These arenes were readily accessible from commercially available starting materials, often in only one or two steps. Tetrabromo-p-xylene was prepared in 90% yield according to the literature method[23] by adding excess bromine to p-xylene in the presence of iron powder at 0°C. Tetraiodobenzene (48) was prepared in good yield according to Yagupolskii's[24] method by mercuration of p-xylene with trifluoromercuriacetate, and iodination of this mercury compound with I_2/KI. Dibromodiiodo-p-xylene (46), which was not a previously known compound, was prepared in 89% yield by dropwise addition of bromine to a solution of 1,4-dimethyl-2,5-diiodobenzene and ferric chloride in nitromethane at 0°C.



46

Compound 47 was synthesized in 54% yield by passing Cl_2 gas through a solution of 1,4-dimethyl-2,5-dibromobenzene and ferric chloride in nitromethane.[25]



47

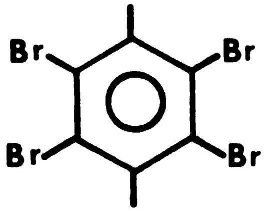
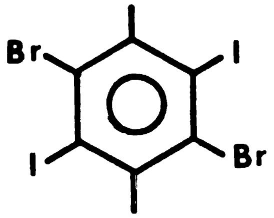
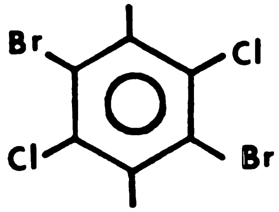
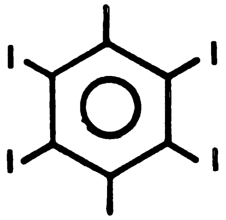
With the use of these arenes in a similar reaction to that used for **25**, one would expect, if the bis-annelation reaction proceeds through common intermediates such as aryne **33** or bis-aryne **35**, a similar anti:syn ratio of the products in all cases. However, if organolithium compounds such as **31** or **34** were involved in the product-determining step (since carbon-halogen bond cleavage is involved in this step), the anti:syn ratio would be expected to vary depending upon the tetrahalo arene used. Table 1 compares the yield and the anti:syn ratio of the bis-adduct **29** which was formed from bis-annelation of these tetrahalo arenes with 2,5-dimethylfuran.

Our experimental results showed that these ratios are similar (57:43) except for tetraiodo-p-xylene; thus we believe that arynes have been formed in the product-determining step, and we can rule out the involvement of organolithium compounds in this step.

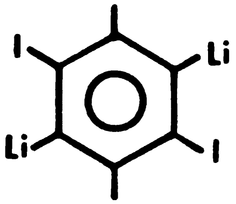
Tetraiodo-p-xylene gave a slightly different anti:syn ratio (61:39). Although we have checked this ratio accurately, it could still be within the experimental

TABLE 1

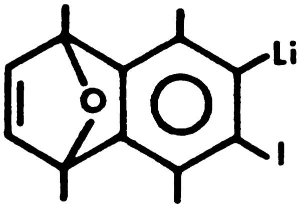
The Yield and Syn:Anti Ratio of Bis-adduct 29 from Tetrahalo-p-xylenes

Arene	Yield of Bis-adduct	Anti:Syn Ratio
 25	78%	57:43
 46	76%	57:43
 47	35%	57:43
 48	68%	61:39

error. It is also possible that intermediates such as 49 and 50 could be involved in the case of the tetraiodoarene.

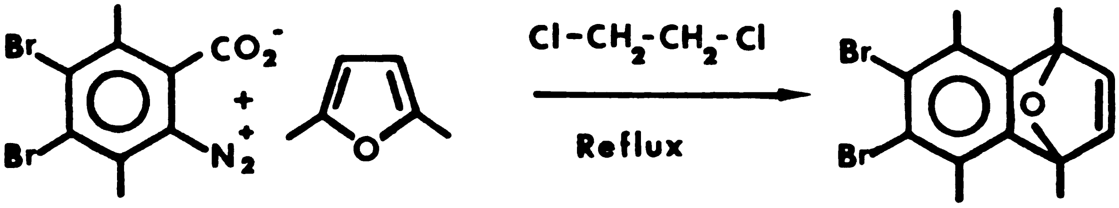


49



50

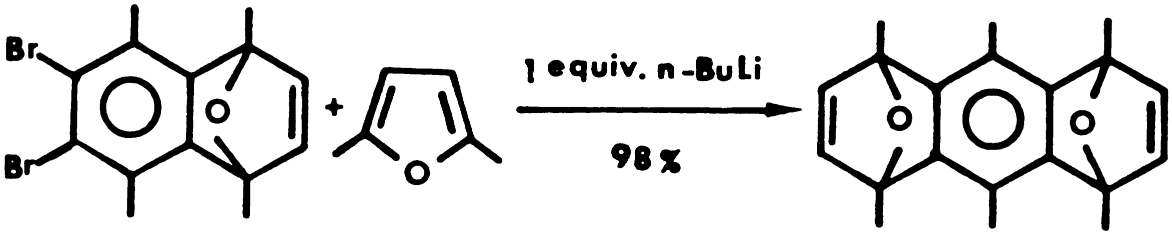
b) If this bis-annelation reaction in fact proceeds stepwise through the formation of mono-adduct 31 (Path A), reaction of this mono-adduct with n-butyllithium in the presence of 2,5-dimethylfuran should result in the formation of the bis-adduct 29 with the same anti:syn ratio as for the bis-adduct formed from tetrabromo-p-xylene. In order to check this, the mono-adduct 31 was synthesized independently. When a suspension of diazonium carboxylate 51 and excess of 2,5-dimethylfuran was heated at reflux in 1,2-dichloroethane a 71% yield of mono-adduct 31 was obtained. The proton NMR spectrum of 31 shows singlets at δ 1.98 (6 H), 2.48 (6 H), and



51 28 31

6.77 (2 H). The anthranilic acid corresponding to 51 was made according to Hart and Ruge.[18]

When one equivalent of the mono-adduct 31 reacted with one equivalent of n-butyllithium in the presence of an excess of 28, a 98% yield of bis-adduct 29 was obtained with the anti:syn ratio (57:43).



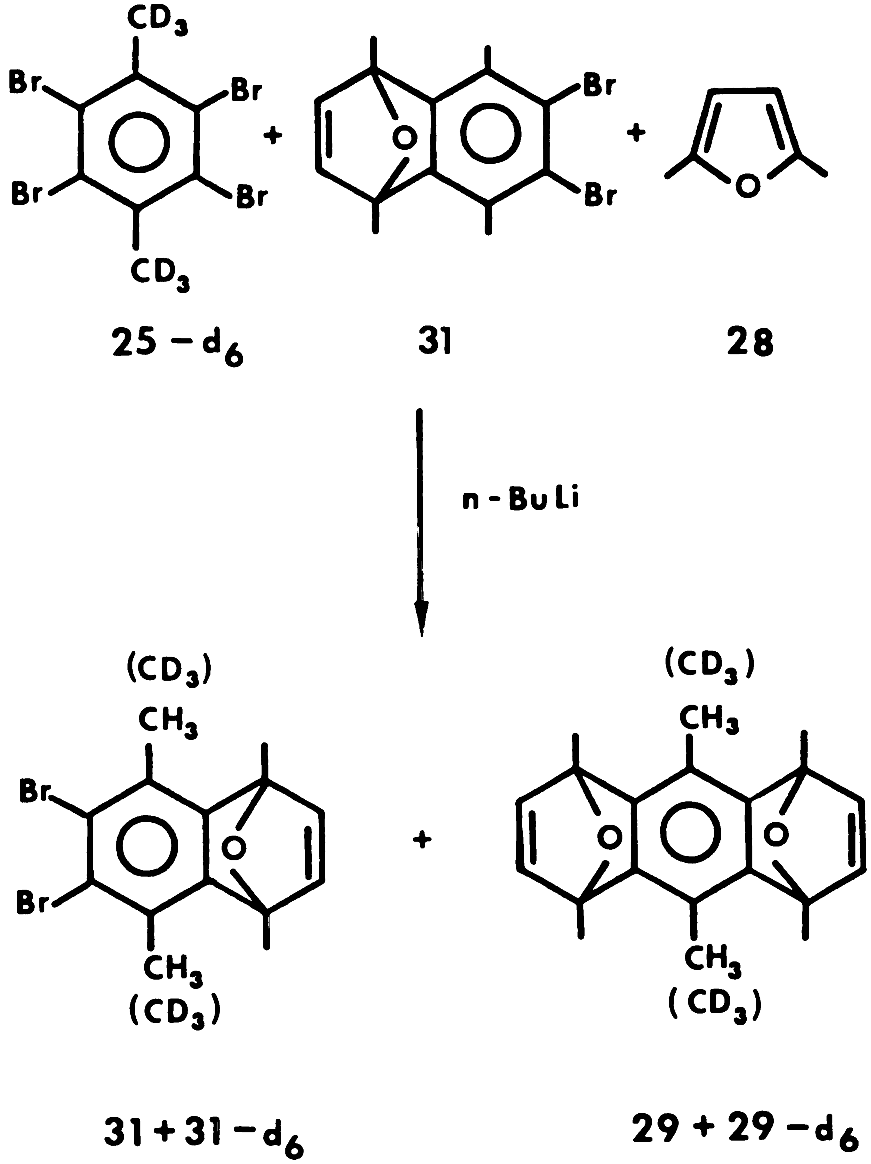
31 28 29

This result supports the stepwise process (Path A), but it does not rule out the bis-metalation (Path B) as a competitive route.

c) A deuterium labeling experiment was designed as follows, which was expected to distinguish Path A from B. If a mixture of mono-adduct 31 and labeled tetrabromo-p-xylene (25-d_6), one equivalent of each, were allowed to react with n-butyllithium (2 equivalents) in the presence of 2,5-dimethylfuran, and if the reaction proceeded through bis-metalation, the reaction product would be expected to contain a mixture of labeled and unlabeled bis-adduct 29 and some unreacted starting materials. If however, the reaction proceeded in a stepwise manner, the reaction product not only should contain bis-adducts

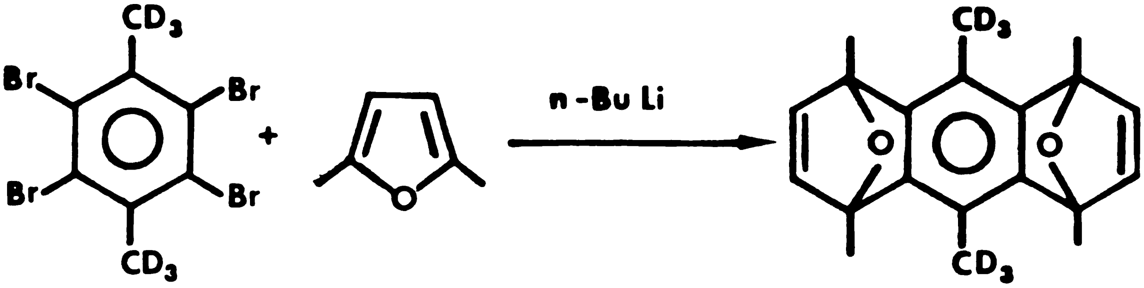
29 and **29-d$_6$**, but also should contain labeled mono-adduct **31** as well (Scheme 4).

Scheme: 4



Tetrabromo-p-xylene-d$_6$ was prepared in almost quantitative yield by bromination of p-xylene-d$_{10}$. When **25-d$_6$** was treated with n-butyllithium in the presence of 2,5-dimethylfuran in a similar manner as for **25** a 98%

yield of bis-adduct **29-d$_6$** was obtained, as a mixture of two isomers. The proton NMR spectrum of **29-d$_6$** clearly shows the absence of the 9,10-methyl signal in **29**.



25-d$_6$ **29-d$_6$**

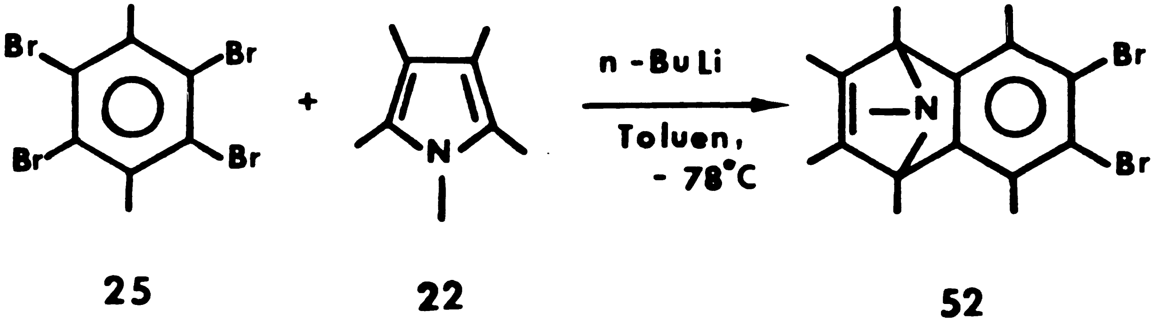
In another experiment, a mixture of **25-d$_6$** and **31** (0.5 equivalents of each) was allowed to react with 1 equivalent of n-butyllithium in the presence of excess 2,5-dimethylfuran (ether, -78°C). In addition to a 58% yield of a mixture of labeled and unlabeled bis-adduct **29** and a 26% yield of unreacted **25-d$_6$**, a 17% yield of mono-adduct **31** was separated by column chromatography. This mono-adduct contained 30-40% deuterium in the aromatic methyls. The presence of deuterium in the mono-adduct **31** was established from its proton NMR spectrum, in that the signal corresponding to the aromatic methyls (δ1.98 ppm) did not integrate equally with the signal at δ2.48 (bridgehead methyls) and was about 30-40% smaller. Also, the mass spectrum of this mixture showed a triplet centered at m/e 363 which is six mass units higher than the triplet observed for M^+ of the non-labeled mono-adduct **31**. The presence of **31-d$_6$** in the reaction mixture clearly proves that the bis-annelation is stepwise (Path A).

Tetrabromo-p-xylene is a highly symmetric compound with very low solubility in ether at -78°C (about 300 mg in 100 mL). Most of it precipitates out when the reaction mixture is cooled to -78°C. On the other hand, mono-adduct **31** is less symmetric and contains functional groups such as the ether bridge and the double bond. Thus it is much more soluble in ether at -78°C than the starting tetrabromo-p-xylene. We suspected that because of this greater solubility, **31** would react preferentially with the n-butyllithium. Thus, regardless of whether one or two equivalents of n-butyllithium were used, the product would always be the bis-adduct **29**.

A better solvent for tetrabromo-p-xylene was therefore sought. THF gave the same result as ether. But when toluene was used as the solvent in the synthesis of bis-adduct **29**, the yield was increased from 78% to 93%. Also, with toluene as solvent, when only one equivalent of n-butyllithium was used, mono-adduct **31** was obtained in 95% yield (it had the same physical constants as **31** which was prepared independently). The fact that by changing the solvent to toluene an almost quantitative yield of mono-adduct **31** was obtained is further evidence to prove that the reaction does not proceed through bis-metalation competing with the stepwise process.

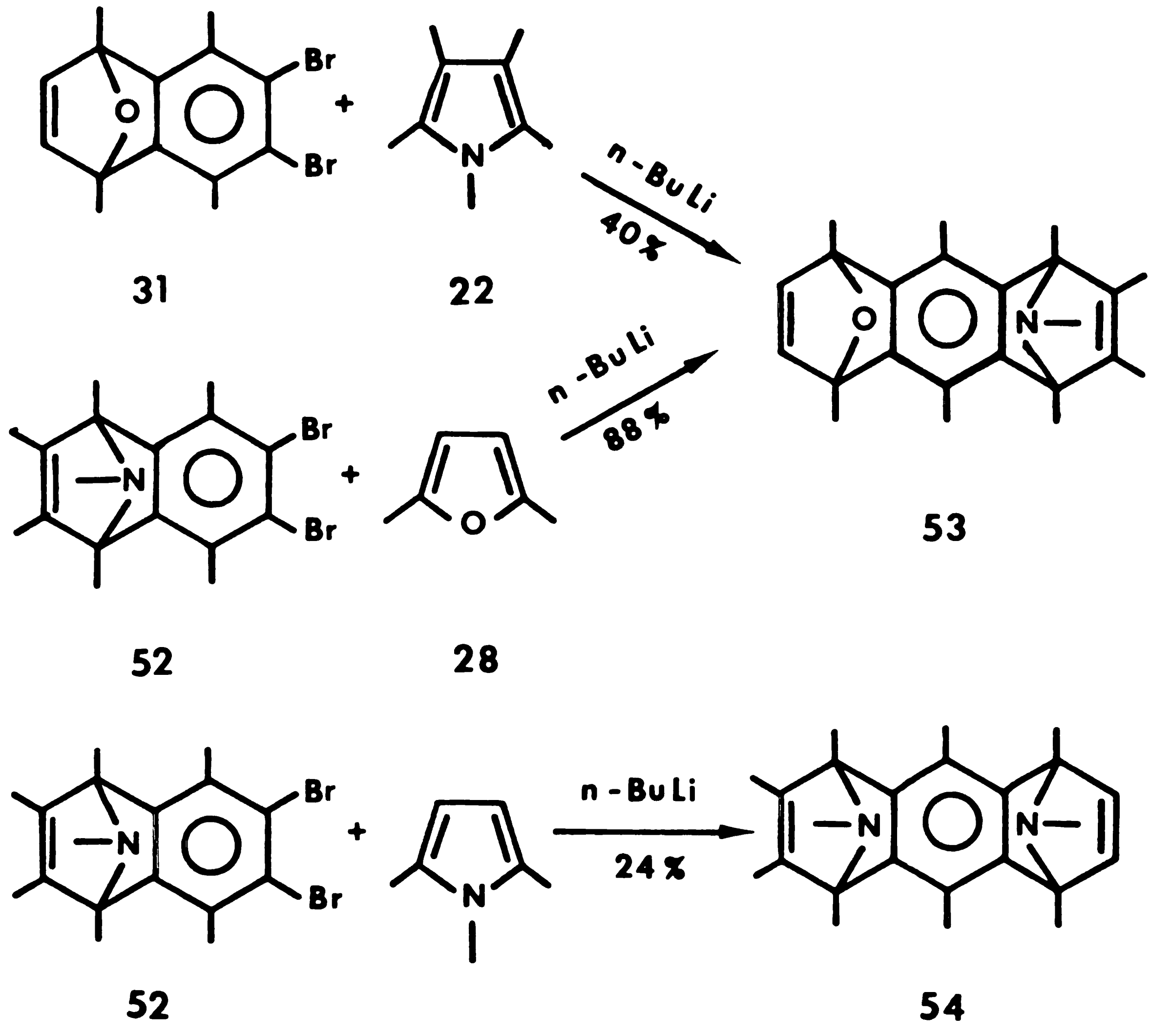
From the results of these experiments we conclude that bis-aryne (35) is not an intermediate in the reaction. However since the products are those which would be obtained if a bis-aryne were an intermediate, we call the tetrahalo arene precursors bis-aryne equivalents.

Discovery of toluene as a solvent not only increased the yield of the bis-adducts in most of the reactions, but also made possible the synthesis of mono-adducts such as 52. In a similar procedure as for 31, when a solution of 25 (1 equivalent) and pentamethylpyrrole 22 (1 equivalent) in toluene was reacted with n-butyllithium (1 equivalent), an 88% yield of mono-adduct 52 was obtained.



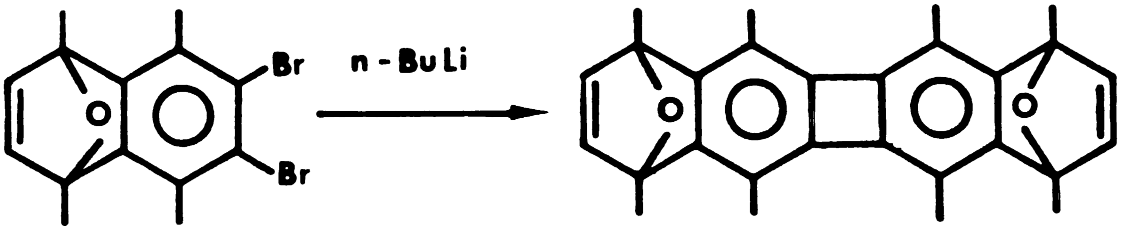
The fact that these mono-adducts could be synthesized in good yields added versatility to this bis-annelation in that the two new fused rings could be different from one another. Thus, unsymmetric bis-adducts 53 and 54 were synthesized (Scheme 5).

Scheme 5



Such unsymmetric adducts are not only novel compounds themselves, but one could also use standard methods to remove the nitrogen or oxygen bridges to obtain unsymmetrically substituted anthracenes.

The mono-adducts could also be used to synthesize binaphthylene derivatives such as 55. For example, when a solution of 31 in toluene at -78°C under argon was treated with n-butyllithium, an 8-10% yield of 55 was obtained as a mixture of syn and anti isomers. No attempt was made to optimize the yield.



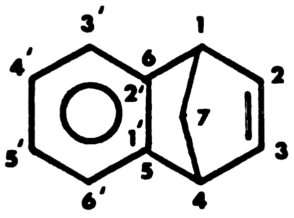
31 **55**

Compound 55 presumably was formed by the [2+2] cyclodimerization of the aryne intermediate.[26]

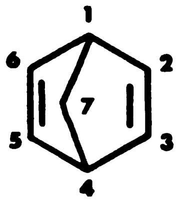
In conclusion, experimental data have been provided which prove that the bis-annelation of 25 occurs in a stepwise manner through the mono-adduct 31, rather than through bis-metalation and bis-aryne (35). Also, it was established that arynes, rather than organolithium compounds, are involved in the product-determining step. The stepwise nature of this bis-annelation reaction was used in the synthesis of unsymmetric bis-adducts such as 53 and 54, which could be considered as precursors for unsymmetrically substituted anthracenes. Mono-adduct 31 was also used to synthesize a binaphthylene derivative (55).

2. Bis-Annelation of Bis-Aryne Equivalents with Cyclopentadienes.

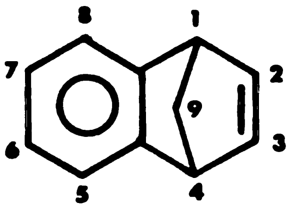
Meinwald and coworkers[27] were the first to synthesize benzonorbornenes (I). The choice of this name was motivated by the desire to relate this sytem to the parent compound norbornadiene (II); however the Ring Index would designate this system as a 1,4-dihydro-1,4-methanonaphthalene (III).



I

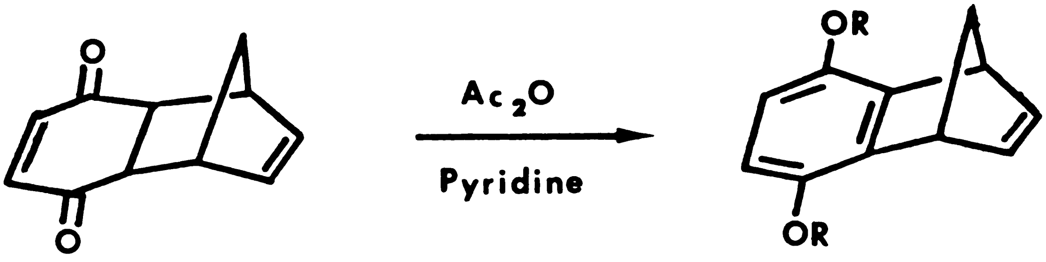


II



III

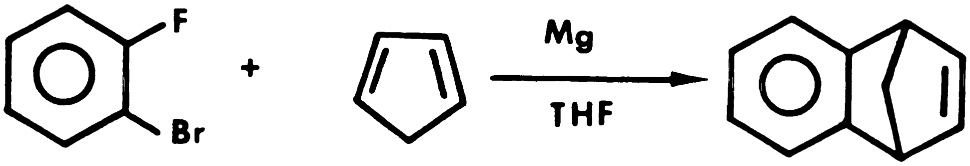
The starting material for this synthesis was the well known 1:1 cyclopentadiene-quinone adduct 56.[28] Treatment of 56 with acetic anhydride and pyridine gave the expected diacetate 57 in excellent yield.



R=COMe

56 **57**

Later, Wittig[15] used benzyne to synthesize the parent compound **60**. When a solution of o-fluorobromobenzene and cyclopentadiene in dry THF reacted with Mg, a 66% yield of **60** was obtained. This elegant procedure made



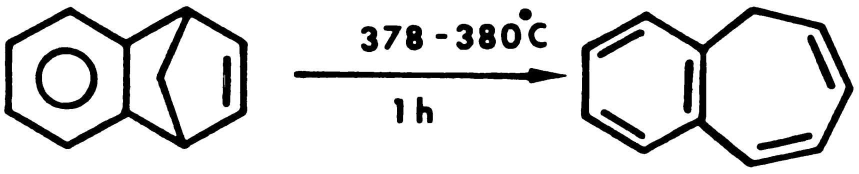
58 **59** **60**

benzonobornene **60** readily available. Shortly afterwards, Bartlett[29] used this compound as an intermediate in the synthesis of benzo analogs of endo-, exo- and 7-norbornenol, to study their rates of solvolysis.

Compound **60** has also been synthesized in 40% yield by the same strategy by using benzenediazonium carboxylate as the benzyne precursor.[30]

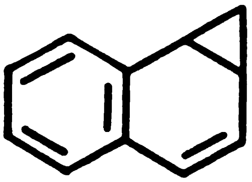
Huisgen[31] and Wittig,[32] in their studies of nucleophilic aromatic substitution reactions (for example the reaction of n-butyllithium and o-halobenzenes), concluded that the formation of benzyne occurs in two steps: the metalation and subsequent elimination of metal halide. Huisgen[31] proposed that the rate-determining step was generally the metalation reaction, and that the rate of elimination of halogen anions occurred in the order of iodine > bromine > chlorine >> fluorine. Later, Tanida et al.[16] studied the formation of benzynes from several o-dihalobenzenes. The arynes were intercepted by cyclopentadiene. From these studies Tanida concluded that metalation or elimination could be rate-determining, depending upon the particular case. For example reaction of 2,5-dibromo-1-iodobenzene with cyclopentadiene and magnesium not only produced the desired 6-bromo-1,4-dihyro-1,4-methanonaphthalene, but also a considerable amount of p-dibromobenzene and 3-bromoiodobenzene were formed. Formation of the last two arenes suggested that the metalation reaction took place without the subsequent elimination, whereas the reaction of arenes such as 4-bromo-3-iodoanisole, 3-bromo-4-fluorobenzene or 2-bromo-4-chlorobenzene with cyclopentadiene and magnesium gave only the desired cycloadduct. Therefore Tanida suggested that Huisgen's discussions and Wittig's findings are probably valid in terms of their own experiments and that which step is the rate-determining step depends primarily upon the particular case.

In general, bicyclo[2.2.1]heptanes and other compounds with this skeleton have received wide attention. They often have been employed in the development of modern organic theories because of their special fixed stereochemistry and the high strain of the ring system. Extensive studies have been done on both the thermal and photochemical rearrangements of benzonorbornadiene. Pyrolysis of 60 at 370-380°C for ∿1 h resulted in an 85% conversion to 61.[33]

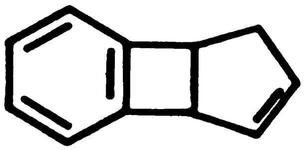


60 61

Deuterium labeling studies suggested that the rearrangement possibly goes through intermediates such as 61a or 61b or both.[33]

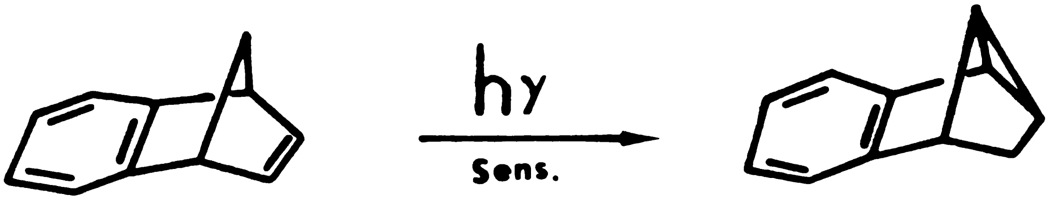


61a



61b

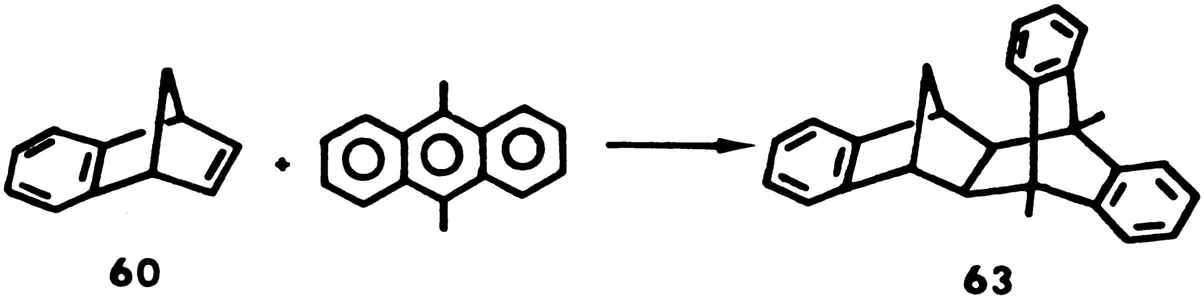
The photoarrangement of 60 has also been explored

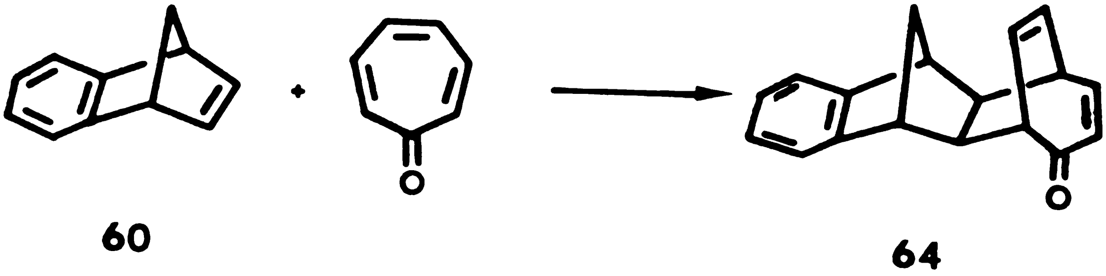


60 **62**

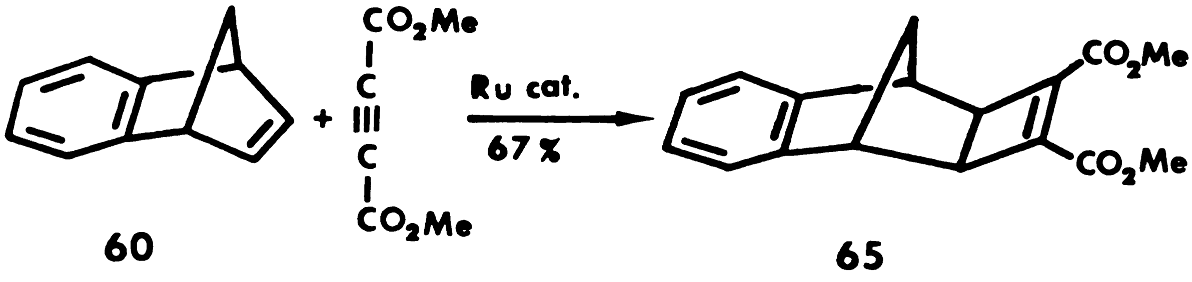
extensively.[34] Prolonged direct irradiation did not appear to give any 62, while acetophenone sensitization gave good conversion. The mechanism of this photoprocess (di-π-methane-rearrangement) has been established.[35]

Benzonorbornadiene 60 has also been widely used in organic synthesis, a few examples will be mentioned in order to further demonstrate the applications of such a system. Tanida and coworkers[36] used norbornadienes and their derivatives acting as dienophiles toward dienes such as tropone and 9,10-dimethylanthracene, in order to study the participation of non-conjugated double bonds in the Diels-Alder reaction. For example, adducts such as 63 and 64 were prepared.





Mitsudo[37] showed that **60** readily reacts with an equimolar amount of dimethyl acetylenedicarboxylate in the presence of a ruthenium catalyst in benzene at 80-100°C to give the corresponding [2+2] cross-adduct **65**.



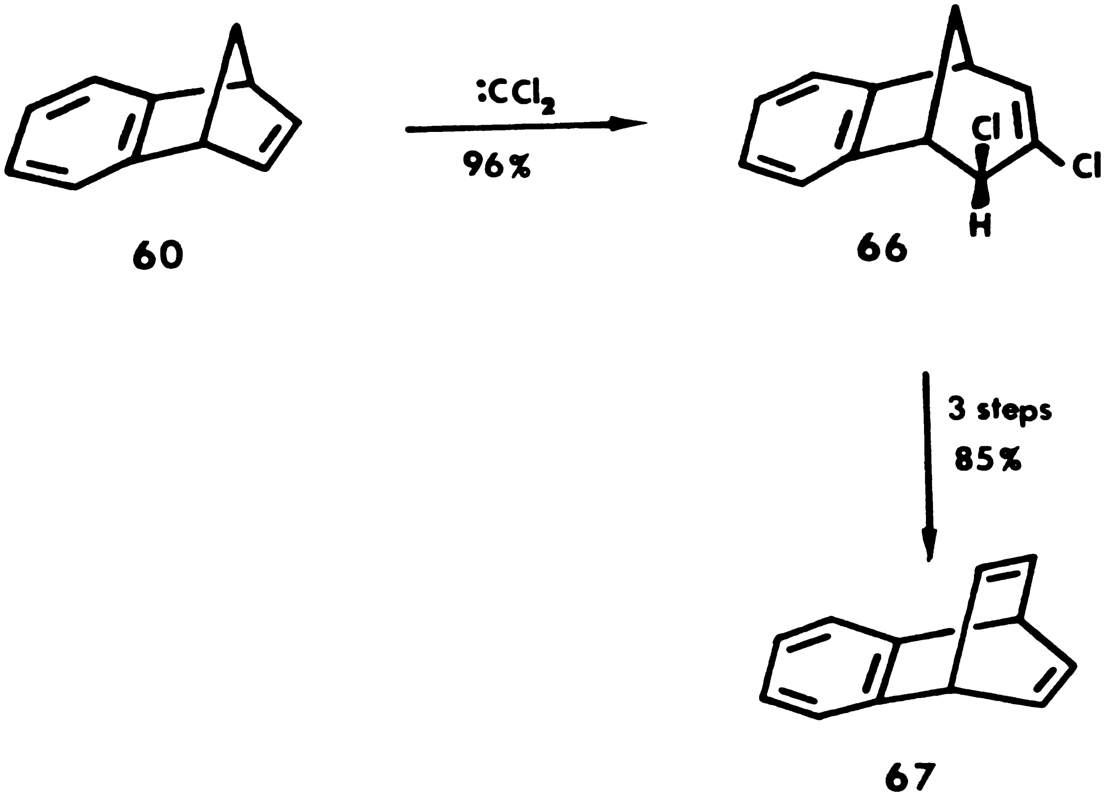
Compound **60** has also been conveniently used in the large-scale preparation of benzobarrelene (**67**) through its dichlorocarbene adduct **66**.[38]

tadi

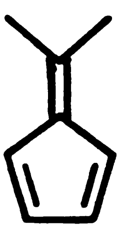
[4,2

(71)

68



Cycloadducts of benzyne with substituted cyclopentadiene systems such as 6,6-dimethylfulvene (68), spiro [4,2]hepta-4,6-dienes (70) and spiro[4,4]-nona-1,3-diene (71) have been prepared.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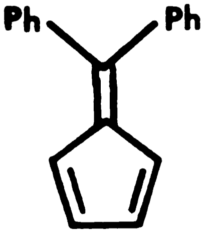

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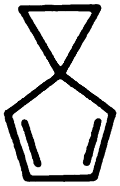
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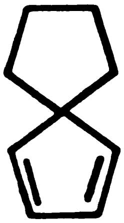
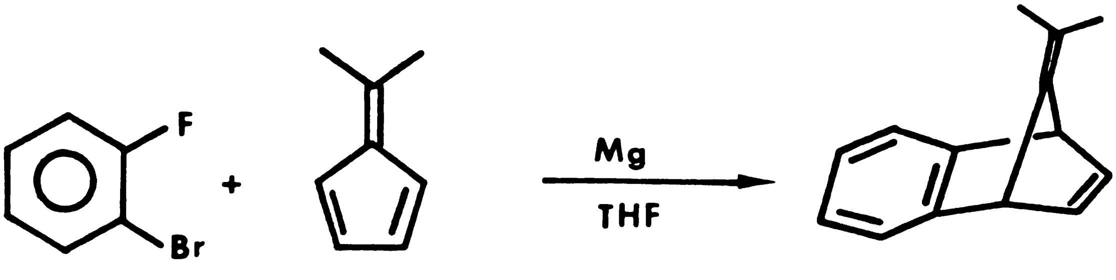
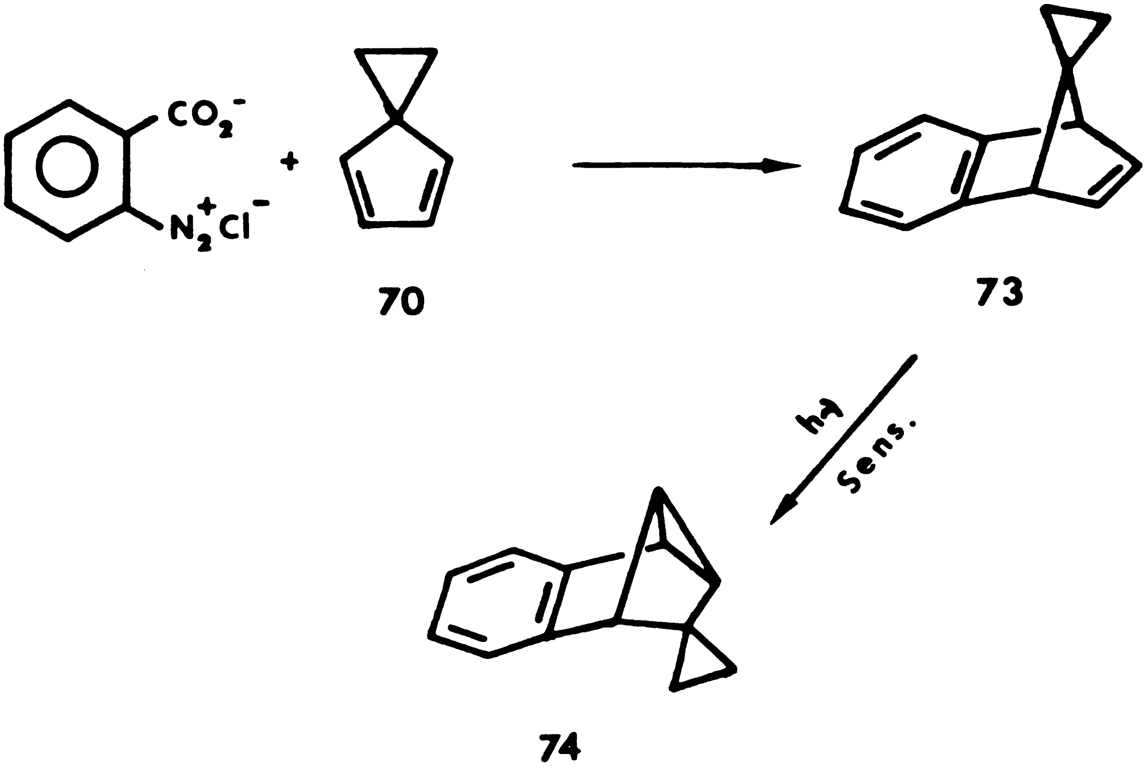

71

Tanida and his coworkers,[39] because of an interest in the homobenzylic behavior observed at the 7-position of benzonorbornadiene derivatives, synthesized 7-isopropylidenebenzonorbornadiene (72) in 31% yield through cycloaddition of benzyne generated from o-bromofluorobenzene and magnesium with 68. The cycloadduct of benzyne and fulvene was also prepared in low yield[40] and used in the synthesis of isobenzofulvene.[41] Compound 72 was used by Tanida[36] as a dienophile in a similar Diels-Alder reaction to that mentioned for 60. Sasaki and coworkers[42] very recently reported regio and stereo selective cycloaddition reactions of 72.



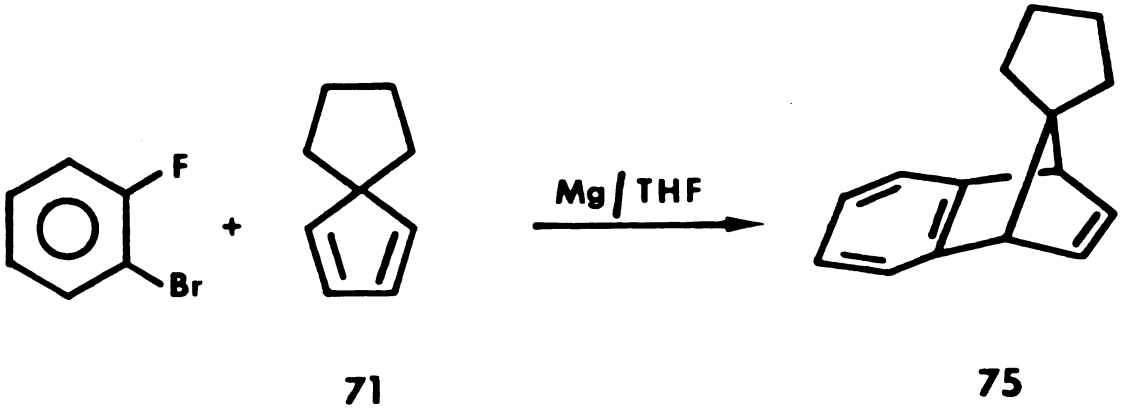
68 **72**

In order to study the effect of cyclopropyl conjugation on the photochemical isomerization of divinyl methane systems, Trost[43] investigated the direct and sensitized irradiations of spiro[cyclopropane-1,9'-1',4'-dihydro[1,4]methanonaphthalene] 73. This compound was prepared in 63% yield by the addition of benzyne to 70.



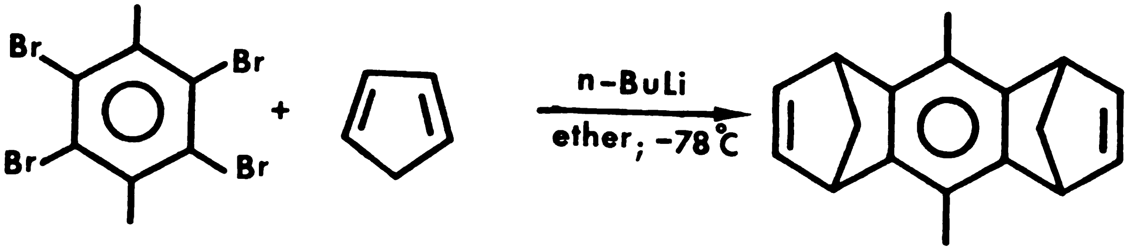
Irradiation of a 1% solution of **73** in ether containing 0.01% acetophenone gave a 65% yield of **74**. These results, which are analogous to those obtained with **60** (p. 38), indicated that the cyclopropane ring has no effect on the course of the reaction.

Spiro[cyclopentane-1,9'-1',4'-dihydro[1,4]methanonaphthalene] (**75**) was also prepared by Wittig's method.[44]



In light of all the known chemistry of the benzonorbornadiene system, we thought it would be worthwhile to extend the bis-annelation reaction with bis-aryne equivalents to cyclopentadienes. Not only would it be possible to obtain a variety of novel bis-adducts but they could be useful as intermediates in similar studies to those mentioned for 60.

One might possibly think that the use of n-butyllithium to generate arynes would not be compatible with dienes having strongly acidic hydrogens, such as cyclopentadiene. Therefore, the first attempt to bis-annelate with cyclopentadiene was done using excess n-butyllithium, in order to accomodate formation of the cyclopentadiene anion. A solution of tetrabromo-p-xylene (25) (1 equivalent) and cyclopentadiene (2 equivalents) in ether was cooled to -78°C under argon. Four equivalents of n-butyllithium (two to react with the bis-aryne equivalent and two to react with the cyclopentadiene) were added dropwise in 2 h, and the reaction mixture was allowed to warm slowly to room temperature. After work-up a 37% yield of bis-adduct 76 was obtained as a mixture of anti and syn isomers.



25 59 76

All experimental data were consistent with the structure (^1H and ^{13}C NMR spectra and mass spectrum).

To determine whether cyclopentadiene or its anion was involved in the cycloaddition reaction, the above experiment was repeated as follows. Equimolar amounts of cyclopentadiene and butyllithium were allowed to react at -78°C in ether. Thus all the cyclopentadiene was converted to its anion, which precipitated. Then the bis-aryne equivalent, tetrabromo-p-xylene, was added followed by 2 equivalents of n-butyllithium (to generate the aryne). On work up only polymeric material and cyclopentadiene dimer were obtained. No trace of bis-adduct 76 was observed. Thus it is clear that free cyclopentadiene, and not its anion, is essential for the cycloaddition.

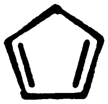
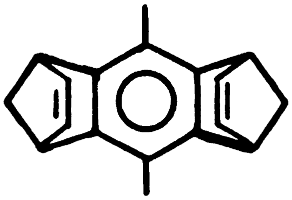
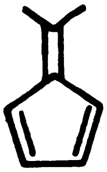
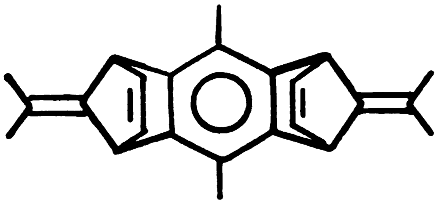
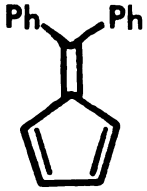
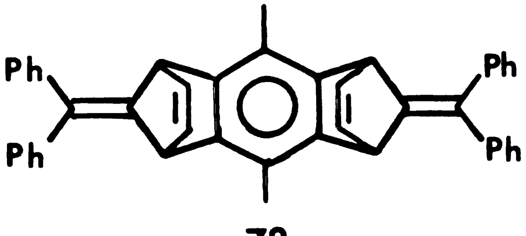
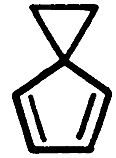
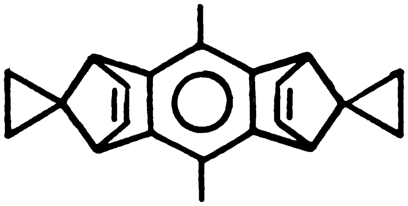
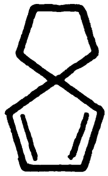
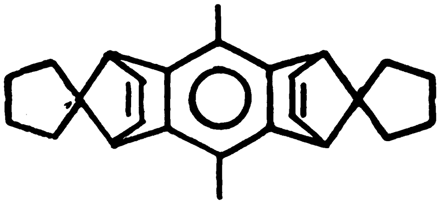
The result of this experiment, combined with the first experiment, suggests that metal-halogen exchange on the benzene ring occurs faster than proton removal from cyclopentadiene. The first experiment was therefore repeated under the same conditions but using only two instead of four equivalents of n-butyllithium. After work up an almost quantitative yield of 76 was obtained. Thus excess n-butyllithium was actually detrimental, since it removed some of the cyclopentadiene from the reaction.

Cyclopentadienes 68-71 were also used to synthesize bis-adducts 77-80 (Table 2). In all cases the reaction product contained a mixture of anti and syn isomers. Often one of the isomers was obtained pure by trituration of the crude product with hexane or methanol. The remaining hexane or methanol solution was later concentrated and the resulting solid was chromatographed on activated alumina to obtain a pure sample containing a mixture of the two isomers. A great effort was not put forth to completely separate these isomers. The ^{1}H NMR, ^{13}C NMR and mass spectra of adducts 77-80 are quite similar to those of bis-adduct 76.

The butyllithium technique for generating benzynes was also used to synthesize the tetramethyl derivatives of 60, 72, 73 and 75. 1,2,3,4-Tetramethyl-5,6-dibromobenzene (21), which was easily available from the bromination of tetramethylbenzene in good yield and large quantity,[45] was used as the benzyne precursor. The benzyne was generated at -78°C under argon by treating

TABLE 2

THE CYCLOADDITION OF A BIS-ARYNE EQUIVALENT WITH CYCLOPENTADIENES

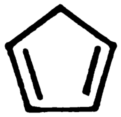
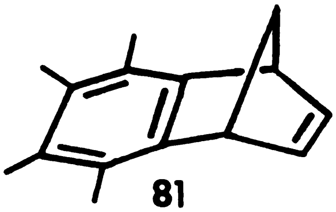
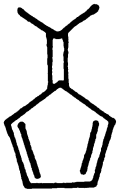
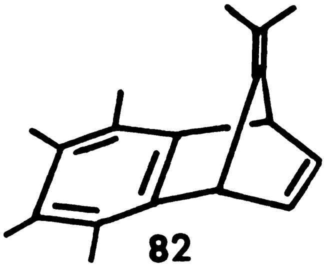
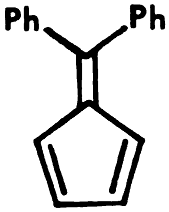
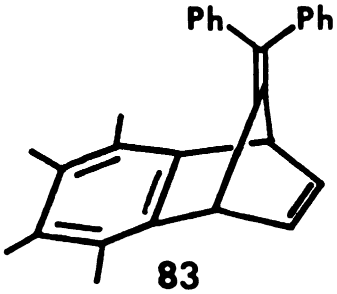
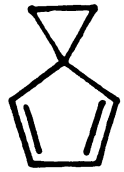
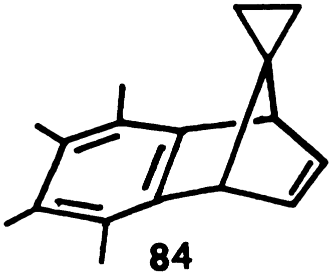
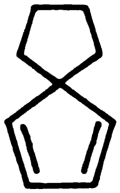
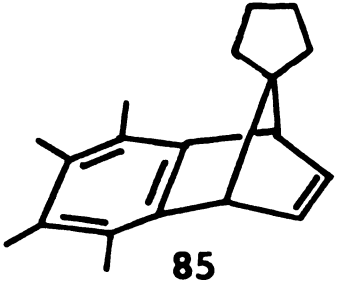
Diene	Solvent	Bis-adduct	Yield (%)
 **59**	ETHER	 **76**	97
 **68**	THF	 **77**	70
 **69**	THF	 **78**	36
 **70**	TOLUENE	 **79**	68
 **71**	TOLUENE	 **80**	58

one equivalent of **21** with one equivalent of n-butyllithium. Interception of this benzyne with dienes **68**-**71** gave the adducts **81**-**85** in good yields (see Table 3). Physical data for these adducts are quite similar to those of the unsubstituted ones and also to their corresponding bis-adducts. Although the lithium halogen exchange reaction of n-butyllithium and o-dihalogenobenzenes has previously been used in generating arynes,[46] the reaction conditions that were worked out here in the synthesis of these mono-adducts represents a considerable yield improvement over the methods which were previously described for adducts **60**, **72**, **73** and **75**.

In conclusion, the bis-adducts which were described in this part of the thesis are novel compounds. Their syntheses are simple, afford the products in good yields, and will enable one to explore their chemistry.

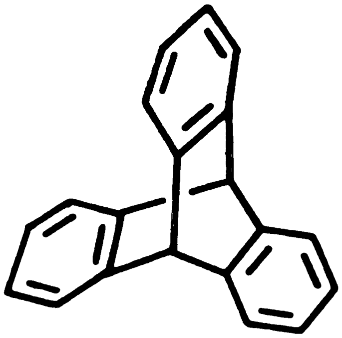
TABLE 3

THE CYCLOADDITION OF TETRAMETHYLBENZYNE WITH CYCLOPENTADIENES

Diene	Solvent	Adduct	Yield (%)
 59	ETHER	 81	97
 68	THF	 82	57
 69	THF	 83	62
 70	TOLUENE	 84	52
 71	TOLUENE	 85	73

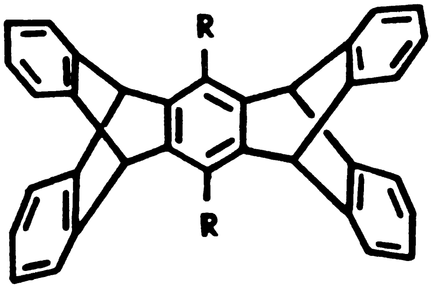
3. Use of Bis-Aryne Equivalents in the Synthesis of Iptycenes.

Bartlett[47] was the first to synthesize triptycene (13), for the purpose of testing certain concepts in physical-organic chemistry. For example, bridgehead-substituted triptycenes were used to generate the corresponding carbonium ions, radicals and carbanions and these were compared with their trityl analogs.[48] Interest in triptycene rose sharply when it was shown by Wittig that it could be synthesized easily in one step from benzyne and anthracene,[14] and at one point the formation of triptycene actually became a test for the efficacy of various benzyne precursors.[49] Eventually, the synthesis of triptycene became a standard undergraduate laboratory "experiment".[50]

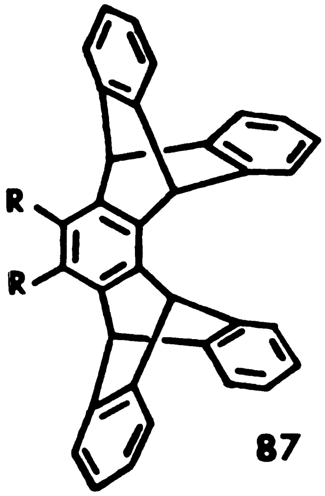

13

Many substituted triptycenes are known, and the benzene rings have also been replaced with a variety of other aromatic rings.[51] The rigid framework is attractive and has been used to study such diverse phenomena as intramolecular charge transfer[52] and restricted rotation about single bonds.[53] In the many structural variations on triptycene, the triptych or tri-planar nature of the structures has been preserved.[54]

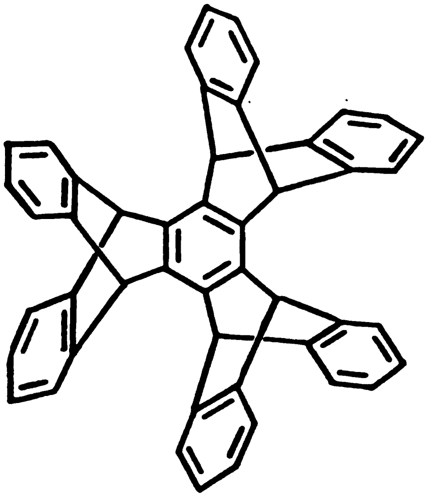
If triptycene is viewed *not* as a benzyne derivative of anthracene but rather as a benzene which is ortho-disubstituted by attachment to the 9,10 positions of anthracene, then one quickly observes that this concept might be extended by connection of two or three anthracenes as shown in **86**-**88**. We propose that these substances be given the trivial name of 'iptycenes'.



86

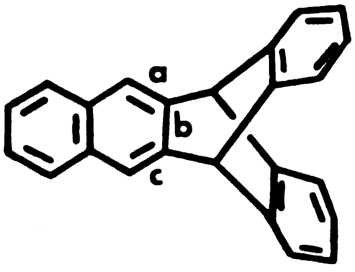


87

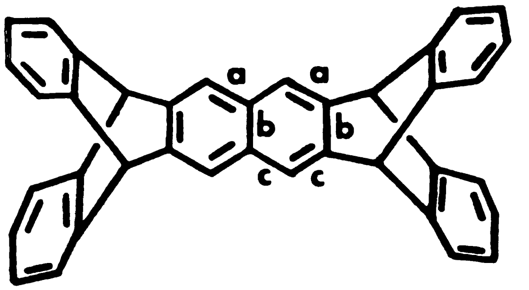


88

The name 'iptycene' emphasizes the relationship between these compounds and the parent structure triptycene. A prefix indicates the number of separated arene planes; thus 13 is triptycene (3 planes), 86 and 87 are pentiptycenes (5 planes) and 88 is a heptiptycene (7 planes). We believe that only three descriptors need be added to these names to precisely define the structures. The use of two of these descriptors is illustrated in the following names: for 86 (R = H), [1.1.1^{b}.1.1]pentiptycene; for 87 (R = H), [1.1.1^{a}.1.1]pentiptycene; for 88, [1.1.1^{a,c}.1.1.1.1]heptiptycene. The 1's indicate that each ring is benzenoid, and the appropriate number would be replaced by 2 if naphthalenoid or 3 if anthracenoid or phenanthrenoid, etc. The superscripts refer to the bond (a, b or c) to which the sp^{3} carbons are attached. We further suggest that these trivial names be abbreviated for prototype compounds. Thus we will use the names para- and ortho-pentiptycene for 86 and 87 respectively.



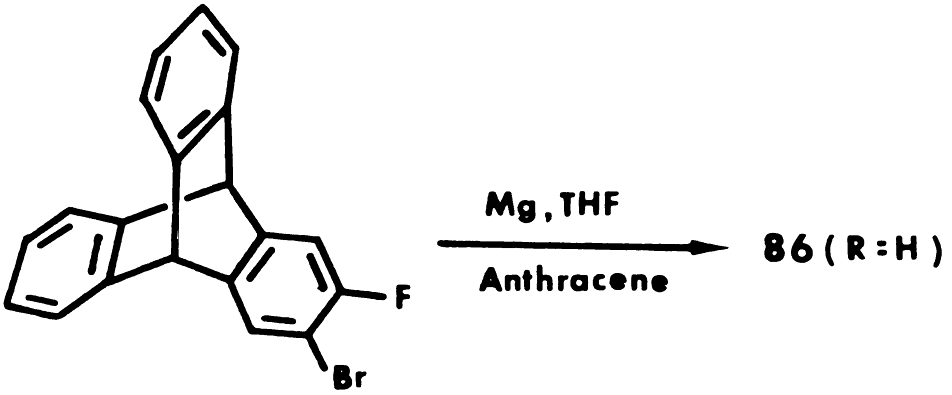
[2^{b}.1.1] triptycene



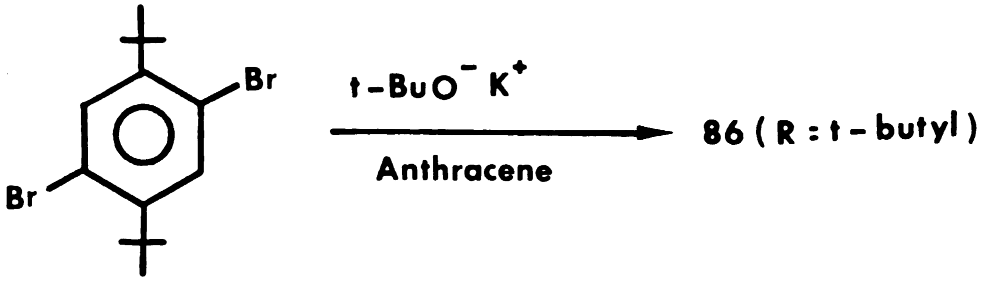
[1.1.2(b)^{b}.1.1] pentiptycene

A third descriptor, to indicate points of ring fusion, may also be necessary; it consists again of a bond (a, b or c) and is placed in parentheses. The examples on the preceeding page illustrate the system. These trivial names are, we believe, simpler to use than the systematic CAS names, which are for 86 (R = H): 5,7,12,14-tetrahydro-5,14[1',2']:7,12[1",2"]dibenzenopentacene: for 87 (R = H): 4,8,13,14-tetrahydro-5,14[1',2']:8,13[1",2"]dibenzenopentaphene; and for 88: 5,6,11,12,17,18-hexahydro-5,18[1',2']: 6,11[1",2"]: 12,17[1‴ ,2‴]tribenzenotrinaphthylene.

Some compounds of this type already appear in the literature.[56] Thus 86 (R = H) was prepared by the addition of 2,3-triptycyne to anthracene. The yield was 10%, and the required fluorobromotriptycene had to be synthesized from triptycene (in four steps, via nitro-, amino- and 2-bromo-3-aminotriptycenes), so that the overall yield from readily accessible starting materials was quite low. Compound 86 (R = *t*-butyl) was synthesized

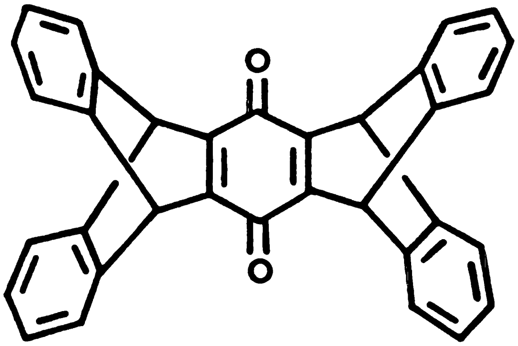


in low yield (3.7% crude, 2% purified) via bis-aryne equivalent 89 by treatment with strong base.[57] Although not fully aromatic, the pentiptycene quinone 90 properly belongs among these compounds. It was originally reported



89

fifty years ago[58] and can be considered as a substance readily available in high yield from inexpensive precursors, benzoquinone and anthracene.

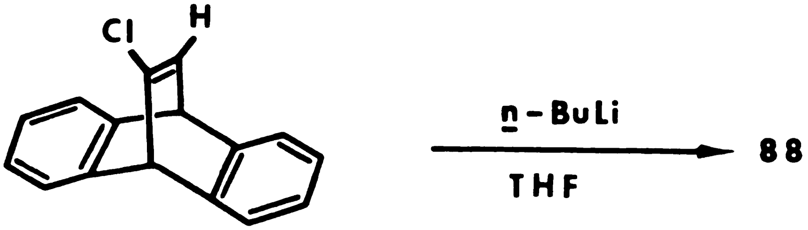


90

As far as we are aware, no ortho-iptycenes such as structure 87 have been previouly described.

Compound 88 was obtained in low, unspecified yield as a minor product from the reaction of 11-chloro-9,10-

dihydro-9,10-ethenoanthracene (**91**) with butyllithium.[59]



91

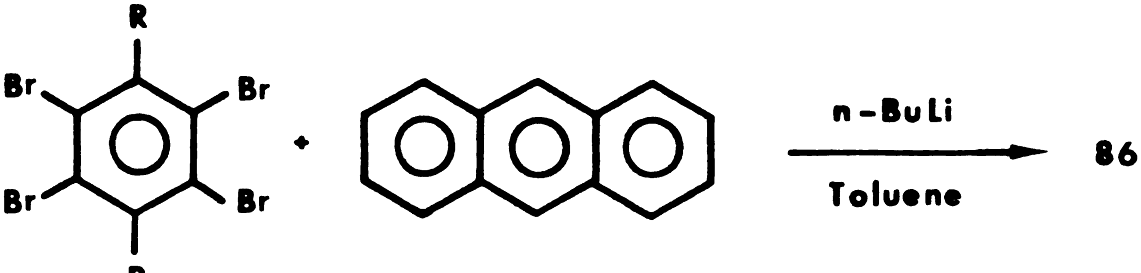
The structure assignment was based on spectra and the space group of its crystalline 1:1 chlorobenzene complex. Compound **88** is reported to have the remarkable melting point, without decomposition, of 580°C.

Extension of our bis-annelation technology to cycloadditions with anthracenes has led to a short general synthesis of pentiptycenes **86** and **87** which will be described here. The synthesis of **88** has also been re-examined and improved, and the cycloalkyne intermediate derived from **91** has been trapped with several dienes.

A. Pentiptycenes with General Structure **86**.

A toluene solution of anthracene and tetrabromo-p-xylene (**25**), when treated with n-butyllithium in hexane at -10°C gave pentiptycene **86** (R = CH_3) in 35% yield (based on consumed anthracene). The product melts at 460-462° without decomposition.

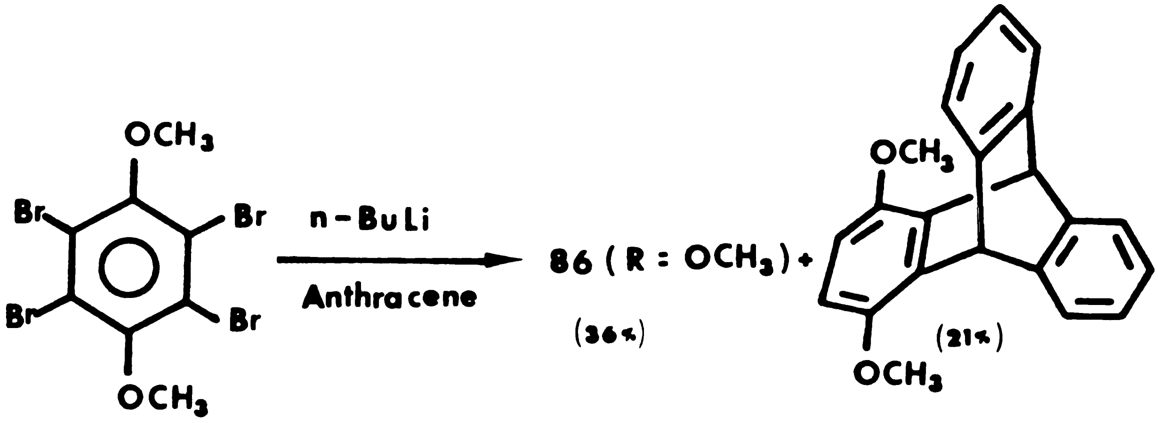
The structure of **86** (R = CH_3) is based on its spectroscopic properties. The mass spectrum showed a



25

parent peak at *m/e* 458 and major fragmentation peaks at 443 ($M^+ - CH_3$), 427 ($M^+ - 2CH_3$), 280 (M^+ - anthracene) and 178 $(\text{anthracene})^+$. The ^{13}C NMR spectrum of this 36-carbon compound showed only 7 peaks, consistent with its D_{2h} symmetry. The methyl carbons appeared at δ 14.36, the bridgehead carbon at δ 50.84 and the remaining five peaks were in the aromatic region. The proton NMR spectrum of **86** ($R = CH_3$) consisted of a singlet at δ 2.65 (6 H) for the methyls, a singlet at δ 5.59 (4 H) for bridgehead hydrogens, and aromatic multiplets at δ 6.90 (8 H) and 7.28 (8 H). These data are quite similar to those of the parent pentiptycene **86** (R = H) which was prepared by Dr. Y. Takehira in our group. A similar procedure, but with 1,2,4,5-tetrabromobenzene as the bis-aryne equivalent precursor, gave an excellent yield of **86** (R = H) (94% based on consumed anthracene).

Other substituted pentiptycenes were also synthesized. For example **86** (R = OCH_3) was prepared in 36% yield and one step from the reaction of tetrabromohydroquinone dimethyl ether (**92**) with anthracene and n-butyllithium; some reduced mono-adduct **93** was also formed. Compound **86** (R = OCH_3) melts at 400-402°C without decomposition. The proton NMR spectrum shows peaks at δ 3.76 (s, 6 H, OCH_3), 5.50 (s, 4 H, bridgehead hydrogens), and aromatic multiplets at δ 6.73 (8 H) and 7.10 (8 H). The ^{13}C NMR spectrum showed only 7-peaks. A single crystal X-ray structure on **86** (R = OCH_3) also confirmed the structure.

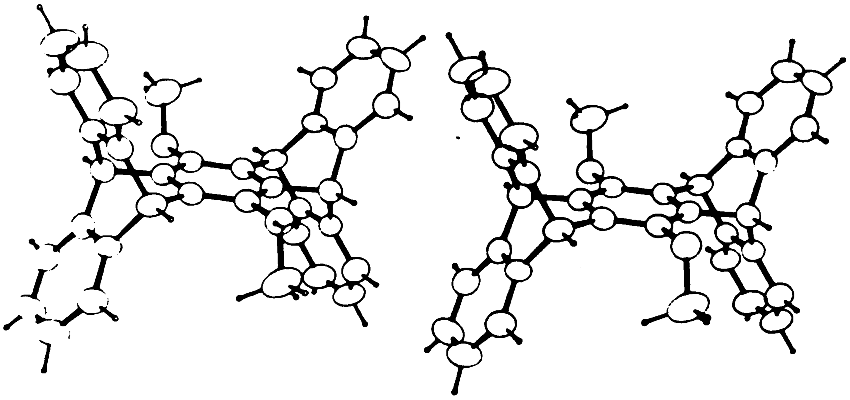


92

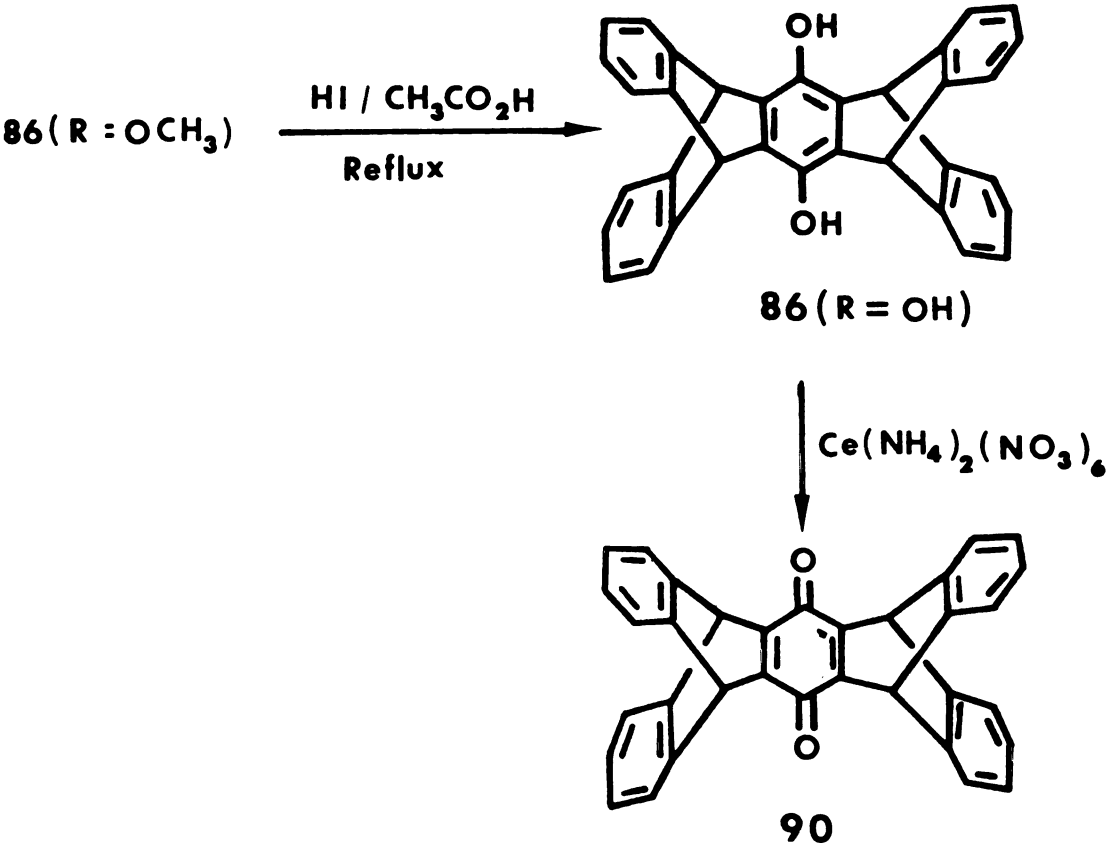
93

Figure 2 shows the stereo drawing of this compound. Appendix 2 gives the tables of bond distances and bond angles.

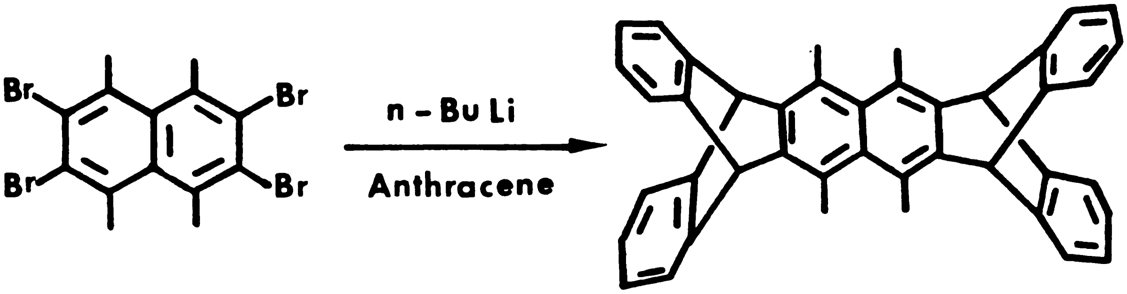
Figure 2



Cleavage of the dimethyl ether 86 (R = OCH_3) with hydrogen iodide and acetic acid gave 86 (R = OH) in 97% yield, mp 427-430°C (dec). Oxidation of 86 (R = OH) with ceric ammonium nitrate gave the known quinone 90 in 86% yield.



A pentiptycene with a central naphthalene ring was obtained in good yield from tetrabromo-tetramethylnaphthalene (**94**).[60] The structure of **95**, mp 358-360°C, follows from its method of synthesis and spectra.

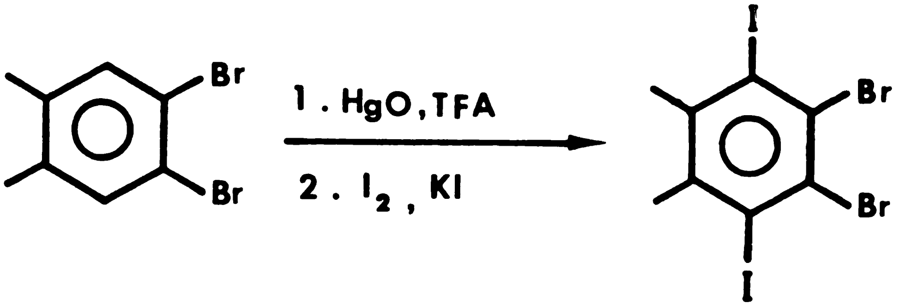


94 **95**

B. Pentiptycenes with General Structure 87.

As far as we are aware, no examples of compounds with this general structure were previously known. The technique of ortho-bis-annelation, however, has been used previously.[61]

The bis-aryne equivalent selected was 4,5-dibromo-3,6-diiodo-o-xylene (97), which was synthesized in two steps and high yield from the corresponding dibromo compound 96. This ortho bis-aryne precursor was selected in order that initial lithiation, which is faster at iodine than at bromine, be directed in such a way as to



96 **97**

produce the desired product. If the tetrabromo analog of 97 is used, initial lithiation and lithium bromide elimination can occur in an undesired manner.

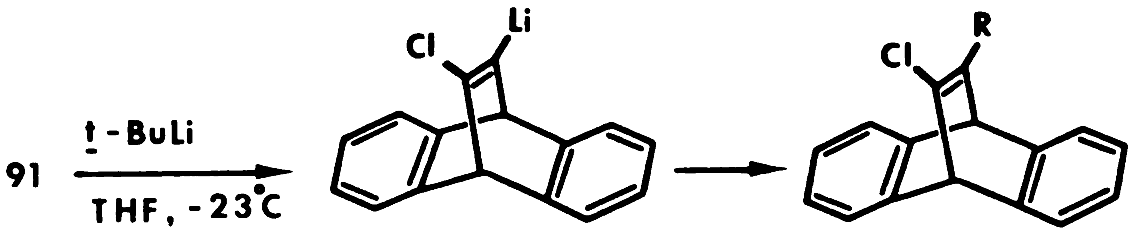
Treatment of 97 with anthracene and butyllithium gave 87 (R = CH_3) in 14% yield, mp 382-384°C. The C_{2v} symmetry of 87 (R = CH_3) requires only twelve different 'kinds' of carbons, and this is precisely what

$$97 \ + \ \text{anthracene} \ \xrightarrow[\text{toluene } -23°\text{C}]{\text{n-BuLi}} \ 87 \ (\text{R} = \text{CH}_3)$$

was seen in the ^{13}C spectrum. There is one methyl signal (δ 15.32) but there are two bridgehead carbon signals (δ 50.18, 50.93) and appropriate aromatic peaks. The mass spectrum of 87 (R = CH_3) showed an intense M^+ peak (*m/e* 458, intensity 97), a base peak at *m/e* 280 (M^+-anthracene) and a fairly intense peak at *m/e* 178 (anthracene, intensity 52).

C. Heptiptycene 88 and Cycloalkyne 104.

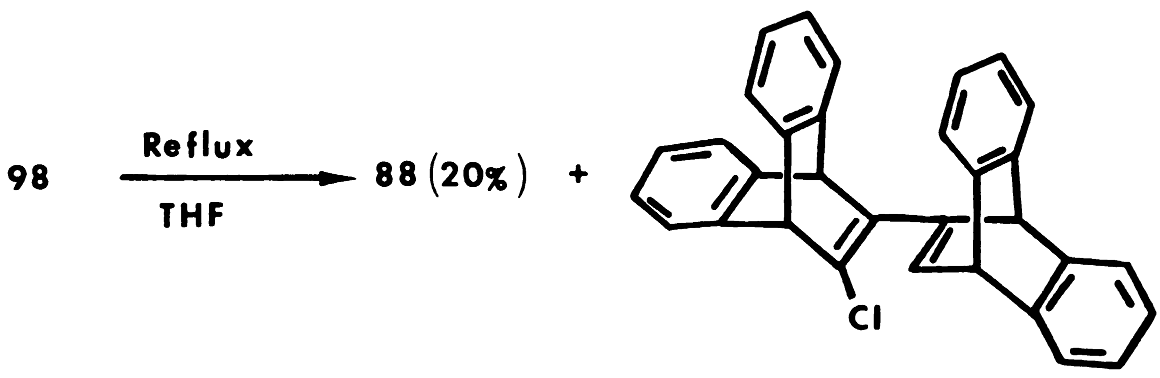
Huebner, et al. showed[59] that at -78°C in THF 91 was metalated by n-butyllithium to give the α-lithio derivative 98 which on carbonation gave the chloro acid 99. We verified this result using t-butyllithium at -42°C. Quenching of 98 with CH_3OD or CH_3I or $BrCH_2$-CH_2Br gave 100, 101 and 102 respectively. Thus 98 is relatively stable toward elimination of lithium chloride.



98

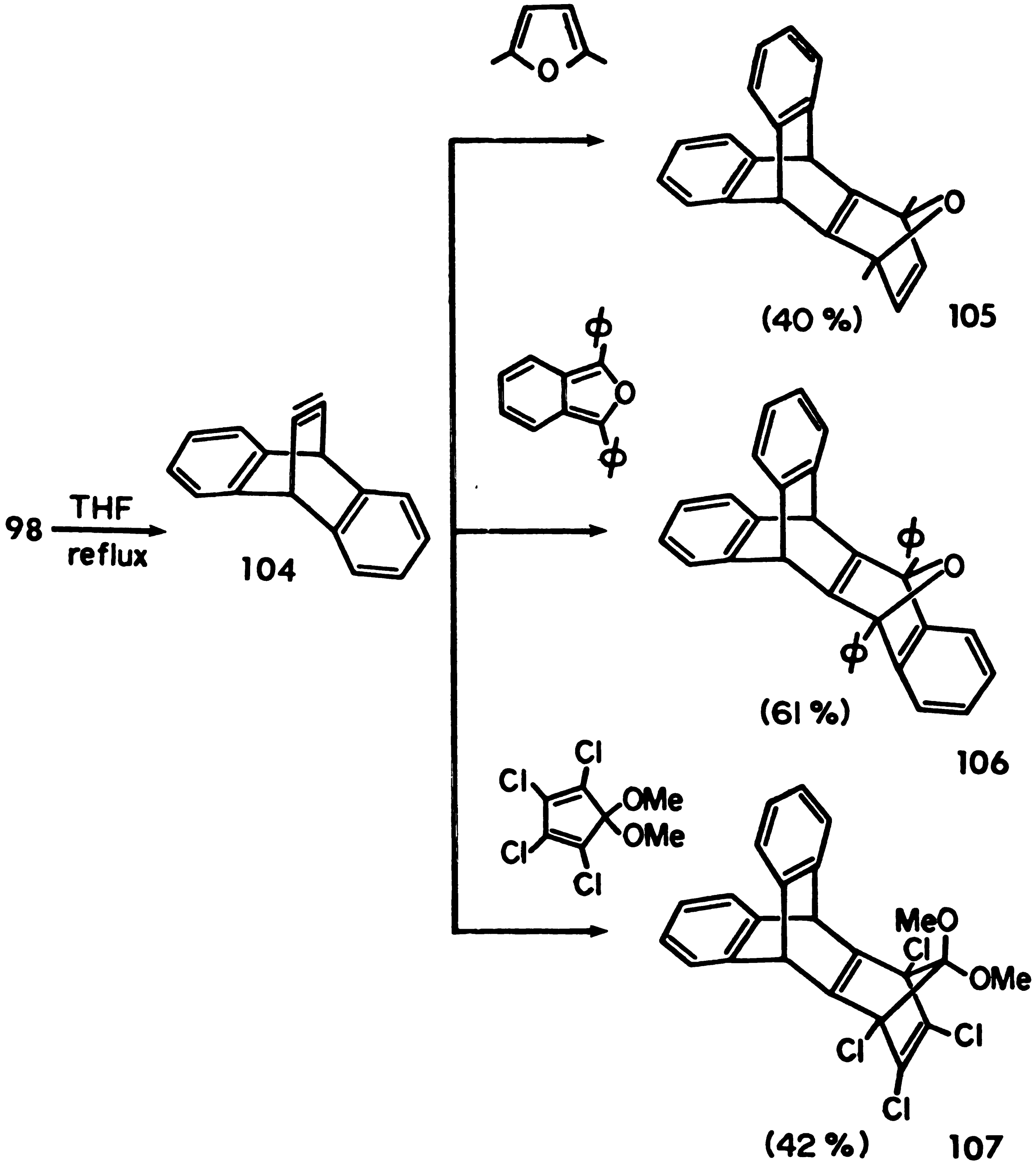
99 ($R : CO_2H$)
100 ($R : D$)
101 ($R : CH_3$)
102 ($R : Br$)

When a solution of 98 (prepared at -42°C using t-butyllithium) was warmed quickly to room temperature and then heated under reflux for 2 h a 20% yield of the heptiptycene 88 and a 39% yield of coupling product 103 was obtained. This procedure represents some yield improvement over the literature.[59]



103 (39%)

The presumed intermediate in the formation of 88 is the cycloalkyne 104. To trap this intermediate, solutions of 98 were prepared at -42°C and added dropwise to



refluxing THF containing various dienes. In this way, adducts 105-107 were prepared in reasonable yields.

Reaction of organolithium reagents with cyclic vinyl halides has been discussed as a route to strained cycloalkynes.[62] For example, recently Gassman and coworkers[63] reported generation of bicyclo[2.2.1]hepta-2-yne and its trimer. But cycloalkyne 104 appears not to have been trapped previously and synthetic utility of this easily accessible reactive intermediate and the formation of related derivatives could be explored. In the experimental section we describe an improved synthesis of its precursor 91.

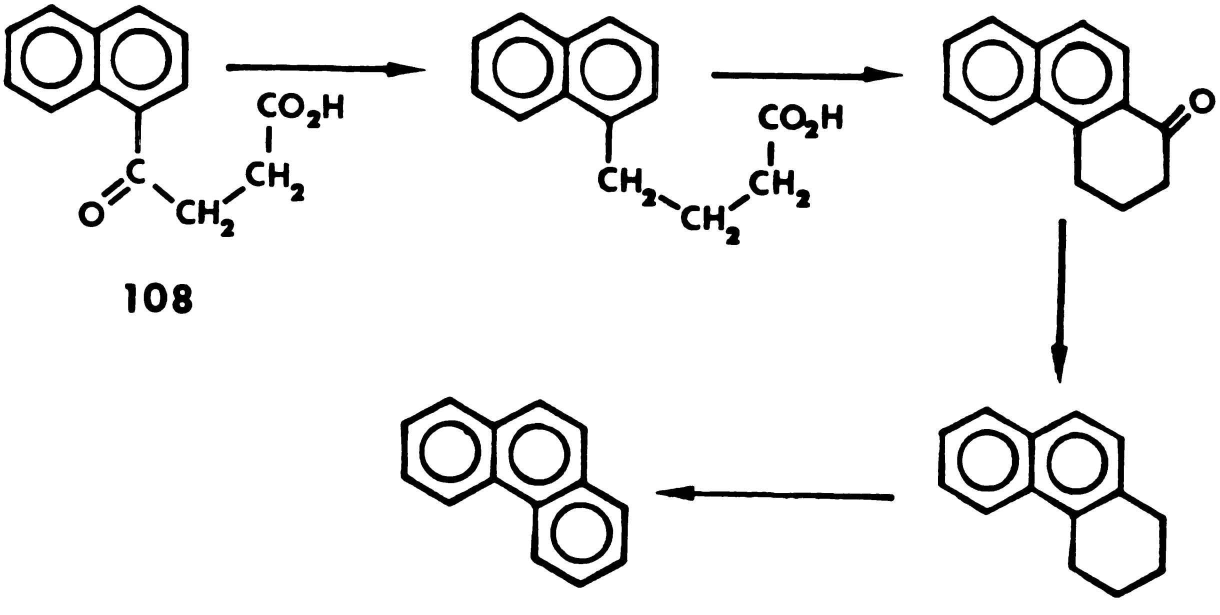
In conclusion, a short, reasonably efficient synthesis of pentiptycenes with the general structures 86 and 87, a synthesis which will permit exploration of the chemistry of these novel compounds and their derivatives, has been developed. The yield of heptiptycene 88 has been improved by using t-butyllithium in place of n-butyllithium in the metalation of 91 and the presumed intermediate in its formation, cycloalkyne 104, has been trapped with various dienophiles. The chemistry of triptycene analogs such as 86-88 can now be explored.

4. Application of Bis-Aryne Equivalents to the Synthesis of Phenanthrenes.

Phenanthrene was first discovered in coal-tar in 1872.[64] Today, coal-tar is still the most important raw material for its preparation. However, there are numerous syntheses of phenanthrene and its derivatives. In this section, synthesis of methyl derivatives, and especially hindered phenanthrenes, will be emphasized, as well as our new and simple synthesis of phenanthrenes.[64a]

Phenanthrene synthesis from succinic anhydride, naphthalene and aluminum chloride is particularly important for the preparation of homologues.[65] Scheme 6 shows

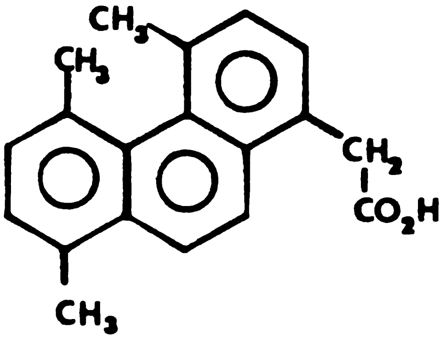
Scheme 6



this general procedure. The keto-acid 108 is reduced by the Clemmensen method, the ring is closed, the product is then reduced as before and dehydrogenated. A variety of reagents have been used by different authors in these steps.[65] In 1965, A. Cornu and J. Ulrich[66] used this already well-known method to synthesize 18 alkyl phenanthrenes.

Considerable interest is associated with 4,5-dimethylphenanthrene (115) because of the steric hindrance associated with such a structure. These 4,5-positions were called "impossible" positions.[67] Newman,[68] in 1940, predicted that molecules containing the 4,5-dimethylphenanthrene system might be capable of optical resolution due to interference between the methyl groups in the hindered positions. Three possible geometries were suggested for this system: (1) the methyl groups may bend away from each other but still lie in the same plane as the aromatic rings; (2) the aromatic rings may be distorted in some way; (3) the methyl groups may be bent out of the plane of the aromatic rings. If the first alternative were correct, there would be no asymmetry and the molecule would not be resolvable. However if the second or third alternative, or combination of these two, were correct the molecule would be capable of resolution.

Newman showed that alternative 2 or 3 is correct by the successful resolution of 4,5,8-trimethyl-1-phenanthrylacetic acid (109).[69]

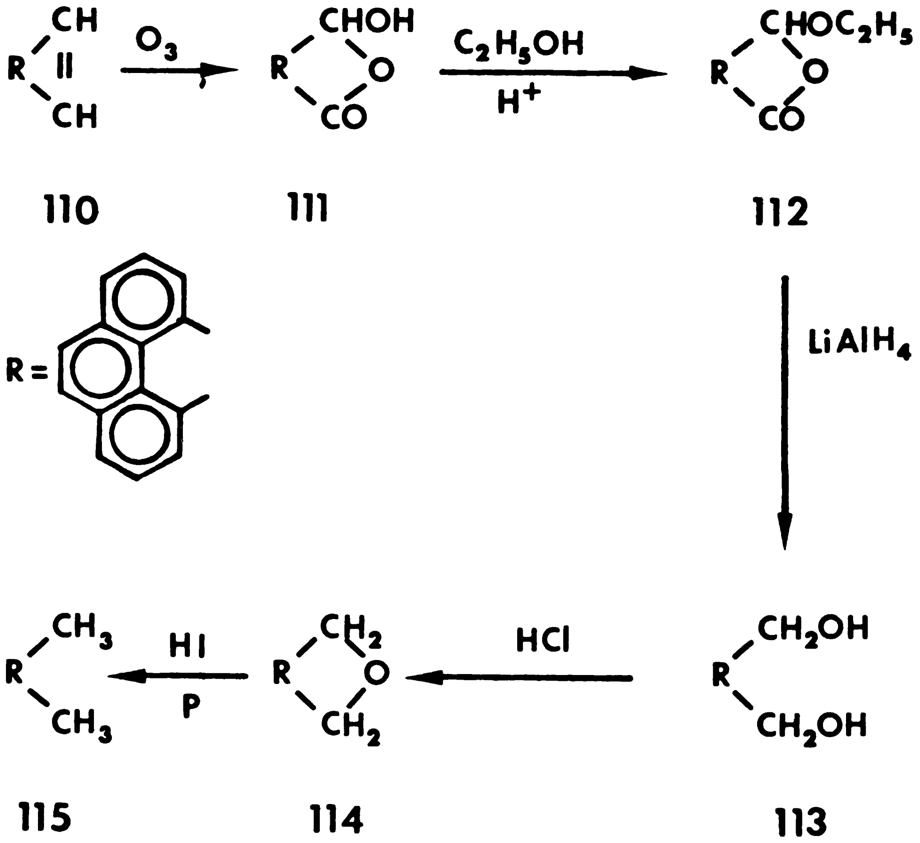


109

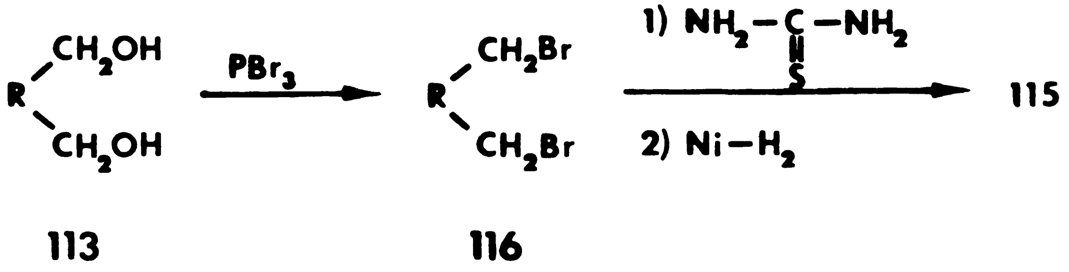
X-ray crystallographic investigation of the structures of overcrowded aromatic compounds by Schmidt and coworkers[70] showed that the asymmetry introduced into a molecule by intramolecular overcrowding is caused by a combination of the two alternatives previously mentioned; that is, by a folding of the benzene rings, and, if there are groups present in the hindered positions, by the assumption of non-coplanar positions for these groups.

Unsuccessful attempts to synthesize 4,5-dimethylphenanthrene were reported by several authors.[71] In 1949, Newman and coworkers[67] were successful and reported the first synthesis of 4,5-dimethylphenanthrene (115) (Scheme 7). Ozonization of pyrene (110) gave the aldehydo-acid 111, which was converted to its ethyl ester 112. Subsequent reduction of 112 with lithium aluminum hydride gave the diol 113 which was converted to cyclic ether 114 by acid. Reduction of 114 with hydroiodic acid and red phosphorus under very careful conditions gave 115. The last step afforded only 17% of 115.

Scheme 7:

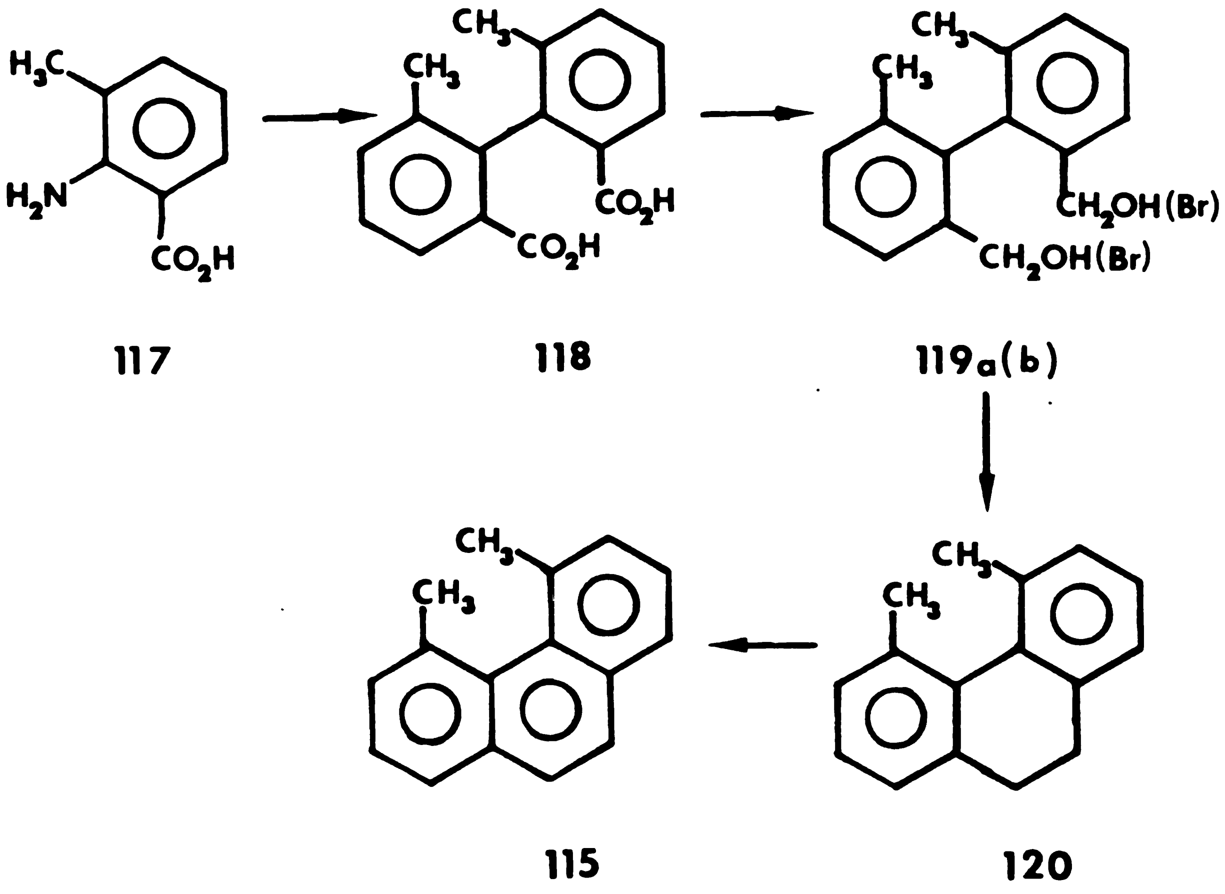


A few months later Badger and Campbell [72] independently reported a synthesis for 115. Their strategy was somewhat similar to that of Newman. After preparation of the diol 113 by a similar procedure, it was converted to its corresponding dibromide 116. Direct reduction of 116 was unsuccessful. Therefore 116 was converted to its diisothiuronium dibromide which underwent smooth hydrogenolysis with Raney nickel to give 115 in 76% yield.



Wittig and Zimmerman, in 1953,[73] used a completely different method to synthesize 115 (Scheme 8).

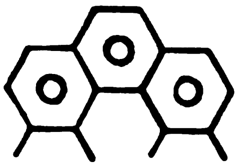
Scheme 8



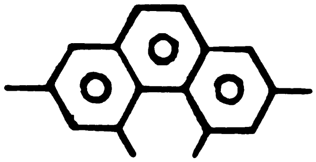
In this synthesis anthranilic acid 117 was prepared from corresponding isatin. The diazonium carboxylic acid derived from 117 was coupled in the presence of cupric sulfate to give 118. Reduction of 118 with lithium aluminum hydride gave diol 119a which upon treatment with phosphorus tribromide gave dibromide 119b. Cyclization of 119b was achieved in good yield using phenyllithium, to give 120. The final dehydrogenation was carried out in a steel bomb at 300-305°C in the presence of 5% rhodium on alumina. The total yield of 115 starting from anthranilic acid 117 was about 25%. This method was adopted by Newman in 1965,[74] for the synthesis of 3,4,5,6- and 2,4,5,7-tetramethylphenanthrenes.

Newman's interest in the synthesis of compounds containing methyl groups in close proximity to each other developed from the problem of their chemical carcinogenity. He determined the strain energies in these hydrocarbons from their heats of combustion.[75] His data showed that 4,5-dimethylphenanthrene is more strained than the 2,7-dimethyl isomer 121 by 12.6 ± 1.5 kcal/mol and 122 is more strained than 123 by 7.2 ± 1.4 kcal/mol, due mainly to the buttressing effect.[76]

Recently,[77] Newman reported a synthesis for 9-bromo derivatives of 122 and 123, in order to compare rates of reaction by an electrophilic substitution mechanism in strained and unstrained polycyclic aromatic



122



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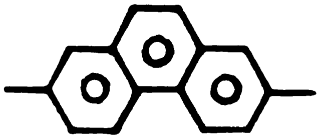

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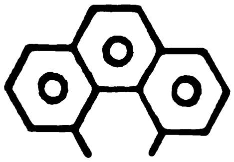
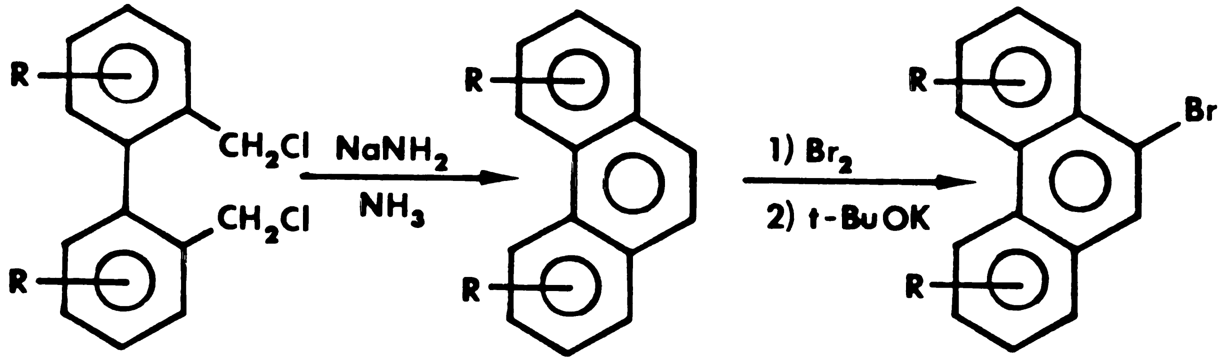


115

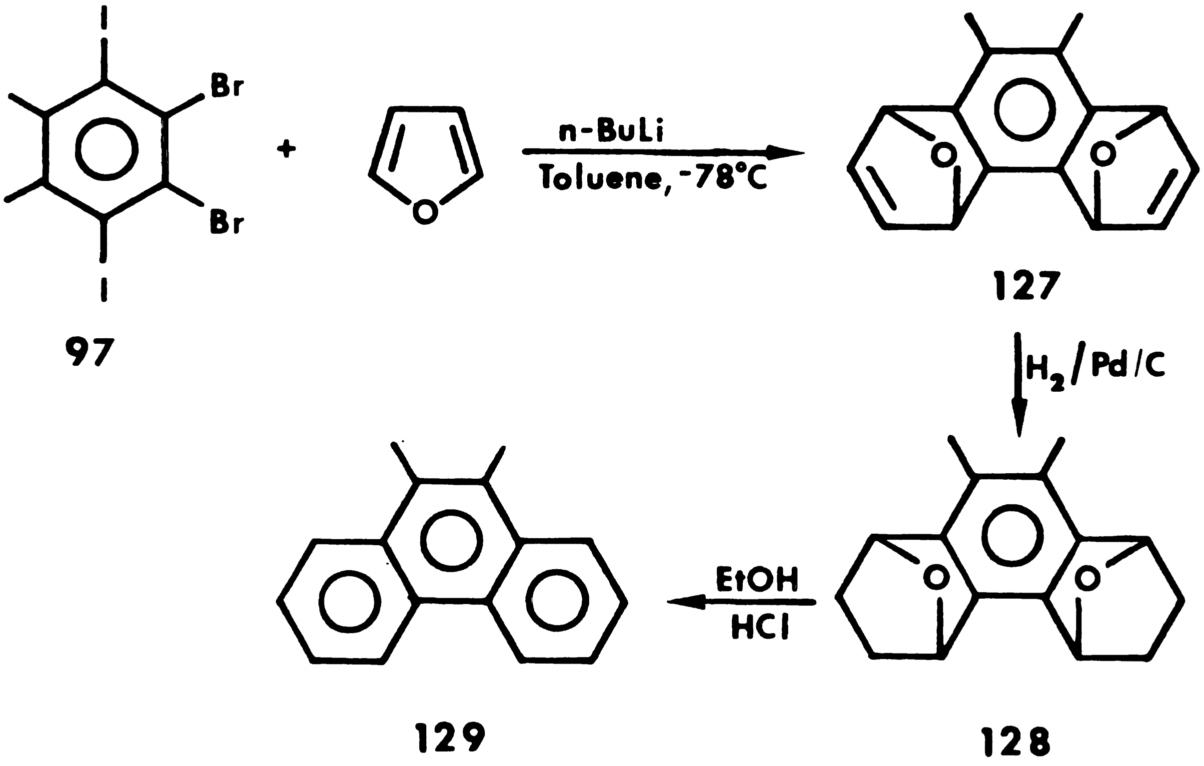
hydrocarbons.[78] In this work he reported an improved method for cyclization of 124. Treatment of 124 with sodium amide in liquid ammonia directly gave the desired phenanthrene 125. The cyclization occurred only when a stainless-steel stirrer was used. When a nylon-coated magnetic stirrer was used, the starting dichlorides were recovered and the nylon stirrer was black.



124 **125** **126**

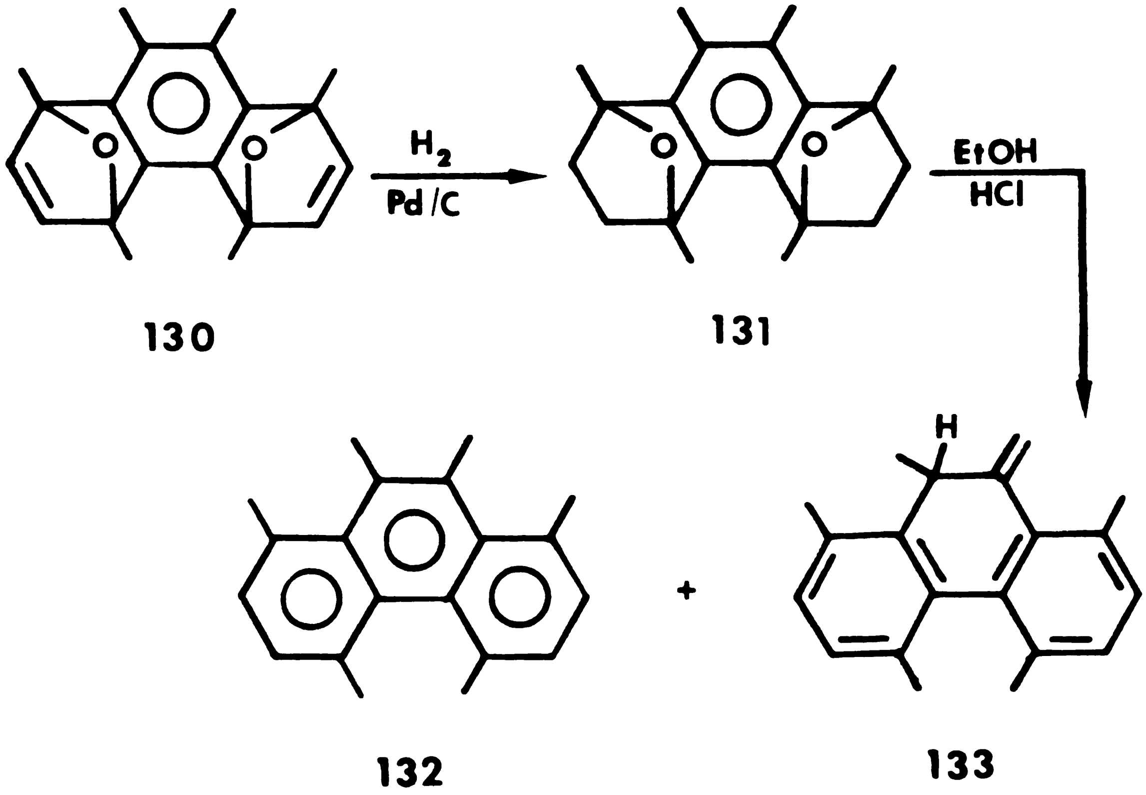
Addition of bromine to the 9,10-bond of 125 yielded a 9,10-dibromo-9,10-dihydrophenanthrene. Subsequent elimination of hydrogen bromide yielded the desired phenanthrenes 126.

Success in using the o-bis-annelation technique to synthesize o-pentiptycene **87** led us to explore a new and simple phenanthrene synthesis. As described in the synthesis of **87**, dibromodiiodo-o-xylene **97** functions as an o-bis-aryne equivalent upon treatment with n-butyllithium. When a solution of **97** (1 equivalent) and furan (excess) in dry toluene at -78°C under argon was reacted with 2 equivalents of n-butyllithium a 71% yield of bis-adduct **127** was obtained as a mixture of syn and anti isomers.



The ^{1}H NMR spectrum ($CDCl_3$) of this mixture does not show separate peaks for the two isomers; rather, the peaks are either overlapped or slightly broadened. A sharp singlet at δ 2.13 (6 H, methyls), a broad singlet at δ 5.60 (4 H, bridgehead hydrogen), and a broad singlet at δ 6.80 (4 H, vinyl hydrogens) were observed. Further identification of **127** was achieved by its conversion to the known 9,10-dimethylphenanthrene **129**.[79] To remove the oxygen bridges, a solution of **127** was hydrogenated over palladium on charcoal. Treatment of the reduced product **128** with a saturated solution of HCl in ethanol gave **129** in greater than 90% yield, mp 140°C (lit.[79] 140.5°C).

Using 2,5-dimethylfuran in a similar reaction gave a 34% yield of bis-adduct **130** as a mixture of syn and anti isomers. This mixture was separated by column chromatography on alumina. The major isomer, which was eluted first, had a proton NMR spectrum consisting entirely of singlets, at δ 1.86 (6 H), 1.90 (6 H), 2.13 (6 H), and 6.50 (s, 4 H), whereas the spectrum of the minor isomer showed a doublet of doublets for the vinyl hydrogens and three other singlets with approximately the same chemical shifts as for the major isomer. The ^{13}C NMR spectrum of each isomer consisted of 10 signals for this C$_{20}$-compound, which shows the presence of a plane or C$_2$ axis of symmetry. For the major isomer the signals are at δ 14.30, 19.15, and 20.27 (methyls), 88.51, 89.31 (bridgehead carbons), and five peaks in the aromatic region.

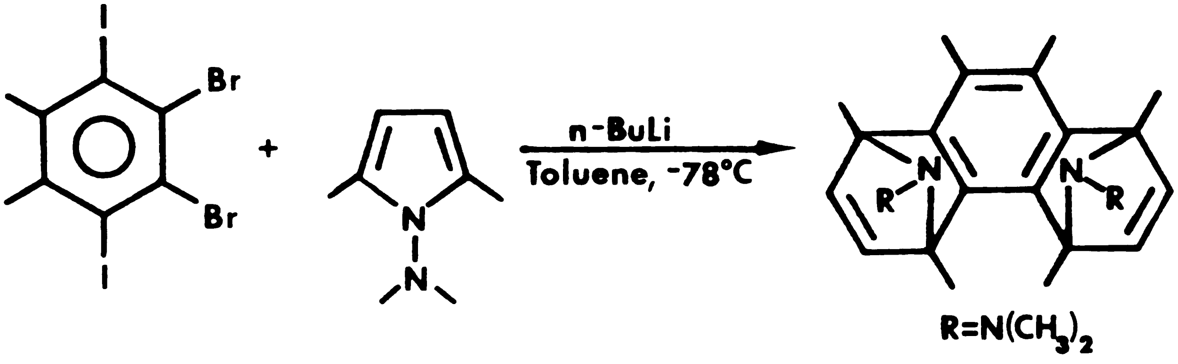


When a procedure similar to that used for 127 was used to remove the oxygen bridges from 130, a 1:3 mixture of hexamethylphenanthrene (132) and the rearranged hydrocarbon 133 was obtained. The physical properties of 132 will be described later in this section. The mass spectrum of 133 showed that it is an isomer of 132. The structure of this isomer was determined from its proton NMR spectrum: δ 0.88 (d, *J* = 8 Hz, 3 H), the aliphatic methyl; 2.23 (s, 6 H), 2.33 (s, 3 H), 2.40 (s, 3 H), the aromatic methyls, 3.43 (q, *J* = 8, 2 Hz, 1 H) the hydrogen next to the aliphatic methyl, 4.93 (d, *J* = 2 Hz, 1 H) and 5.20 (d, *J* = 2 Hz, 1 H), the vinyl hydrogens; 6.86 (s, 2 H) and 7.00 (s, 2 H), the aromatic hydrogens.

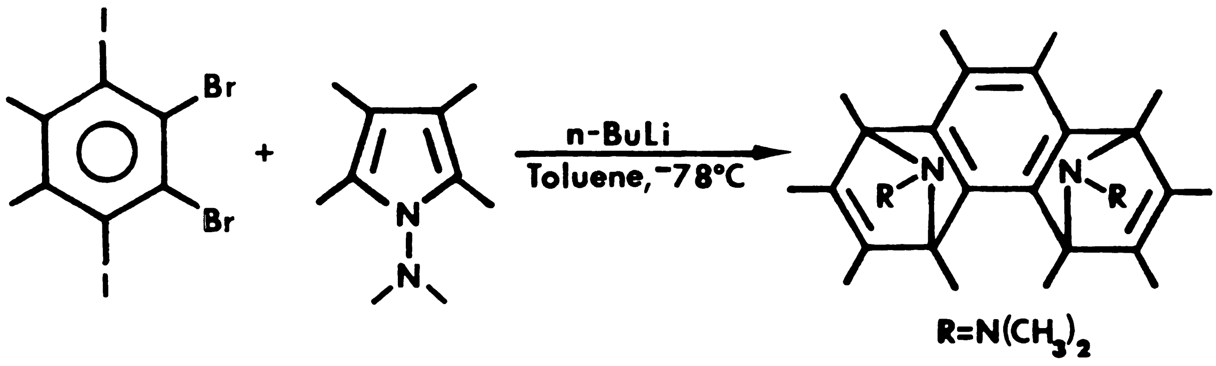
In order to find out whether 133 is a primary product of the reaction of 131 with acid or whether it is formed as a secondary product from further reaction of hexamethylphenanthrene 132 with acid, a solution of 132 was treated with ethanol saturated with HCl, under exactly the same conditions as for 131. After work-up the reaction mixture contained 76% of 133 and 24% of unreacted 132. Thus 133 is a secondary reaction product.

The unsatisfactory removal of the oxygen bridges from 130, which gave mainly the undesired rearranged product 133, led us to look for a different diene, the bis-annelation product of which could be aromatized in good yield without rearrangement. Dimethylaminopyrroles were previously used in our laboratory in the synthesis of some polymethylarenes.[20,80] Aromatization of the bis-adducts derived from these pyrroles was achieved either by m-chloroperbenzoic acid oxidation or by pyrolysis. The nitrogen bridges were eliminated to give the corresponding polyarenes in excellent yields. This method was discovered by Schultz.[81]

Pyrroles 134[82] and 135[80] were prepared in good yields by azeotropic distillation of the corresponding 2,5-hexanediones and 1,1-dimethylhydrazine. Bis-annelation of pyrrole 134 and arene 87 gave a 46% yield of bis-adduct 136 as a mixture of syn and anti isomers. The major isomer was purified by trituration of the crude product with hexane. The proton NMR spectrum of this isomer consisted of singlets at δ 1.80 (6 H)



87 **134** **136**



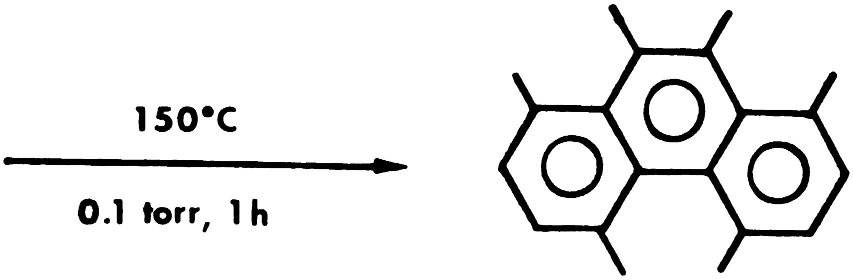
87 **135** **137**

and 1.83 (6 H), 1,4,5,8-methyls; singlet at δ 2.16 (6 H), 9,10-methyls; a broad singlet at δ 2.28 (12 H), N-methyls, and a broad singlet at δ 6.43 (4 H), vinyl hydrogens. The ^{13}C NMR spectrum of this isomer showed peaks at δ 14.93 (9,10-methyl), 18.72, 19.43 (1,4,5,8-methyls), 45.69 (N-methyls) 74.71, 76.15 (bridgehead carbons) and 126.44, 145.75 146.00, 146.52, 146.75 (sp^2 carbons). The electron impact mass spectrum of 136 did not show a parent peak but had a base peak at *m/e* 262 corresponding to $[M^+ - 2N(CH_3)_2]$; however, the chemical ionization mass spectrum gave an $(M + 1)^+$ peak at *m/e* 379.

Bis-adduct **137** was also prepared by a procedure similar to that used for **127**, from the bis-annelation of pyrrole **135** and arene **87**. The yield of the mixture of syn and anti isomers of **137** was 44%. The proton NMR spectrum of the major isomer showed singlets at δ 1.56 (6 H), 1.60 (6 H), 1.76 (6 H), 1.80 (6 H), 2.16 (6 H), 2.43 (12 H); the ^{13}C NMR (spectrum) was similar to that of **136** and consisted of peaks at δ 10.50, 11.38, (2,3,-6,7-methyls), 14.77 (9,10-methyls), 17.63, 18.69 (1,4,-5,8-methyls), 45.83 (N-methyls), 76.12, 76.30 (bridgehead carbons), and four other peaks in the aromatic region. The electron impact mass spectrum did not show a parent peak, but a base peak at *m/e* 318 corresponding to $[M^+ - 2N(CH_3)_2]$. However, the chemical ionization mass spectrum gave an $(M + 1)^+$ peak at *m/e* 435.

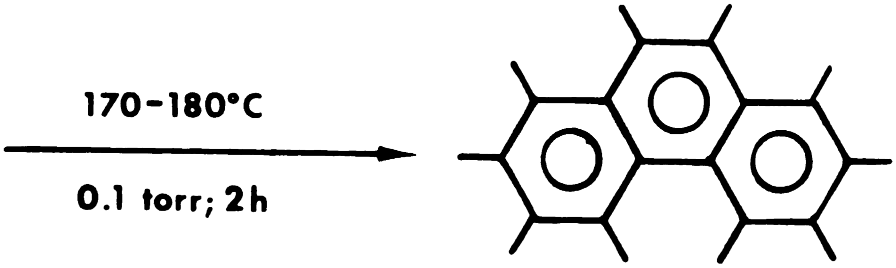
As previously pointed out, the mass spectra of adducts **136** and **137** failed to show parent peaks; rather they gave base peaks corresponding to the bridge-removed products. This indicated that pyrolysis of **136** and **137** could very well lead to hexamethylphenanthrene (**132**) or decamethylphenanthrene (**138**), respectively.

136



132

137



138

When 136 (50 mg) was pyrolyzed at its melting point (147-149°C) at 0.1 torr for 1 h it gave a 90% yield of 1,4,5,8,9,10-hexamethylphenanthrene (132). The proton NMR spectrum of 132 showed singlets at δ 2.449 (6 H), 2.631 (6 H), 2.817 (6 H), and an AB quartet for the aromatic protons centered at δ 7.171. The ^{13}C NMR spectrum consisted of 10 peaks for this C_{20}-carbon compound, three peaks at δ 20.79, 22.02, 25.47, for the three types of methyl groups, and 7 peaks in the aromatic region. The mass spectrum showed the parent peak, which was also the base peak, at *m/e* 262. The ultraviolet absorption spectrum of 132 in heptane showed

λ_{max} at 324 nm (log ε 4.43), 266 (4.90), 241 (4.64).

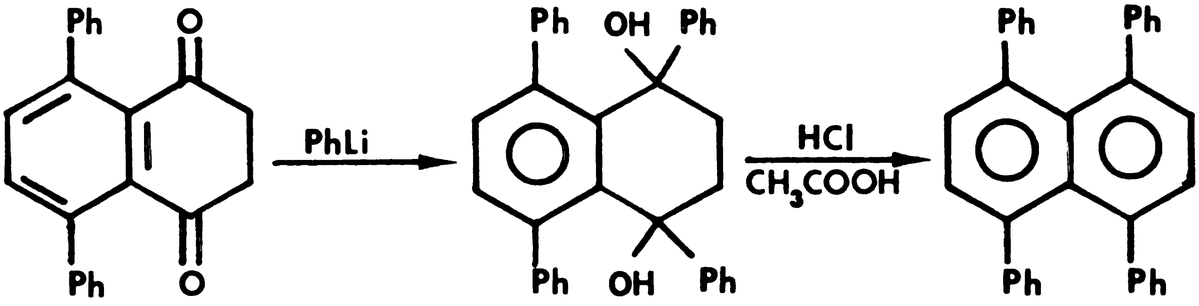
Decamethylphenanthrene (**138**) was prepared similarly in 87% yield by pyrolysis of **137** (100 mg) at around its melting point (170-180°C) at 0.1 torr for 2 h. The proton NMR spectrum of **138** in chloroform showed a broad singlet at δ 2.33 (18 H), and singlets at 2.64 (6 H) and 2.53 (6 H); the proton NMR spectrum at 180 M Hz in C_6D_6 showed singlets at δ 2.227 (12 H), 2.536 (6 H), 2.368 (6 H), 2.491 (6 H). The ^{13}C NMR spectrum showed four peaks at δ 16.57, 20.88, 21.08, 21.96 (two of the methyl carbons are overlapped), and six peaks in the aromatic region (two of the sp^2 carbons are also overlapped). The mass spectrum showed a parent peak which was also the base peak at *m*/*e* 318. The ultraviolet spectrum in heptane showed λ_{max} at 325 nm (log ε 4.14) and 277 (4.73).

In conclusion, a simple and general synthesis of phenanthrenes has been developed which is especially applicable to the synthesis of hindered derivatives. The yields are good and comparable to the previously described methods, with fewer steps.

5. Polyphenylarenes: Groups Sandwiched Between Phenyl Faces.

In the past 20 years, many anthracene and naphthalene derivatives which contain at least two aryl substituents at peri positions have been synthesized in order to study their chemical and physical properties. Of the many methods which have appeared in the literature, only a few examples will be mentioned.

1,4,5,8-Tetraphenylnaphthalene[83] (141) was synthesized by reaction of 139 with phenyllithium to give the two stereoisomers of 140. Dehydration of 140 with HCl/CH_3COOH gave 141.

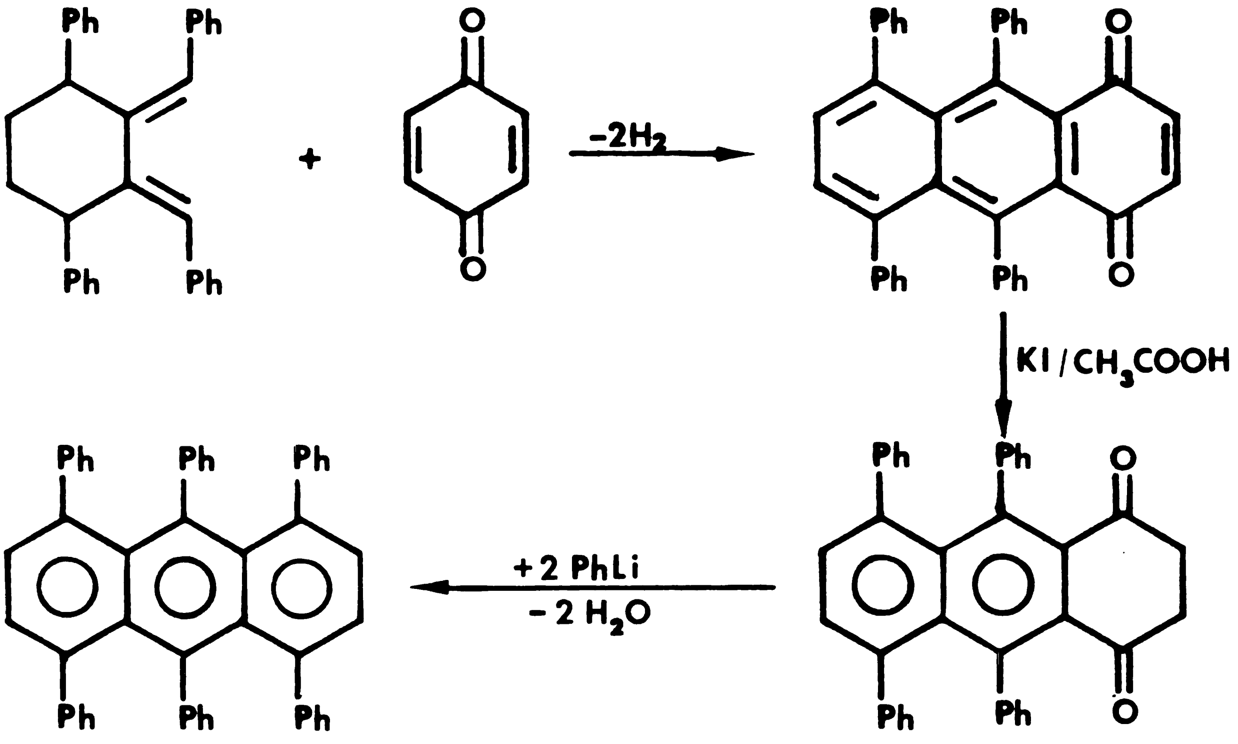


139 140 141

A similar procedure was used to synthesize 1,4,5,8,9,10-hexaphenylanthracene[84] (142) (Scheme 9).

Cycloaddition of benzyne and 3,6-diphenylisobenzofuran was used by Wittig[13] to synthesize 9,10-diphenylanthracene (12), as previously mentioned (p. 8). Stevens[85] later used the same strategy to synthesize 1,2,3,4,9,10-hexaphenylanthracene, by cycloaddition of benzyne to hexaphenylisobenzofuran.

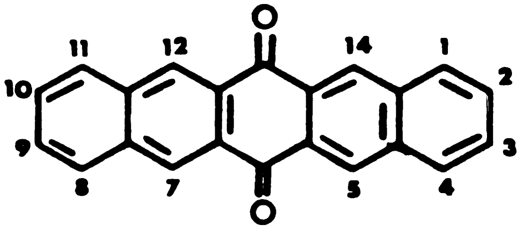
Scheme 9



142

House and coworkers[86] have tried several different procedures to synthesize phenyl substituted anthracenes and naphthalenes, in order to study the restricted rotation of the phenyls at the peri positions. 1,8-Diphenylnaphthalene was synthesized by the coupling reaction of 1,8-diiodonaphthalene and Ph_2CuLi. Also, 1,2-addition of phenyllithium to quinones was used in a number of cases.[87]

Pentacene and its derivatives have also been used in various studies such as determination of resonance energies of polyacenes,[88] the rate of the reactivity of benzenoid hydrocarbons[89] (i.e., in Diels-Alder reactions), and semi-empirical SCF-pi-molecular orbital studies.[90] Many of the substituted pentacenes have been prepared from pentacene itself. 6,13-Diphenylpentacene and 5,7,12,14-tetraphenylpentacene were prepared by the action of either a Grignard reagent or phenyllithium on 6,13-pentacenequinone (143) and 5,7,12,14-pentacenediquinone (144), respectively.[91]



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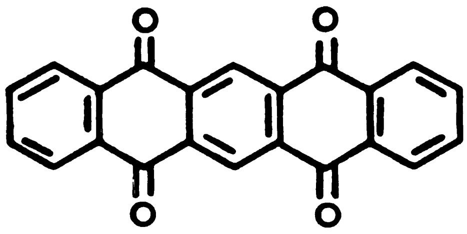

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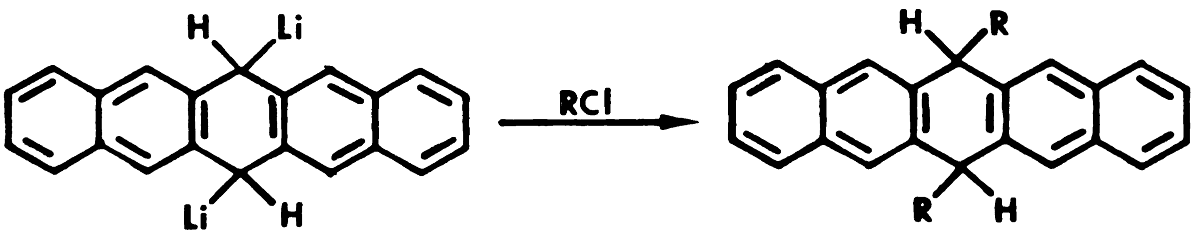
6,13-Dilithiopentacene (145) was obtained by the action of Li on pentacene.[92] The 6,13-dialkyl dihydro derivatives 146 were obtained from action of the dilithium compound 145 with alkyl chlorides.[93]



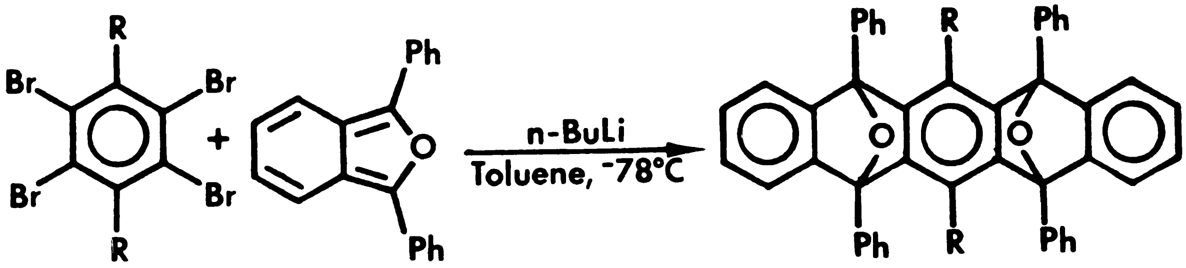
145 **146**

Pentacenes are very reactive and, in solution, absorb atmospheric oxygen (very rapidly in sunlight) to give a peroxide.[91] The photooxidation rate decreases from pentacene > naphthacene > anthracene.[91]

It was thought that the bis-annelation reaction could furnish a simple route to these polyphenylarenes, provided an efficient method could be found to remove the bridges from the corresponding bis-adducts. 2,5-Diphenylfuran (**147**) or 3,6-diphenylisobenzofuran (**148**) were selected for cycloadditions with bis-aryne equivalents to further demonstrate the capability of this bis-annelation reaction.

A toluene solution of 3,6-diphenylisobenzofuran (**148**) and tetrabromo-p-xylene (**25**), when treated with n-butyllithium in hexane at -78°C gave 67% of bis-adduct **149** ($R = CH_3$) as a mixture of two geometric isomers. The structure of **149** ($R = CH_3$) is based on spectroscopic properties which were obtained for the major isomer. The mass spectrum showed a parent peak at *m/e* 642. The ^{13}C NMR spectrum of this C_{48}-carbon compound showed only 13 peaks, at δ 17.43 (methyl), 91.67 (bridgehead), and the expected aromatic peaks. The proton NMR spectrum of **149** ($R = CH_3$) showed a singlet at δ 1.43 (6 H) which is shifted upfield 0.8 ppm compared to the 2,5-dimethylfuran adduct **29**. This upfield shift is because of the ring current of the benzene rings. The aromatic hydrogens appeared as a multiplet at δ 7.30-7.85 (28 H).

Bis-adduct 149 (R = OCH_3) was also prepared in one step and 42% yield from the reaction of tetrabromohydroquinone dimethyl ether (92) and diphenylisobenzofuran, as a mixture of anti and syn isomers. The mass spectrum with chemical ionization showed (M^+ + 1) = 676. The ^{13}C NMR spectrum showed only 13 peaks for this C_{48}-carbon compound. In the proton NMR spectrum the methoxyl signal appeared at δ 2.66, which is shifted appreciably upfield compared to an ordinary methoxyl group.

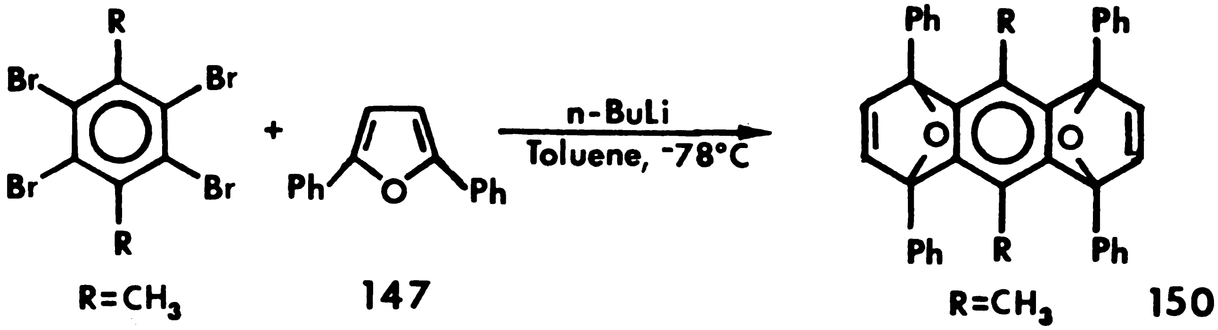


25 R=CH_3
92 R=OCH_3

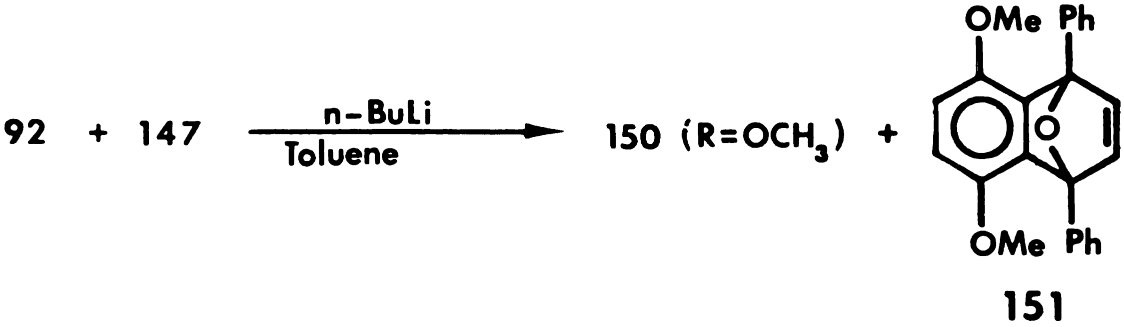
148

149 R=CH_3
R=OCH_3

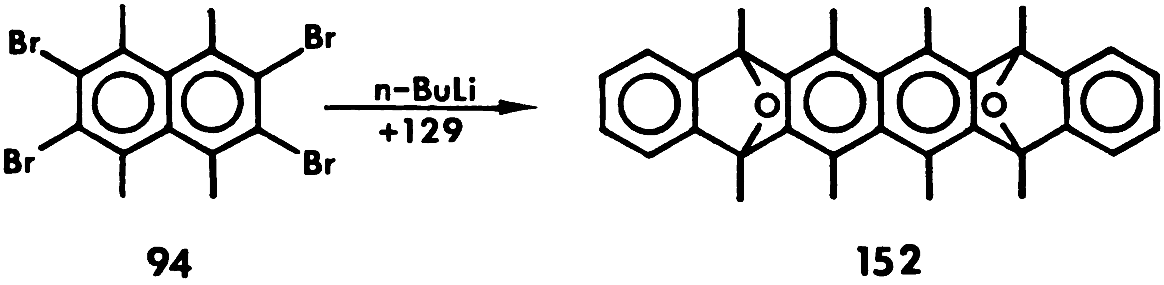
Reaction of tetrabromo-p-xylene (25) with 2,5-diphenylfuran (147) and n-butyllithium at 0°C gave 150 (R = CH_3) in 52% yield (based on diphenylfuran used). The product was identified by its spectroscopic data.



When arene **92** was used with 2,5-diphenylfuran some reduced mono-adduct **151** was also formed.

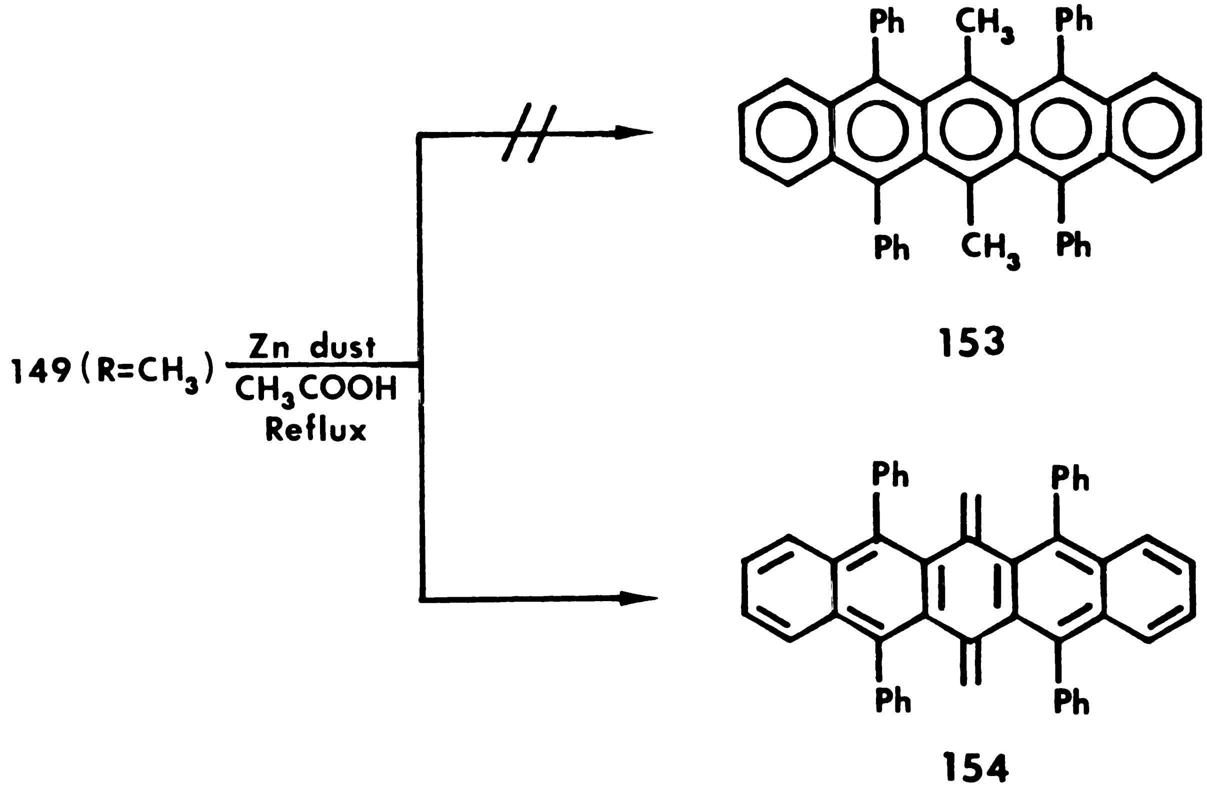


The hexacene derivative **152** was prepared in 82% yield from the reaction of tetrabromo-tetramethylnaphthalene (**94**) with **148** and n-butyllithium, and was obtained as a mixture of two isomers. The structure of **152**



follows from its method of synthesis and spectra.

Known literature procedures were applied to the aromatization of these bis-adducts, in order to obtain the corresponding pentacene or anthracene derivatives. However, when 149 (R = CH_3) was refluxed in acetic acid with zinc dust for 2 h, reaction did not proceed to give pentacene 153; rather, it gave the quinonedimethide 154 in quantitative yield.



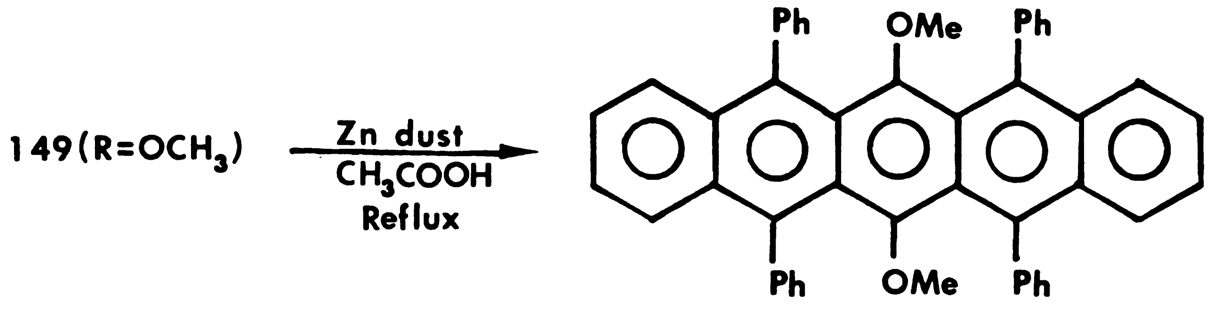
153

154

Compound 154 was characterized by its spectroscopic data. The ^1H NMR spectrum showed a broad singlet at δ 4.86 (4 H) for the vinyl protons and a multiplet at δ 7.0-7.40 (28 H). The mass spectrum showed the parent peak at m/e 608.

In another attempt to remove the oxygen bridges, 149 (R = CH_3) was treated with n-butyllithium in the presence of anhydrous ferric chloride.[94] No reaction occurred and the starting material was recovered.

Bis-adduct 149 (R = OCH_3) was also treated with zinc dust in acetic acid in the dark and under argon. The reaction mixture became blue after 15 minutes of reflux, and the color continued to darken, up to 1 h. The formation of a blue solution is very strong evidence for the formation of a pentacene. The reaction was stopped after 2 h at reflux, and the mixture was cooled to room temperature. Deoxygenated water was added and the solution was filtered under an argon atmosphere in darkness. A greenish-blue solid remained. A proton NMR spectrum of this crude product showed a singlet at δ 3.61 (6 H) and a multiplet at 6.90-7.30. The mass spectrum showed a parent peak at *m/e* 642, corresponding to the expected pentacene 155.



155

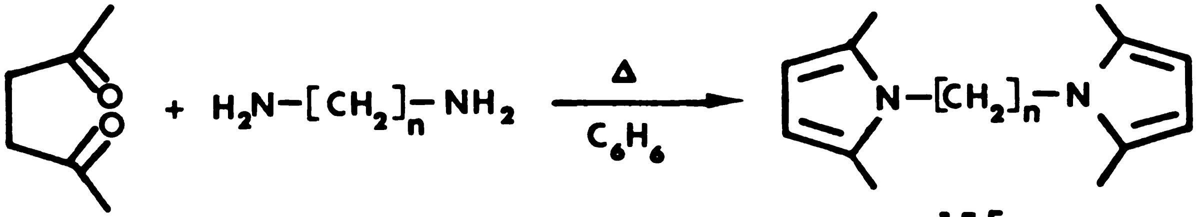
Attempts to purify this compound were not successful because the blue product changed to a colorless compound which showed several spots when subjected to TLC. Perhaps more careful conditions (total absence of oxygen and light) are required to purify pentacene **155**.

In conclusion, the bis-annelation technique is capable of being used to synthesize polynuclear aromatic compounds provided an efficient procedure is available to remove the oxygen bridges. At this point more study is required in order to find a method to efficiently aromatize bis-adducts of this type.

6. Attempted Synthesis of N-N Bridged Bis-Adducts of Bis-Aryne Equivalents: Basket-Type Compounds.

The synthesis of bridged aromatic compounds has long been a challenge for organic chemists.[95] There are several general reasons for studying bridged aromatics. Perhaps the most interesting question arises from the geometry of the compounds. Generally, these species have a definite fixed geometry with limited or restricted rotation around the covalent single bonds, and such rigidity and deformation in some cases give unusual properties to the compounds.

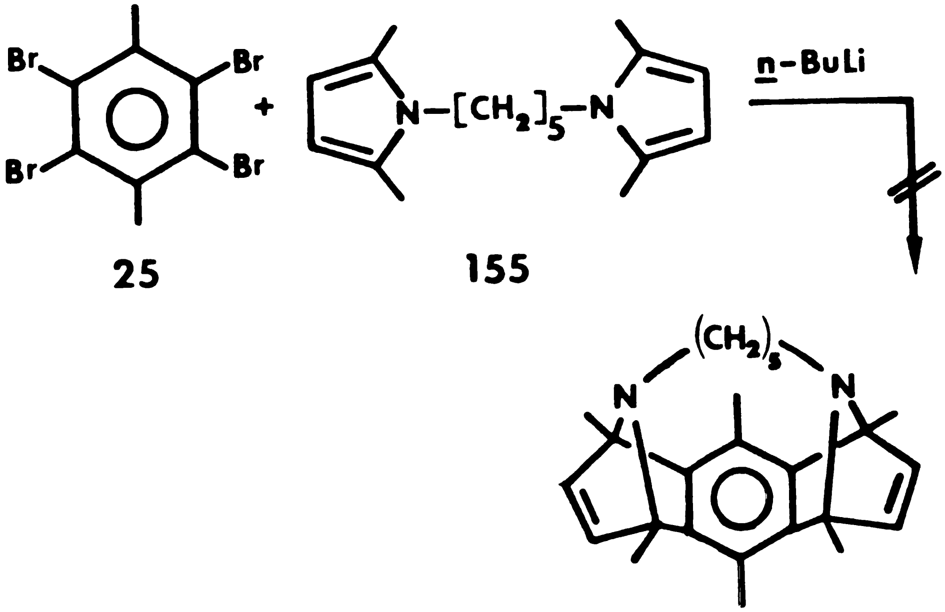
In further attempts to extend the utility of the bis-annelation technique, the synthesis of some bridged aromatics such as 156 was attempted. Since bis-aryne equivalents have two reaction sites it is plausible to expect an inter-intra-molecular Diels-Alder adduct, if a molecule with two diene functionalities is used. Thus, dipyrroles of the type 155, which are readily prepared in excellent yield from diamines and 1,4-diketones,[96] were considered.



155

n= 3 ,4 ,5

Two strategies were used in the attempted synthesis of 156. The first approach was a simple one-step synthesis, similar to the general procedure that was used previously in bis-annelation reactions. Thus, a suspension of tetrabromo-p-xylene (25) (10 mmol) and dipyrrole 155 (n = 5) (10 mmol) in toluene at -78°C under argon was reacted with n-butyllithium (20 mmol). After work-up the reaction product contained polymeric materials, suggesting that the reaction proceeded by an intermolecular process rather than intramolecularly. In a similar reaction but using high dilution techniques, there was no change in the composition of the reaction products.[96]



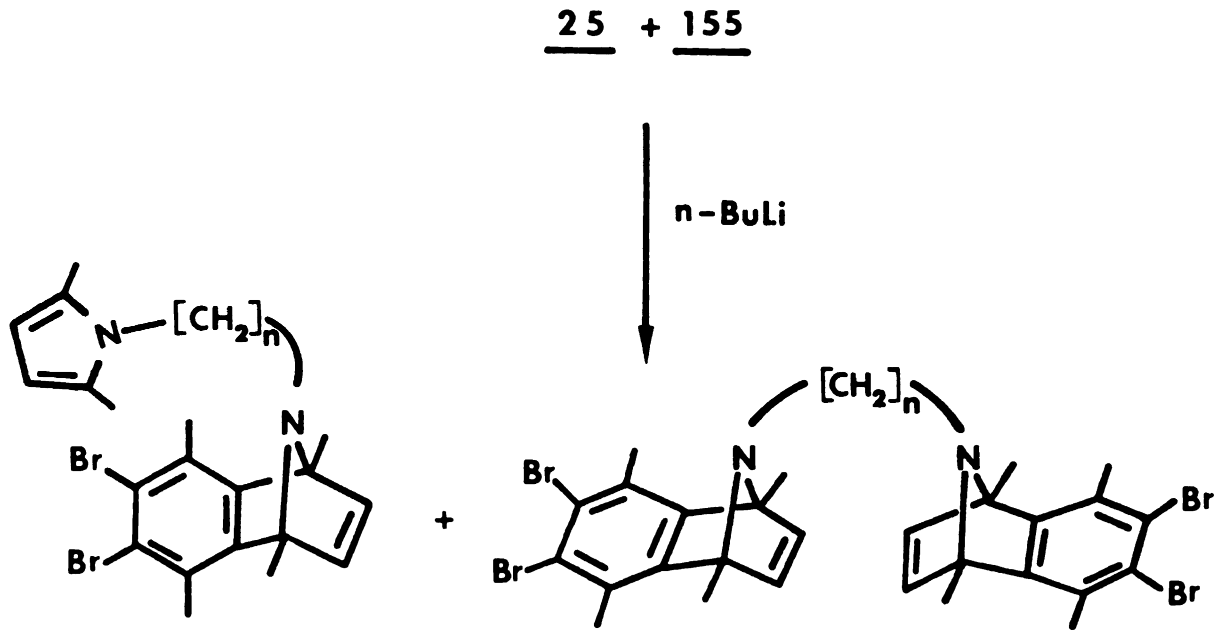
25

155

156

The other approach took advantage of the stepwise nature of the bis-annelation reaction. Treatment of mono-adduct 157 with n-butyllithium using the high dilution technique might afford a good chance for intramolecular cycloaddition, to form 156. Therefore, in an attempt to synthesize mono-adduct 157, a suspension of tetrabromo-p-xylene (25) and dipyrrole 155 (10 mmol each) in toluene at -78°C under argon was reacted with 10 mmol of n-butyllithium. After work-up, the reaction mixture contained not only 1:1 adduct 157, but some 2:1 adduct of tetrabromo-p-xylene and dipyrrole (158). The ratio of the 1:1 adduct to the 2:1 adduct depended upon the number of methylene groups in the starting dipyrroles.

The proton NMR spectrum of 157 ($n = 5$) shows a multiplet at δ 1.03-1.66 (6 H, methylenes), singlets at δ 1.76 (6 H), 2.16 (6 H), 2.46 (6 H) for the three sets of methyl groups, a multiplet at δ 3.43-3.83 (4 H, methylenes next to nitrogens) and singlets at δ 5.65 (2 H, vinyl hydrogens of the pyrrole moiety) and 6.53 (2 H, vinyl hydrogens). The ^{13}C NMR spectrum of this C_{25}-carbon compound showed 15 peaks, as expected from its symmetry, at δ 12.74, 18.41 and 20.60 (methyls), 25.29, 30.91, 31.58 (methylenes in the middle of the chain), 43.49, 45.30 (methylenes next to nitrogen), 77.39 (bridgehead carbon), 105.05 (C_2 and C_5 in the



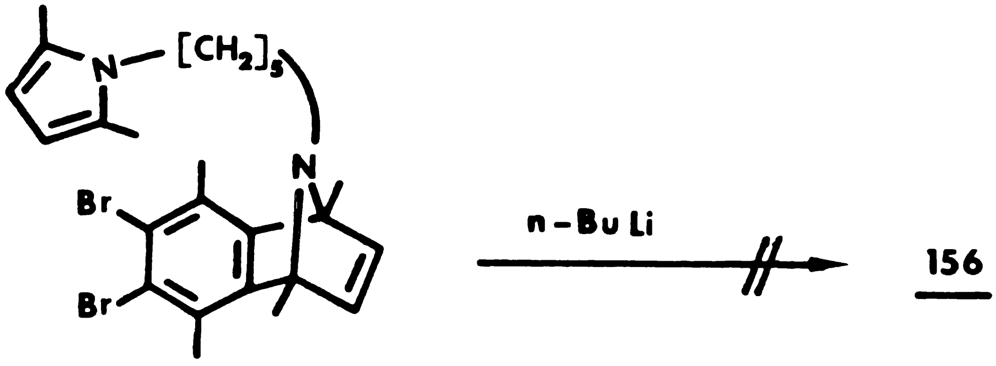
157; 1:1 adduct		158; 2:1 adduct
51 %	n : 3	21 %
15 %	n : 4	47 %
24 %	n : 5	41 %

pyrrole ring) and five expected sp^2 carbons in the aromatic region. The mass spectrum showed a parent peak at m/e 430 and a base peak at m/e 164 [(M$^+$ - (CH$_2$)$_5$-N].

For 158 (n = 5) the proton NMR spectrum consisted of peaks at δ 1.0-1.60 (m, 6 H, methylene hydrogens), 1.76-2.16 (m, 4 H, methylenes next to nitrogens), 1.76 (s, 12 H, methyls on the bridgehead carbon), 2.43 (s, 12 H, methyls on the benzene ring), and 6.50 (s, 4 H, vinyl hydrogens). The ^{13}C NMR spectrum of this C$_{33}$-carbon compound showed only 10 peaks, consistent with its C_{2v} symmetry; the methyl groups appeared at δ 18.42 and 20.62, methylenes at δ 26.09, 31.71 and 45.37, the bridgehead carbon at δ 77.40 and the remaining four peaks in the aromatic region.

The structures of compounds 157 (n = 3,4) and 158 (n = 3,4) were determined by their spectroscopic data. Table 4 compares the ^{13}C NMR spectra of 157 and 158 (n = 3,4,5) and Table 5 compares the ^{1}H NMR spectra of these adducts.

In an attempt to cyclize adduct 157 (n = 5), a solution of 157 (n = 5) (1.5 mmol) in 100 mL of toluene



157(n=5)

and n-butyllithium (3 mmol) in 100 mL of hexane were added dropwise simultaneously to 250 mL of dry toluene at -78°C under argon over a period of 4 h. Attempts to obtain a pure product from the reaction mixture failed. Perhaps some butylated products along with polymeric material were present.

TABLE 4

^{13}C-NMR CHEMICAL SHIFTS (ppm) OF 1:1 ADDUCTS 157 (n=3,4,5) AND 2:1 ADDUCTS 158 (n=3, 4, 5)

Compound	Solvent	Arom. & Vinyl	N-C-bridged	N-CH$_2$	Other Methylenes	Methyls
157 (n=3)	CDCl$_3$	150.3 147.4 132.9 127.1 126.3 126.2 105.1	77.4	42.5 44.0	32.5	20.6 18.4 12.5
157 (n=4)	CDCl$_3$	150.3 147.6 132.4 127.2 126.3 105.1	77.4	45.2 43.5	30.3 29.0	20.5 18.5 12.6
157 (n=5)	CDCl$_3$	150.4 147.5 132.3 127.13 126.2 105.0	77.4	45.3 43.5	31.6 30.9 25.3	20.6 18.4 12.5
158 (n=3)	CDCl$_3$	150.3 147.6 132.3 126.7	77.4	43.9	33.06	20.6 18.6
158 (n=4)	CD$_3$CN + CCl$_4$	151.2 147.3 131.9 125.7	77.3	44.9	29.6	20.5 18.3
158 (n=5)	CDCl$_3$	150.5 147.6 132.3 126.1	77.4	45.4	31.7 26.1	20.6 18.4

TABLE 5

^{1}H NMR CHEMICAL SHIFTS (ppm) OF 1:1 ADDUCTS 157 (n= 3, 4, 5) AND 2:1 ADDUCTS 158 (n= 3, 4, 5)*

Compound	Vinyl H	Pyrrole H	N—CH_2	Other Methylenes	Arom. CH_3	Bridge-head CH_3	Pyrrole CH_3
157 (n=3)	6.50 (s, 2H)	5.63 (s, 2H)	3.43–3.76 (m, 4H)	2.10–2.15 (m, 2H)	2.43 (s, 6H)	1.73 (s, 6H)	2.13 (s, 6H)
157 (n=4)	6.50 (s, 2H)	5.56 (s, 2H)	3.36–3.66 (m, 4H)	1.30–1.66 (m, 4H)	2.40 (s, 6H)	1.76 (s, 6H)	2.13 (s, 6H)
157 (n=5)	6.53 (s, 2H)	5.65 (s, 2H)	3.43–3.83 (m, 4H)	1.03–1.66 (m, 6H)	2.46 (s, 6H)	1.76 (s, 6H)	2.16 (s, 6H)
158 (n=3)	6.50 (s, 4H)		1.73–2.40 (m, 6H)		2.40 (s, 12H)	1.73 (s, 12H)	
158 (n=4)	6.53 (s, 4H)		1.90–2.33 (m, 4H)	1.50–1.66 (m, 4H)	2.40 (s, 12 H)	1.76 (s, 12 H)	
158 (n=5)	6.50 (s, 4H)		1.76–2.16 (m, 4H)	1.00–1.60 (m, 6H)	2.43 (s, 12 H)	1.76 (s, 12 H)	

*Spectra run in $CDCl_3$ as solvent.

It seems likely that the geometry of the mono-adduct **157** is such that it prefers to undergo intermolecular cycloaddition, rather than intramolecular, to form polymeric material. However, attempts by others in this group to synthesize these basket-type compounds are still in progress.

In conclusion, although it was not possible to obtain any N-N bridged basket-type compound, novel adducts such as **157** and **158**, were synthesized the chemistry of which could be explored.

EXPERIMENTAL

1. General procedures

^1H NMR spectra were measured at 60 MHz (Varian T-60), or on a Bruker WM-250 or Bruker 180-MHz spectrometer using $(CH_3)_4Si$ as an internal standard. Chemical shifts are reported in ppm (δ). ^{13}C NMR spectra were measured on a Varian CFT-20 spectrometer. IR spectra were determined on a Perkin Elmer Model 167 spectrometer. UV spectra were obtained on a Cary Model 219 spectrometer. Mass spectra were measured at 70 eV using a Finnigan 4000 spectrometer with the INCOS data system, operated by Mr. Ernest Oliver. High resolution mass spectra were obtained with a Varian CH5 spectrometer. Melting points were determined with an Electrothermal Melting Point Apparatus (Fisher Scientific). To extend the range about 360°C, the apparatus was connected to one or two Variacs (in series) each of which could nominally boost line voltage from 110 V to 140 V and the thermometer was replaced by an iron-constantan thermocouple. The thermometer well was blocked with a glass rod to minimize heat loss, and the thermocouple was placed in a melting point tube well adjacent to the well holding the sample tube. After the approximate mp range was determined, the block was pre-heated to approximately 50° below the expected mp before inserting the sample. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

2. Tetrabromo-p-xylene (**25**)

To a suspension of 1 g of iron powder in 20 g (0.19 mol) of p-xylene at 0°C was added dropwise 96 mL (1.8 mol) of bromine. The reaction mixture was left overnight, then the excess bromine was destroyed by adding saturated aqueous $NaHSO_3$. The solid was filtered and the filter cake was successively washed with 10% aqueous solutions of $NaHSO_3$, $Na_2S_2O_3$, $NaHCO_3$, and finally water. The solid was dried to give 81 g (90%) of **25**, which was recrystallized from chloroform/methanol, mp 249-250° (lit. 251-252°C); ^1H NMR ($CDCl_3$) δ 2.78 (s, 6 H); mass spectrum, *m/e* (relative intensity) 422 (100), 341 (54), 262 (25), 182 (21), 102 (67).

3. Tetrabromo-p-xylene-d_6 (**25**-d_6)

In a procedure similar to that used for **25**, a suspension of 0.4 g of iron powder in 3.1 g (26 mmol) of p-xylene d_{10}[97] was treated dropwise with 15 mL (0.28 mol) of bromine. After work-up 11.25 g (98%) of **25-d_6** was obtained which was recrystallized from $CHCl_3/CH_3OH$; mp 248-250°C; mass spectrum, *m/e* (relative intensity) 428 (11), 347 (6), 268 (3), 187 (21), 108 (100). High resolution mass spectrum: Calcd. for $C_8D_6Br_4$: 425.75562; Found: 425.75693.

4. 1,4,5,8,9,10-Hexamethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-endoxide (29)

To a suspension of 4.22 g (10 mmol) of 25 and 5 g (excess) of 2,5-dimethylfuran (28) in 100 mL of dry ether at -78°C under argon, was added dropwise (2 h) 11 mL (22 mmol) of n-butyllithium (2 M in hexane) which was diluted with 100 mL of hexane. After stirring the mixture for 2 h at -78°C, it was allowed to warm to room temperature and quenched with methanol (1 mL). The ethereal solution was washed with water, dried ($MgSO_4$), and concentrated. Trituration of the crude product with 10 mL of hexane gave 2.19 g (73%) of 29 as a mixture of anti:syn isomers with the ratio of 57:43. Successive washing of this mixture with ether yielded a pure sample of the anti isomer. mp 283-284°C; ^1H NMR ($CDCl_3$) δ 1.94 (s, 12 H), 2.29 (s, 6 H), 6.78 (s, 2 H); mass spectrum, m/e (relative intensity) 294 (9), 251 (37), 225 (81), 209 (22), 193 (21), 178 (26), 43 (100).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53.
Found: C,81.51; H, 7.50.

In this experiment, when anhydrous toluene was used as a solvent under otherwise similar conditions, the yield of 29 was increased to 93% with the same anti:syn ratio.

In this experiment, when only 10 mmol of n-butyllithium was used under otherwise similar conditions, 3.26 g of a crude reaction product was obtained. Chromatography of this crude product on an alumina column using hexane as eluent gave 1.35 g (32%) of unreacted tetrabromo-p-xylene. Further elution with 3:1 hexane:methylene chloride gave 1.58 g (47%) of bis-adduct 29 as a mixture of anti and syn isomers. No trace of mono-adduct 31 was observed.

5. 2,5-Dibromo-4,6-diiodo-1,4-dimethylbenzene (46)

To a solution of 40.8 g (0.114 mol) of 2,5-diiodo-1,4-dimethylbenzene[98] and 37 g (0.224 mol) of anhydrous ferric chloride in 200 mL of nitromethane at 0°C was added dropwise 16 mL (0.3 mol) of bromine. After the mixture was left overnight, the white solid was filtered, washed with nitromethane and acetone to give 52.5 g (89%) of 46 which was recrystallized from ethanol/chloroform, mp 225-227°C; ^{1}H NMR (CDCl$_3$) δ 3.00 (s, 6 H); mass spectrum *m/e* (relative intensity) 516 (4), 389 (2), 262 (7), 181 (15), 127 (93), 102 (100), 75 (88), 51 (89). High resolution mass spectrum: Calcd. for $C_8H_6I_2Br_2$: 513.69305; Found: 513.69202.

6. 2,5-Dibromo-4,6-dichloro-1,4-dimethylbenzene (47)

A solution of 4 g (0.025 mol) of anhydrous ferric chloride and 6.6 g (0.025 mol) of 2,4-dibromo-1,4-dimethylbenzene[99] in 100 mL of nitromethane was poured into a three-necked flask equipped with a thermometer, reflux condenser and gas inlet tube. The flask was cooled in an ice bath and chlorine gas was passed through the solution via a gas inlet tube. As soon as the chlorine was introduced a white solid precipitated (the reaction is highly exothermic). Passage of chlorine was continued for 2 h. The solid was filtered, washed with nitromethane and acetone and recrystallized from chloroform/methanol to give 4.5 g (54%) of **47**, mp 226°C, (lit.[25] 226°C); ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 6 H); mass spectrum, *m/e* (relative intensity) 337 (4), 335 (31), 334 (89), 332 (100), 330 (41), 296 (30), 253 (91), 217 (25), 172 (26), 136 (64), 101 (44), 75 (55).

7. 2,3,5,6-Tetraiodo-1,4-dimethylbenzene (**48**)

This compound was prepared according to the literature method, by mercuration of p-xylene and iodination of the mercury compound with I_2/KI; mp 246-248°C (lit.[24] 245-248°C); ^{1}H NMR ($CDCl_3$) δ 3.30 (s, 6 H); mass spectrum, *m/e* (relative intensity) 610 (1), 483 (2), 356 (2), 229 (36), 127 (33), 102 (100), 75 (61).

8. 1,4,5,8-Tetramethyl-6,7-dibromo-1,4-dihydronaphthalene-1,4-endoxide (**31**)

To a suspension of 1.5 g (0.004 mol) of **51** in 20 mL of 1,2-dichloroethylene was added 4 g (excess) of 2,5-dimethylfuran and 1.5 mL of propylene oxide. The mixture was warmed gradually to avoid vigorous CO_2 evolution, then was heated under reflux for 3 h. After the mixture was cooled to room temperature the solvent was removed by a rotary evaporator. The residue was dissolved in 100 mL of ether and washed three times with 50 mL portions of 10% aqueous sodium hydroxide and finally with water and dried ($MgSO_4$). Concentration of the ether left a brown solid which was washed on activated alumina, eluting with 3:1 hexane: methylene chloride to give 1.03 g (71%) of **31** which was recrystallized from CH_3OH, mp 146-147°C; ^1H NMR ($CDCl_3$) δ 1.984 (s, 6 H), 2.482 (s, 6 H), 6.772 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.61, 20.21, 89.64, 126.11, 129.69, 146.66, 150.53, mass spectrum, m/e (relative intensity) 361 (0.4), 360 (2), 359 (0.8), 358 (4), 155 (91), 153 (86), 152 (85), 139 (61), 129 (45), 128 (100), 127 (48), 115 (57), 77 (40), 76 (40).

Anal. Calcd. for $C_{14}H_{14}OBr_2$: C, 46.96; H, 3.94; Br, 44.63. Found: C, 47.05; H, 3.95; Br, 44.62.

Compound **31** was also prepared as follows: to a suspension of 4.22 g (10 mmol) of **25** and 5 g (excess) of 2,5-dimethylfuran in 100 mL of dry toluene at -78°C under argon, was added dropwise (2 h) n-butyllithium (10 mmol) in 50 mL of hexane. After stirring the mixture for 2 h at -78°C, it was allowed to warm to room temperature and quenched with methanol (1 mL). The toluene solution was washed with water, dried ($MgSO_4$), and concentrated to give 3.56 g (100%) of **31** (the physical data of this compound were similar to that mentioned above).

9. 1,4,5,8-Tetramethyl-9,10-dimethyl-d_6-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-endoxide (29-d_6)

In a procedure similar to that used for 29, a suspension of 1.07 g (2.5 mmol) of 25-d_6 and 2.5 g (excess) of 2,5-dimethylfuran in 50 mL of anhydrous ether, was treated dropwise with 6 mmol of n-butyllithium in 25 mL of dry hexane over a 2 h period. After work-up and purification 0.74 g (98%) of 29-d_6 was obtained as a mixture of anti and syn isomers with the ratio 61:39. ^{1}H NMR ($CDCl_3$) of the mixture: two singlets at δ 1.935 and 1.957 (12 H) correspond to the methyl groups, 2 singlets at δ 6.754 and 6.785 (4 H) correspond to the vinyl hydrogens; mass spectrum, *m/e* (relative intensity) 300 (5), 257 (19), 231 (70), 215 (88), 43 (100). High resolution mass spectrum: Calcd. for $C_{20}H_{16}D_6O_2$: 300.19965. Found: 300.19978.

10. Reaction of mono-adduct 31 and 2,5-dimethylfuran with n-butyllithium

To a solution of mono-adduct 31 (0.358 g, 1 mmol) and 2,5-dimethylfuran (0.5 g, excess) in 20 mL of dry ether at -78°C under argon, was added dropwise 2.5 mmol of n-butyllithium in 10 mL of dry hexane over 1 h. After stirring for 3 h at -78°C the mixture was allowed to warm to room temperature and quenched with methanol (1 mL). The ethereal solution was washed with water, dried ($MgSO_4$) and concentrated. Trituration of the crude product with 5 mL of hexane gave 0.288 g (98%) mixture of the two isomers of **29** with the 57:43 anti to syn ratio (for physical data see p. 98).

11. Reaction of mono-adduct **31** and tetrabromo-p-xylene (**25**-d_6) with n-butyllithium in the presence of 2,5-dimethylfuran

A solution of 2.14 g (5 mmol) of **25**-d_6 and 1.7 g (5 mmol) of mono-adduct **31** and 5 g (excess) of 2,5-dimethylfuran in 100 mL of dry ether was cooled to -78°C under argon (most of the **25**-d_6 precipitated). To this suspension n-butyllithium (10 mmol in 50 mL of hexane) was added dropwise over 2 h. After stirring the mixture for 3 h at -78°C, it was allowed to warm to room temperature and quenched with methanol (1 mL). The ethereal solution was washed with water and dried ($MgSO_4$). Concentration of the ether at low pressure left 3.106 g of a crude product which was chromatographed on activated alumina, eluted with hexane and later 9:1 hexane:methylene chloride to give as the first fraction, 0.746 g (24%) of unreacted **25-d_6**. The second fraction, 0.523 g (17%) was a mixture of mono-adducts **31** and **31-d_6**. The percentage of **31-d_6** in this mixture was determined from the proton NMR, in that the signal corresponding to aromatic methyls (δ 1.98 ppm) was 30-40% smaller in area than the signal corresponding to the bridgehead methyls (δ 2.48 ppm).

Also the mass spectrum of this mixture was similar to that of **31** (p.100) but showed a peak at *m/e* 363 (trace) corresponding to **31-d_6**.

Finally, eluting with methylene chloride gave a 1.816 g (58%) mixture of bis-adducts **29** and **29-d_6**. The percentage of **29-d_6** (30%) in this mixture was determined from integration of the peak at δ 2.92 (aromatic methyls) compared to peak at δ 1.94 (bridgehead methyls).

12. Reaction of **47** with n-butyllithium in the presence of 2,5-dimethylfuran

In a procedure similar to that used for bis-adduct **29**, reaction of **47** (3.33 g, 5 mmol) and **28** (2.5 g, excess) with n-butyllithium (12 mmol) in 100 mL of hexane, gave 0.51 g (35%) of bis-adduct **29** as a 57:43 mixture of anti to syn isomers.

13. Reaction of **46** with n-butyllithium in the presence of 2,5-dimethylfuran

In a procedure similar to that used for bis-adduct **29**, reaction of **46** (2.58 g, 5 mmol) and **28** (2.5 g, excess) in 100 mL of dry ether at -78°C under argon with n-butyllithium (12 mmol) in 100 mL of hexane gave 1.12 g (76%) of bis-adduct **29** as a 57:43 mixture of anti to syn isomers.

14. Reaction of 48 with n-butyllithium in the presence of 2,5-dimethylfuran

In a procedure similar to that used for bis-adduct 29, reaction of 48 (3.05 g, 5 mmol) and 28 (2.5 g, excess) in 100 mL of dry ether at -78°C under argon with n-butyllithium (12 mmol) in 100 mL of hexane gave 1 g (68%) of bis-adduct 29 as a 61:39 mixture of anti to syn isomers.

15. N-Methyl-1,2,3,4,5,8-hexamethyl-6,7-dibromo-1,4-dihydro-naphthalene-1,4-imine (52)

A solution of 25 (4.22 g, 10 mmol) and 22 (1.37 g, 10 mmol) in 100 mL of dry toluene under argon was cooled to -78°C (most of the 25 precipitated). To this suspension n-butyllithium (12 mmol in 50 mL of hexane) was added dropwise over a period of 2 h, then the reaction mixture was slowly warmed to room temperature. The excess n-butyllithium was quenched with methanol (1 mL). Toluene was removed on a rotary evaporator and the remaining solid was dissolved in ether. The ethereal solution was washed with water, dried ($MgSO_4$) and concentrated to give 3.95 g of crude product. Chromatography of this crude product on an alumina column using hexane as eluent gave 3.5 g (88%) of 52, mp 118-120°C; ^1H NMR ($CDCl_3$) δ 1.66 (broad s, 12 H), 1.93 (s, 3 H), 2.42 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.13, 15.74, 20.83, 30.60, 77.04, 126.06, 132.17, 145.47, 149.60; mass spectrum, *m/e* (relative intensity) 402 (3), 398 (8), 355 (22), 320 (10), 277 (45), 197

(14), 128 (16), 115 (50), 70 (44), 56 (100); high resolution mass spectrum: Calcd. for $C_{17}H_{21}Br_2N$: 397.00418; Found: 397.00525.

16. N-Methyl-1,2,3,4,5,8,9,10-octamethyl-1,4,5,8-tetrahydroanthracene-1,4-imine-5,8-endoxide (53)

In a procedure similar to that used for 29, reaction of the mono-adduct 31 (1.79 g, 5 mmol) and 22 (0.68 g, 5 mmol) in 100 mL of dry toluene with n-butyllithium (12 mmol) gave a crude product mixture. Chromatography of this crude product on activated alumina, eluting with methylene chloride, gave 0.69 g (42%) of 53 as a mixture of two isomers. Separation of the isomers was not attempted. The 180 MHz proton NMR spectrum clearly showed the presence of two isomers in the ratio of 60:40. ^1H NMR ($CDCl_3$) of the major isomer, δ 1.65 (s, 6 H), 1.66 (s, 6 H), 1.95 (s, 6 H), 2.03 (s, 3 H), 2.25 (s, 6 H), 6.79 (s, 2 H); ^1H NMR ($CDCl_3$) of the minor isomer, δ 1.61 (s, 6 H), 1.65 (s, 6 H), 1.96 (s, 6 H), 2.03 (s, 3 H), 2.31 (s, 6 H), 6.78 (s, 2 H); mass spectrum, *m/e* (relative intensity) 355 (2), 238 (11), 255 (3), 281 (3), 56 (100). High resolution mass spectrum: Calcd. for $C_{23}H_{29}NO$: 335.22492; Found: 335.22506.

The bis-adduct 53 was also prepared as follows: In a procedure similar to that used above, reaction of mono-adduct 52 (1.67 g, 5 mmol) and 28 (2.5 g, excess) in

100 mL of dry toluene with n-butyllithium (5.5 mmol) gave 1.66 g of a crude product mixture. Chromatography of this crude mixture on activated alumina eluting with methylene chloride gave 1.43 g (86%) of **53** as a mixture of two isomers in the ratio of 71/29.

17. Bis-(N-methyl)-1,2,3,4,5,8,9,10-octamethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-imine (**54**)

In a procedure similar to that used for **29**, reaction of **52** (2.97 g, 7.5 mmol) and N-methyl-2,5-dimethylpyrrole (0.817 g , 7.5 mmol) in 100 mL of dry toluene with n-butyllithium (12 mmol) in hexane gave a crude product mixture. Chromatography of this crude mixture on activated alumina, eluting with 3:1 hexane:chloroform gave 0.418 g (24%) of **54** as a mixture of two isomers. ^{1}H NMR of the mixture ($CDCl_3$) δ 1.63, 1.66, 1.76 (three singlets, 1,2,3,4,5,6-methyls, 18 H), 1.86, 1.90, 1.96, 2.00 (four singlets, N-methyls, 6 H), 2.18, 2.23, (two singlets, 9,10-methyls, 6 H), 6.60 (broad s, vinyl hydrogens): mass spectrum, *m/e* (relative intensity) 348 (5), 293 (15), 278 (12), 268 (29), 238 (23), 220 (9), 205 (27), 56 (100). High resolution mass spectrum: Calcd. for $C_{24}H_{32}N_2$: 348.25656; Found: 348.25838.

18. 1,4,5,6,7,10,11,12-Octamethyl-1,4,7,10-tetrahydrobinaphthylene-1,4;7,10-bis-endoxide (55)

To a solution of mono-adduct 31 (1.79 g, 5 mmol) in 50 mL of dry ether at -78°C under argon, was added dropwise n-butyllithium (2.5 mL, 2 M in hexane) in 25 mL of hexane over a period of 1 h. After stirring for 6 h at -78°C the mixture was quenched with methanol (1 mL). The ethereal solution was washed with water and dried ($MgSO_4$). Concentration of the ether gave a crude product mixture. Column chromatography of this crude mixture on activated alumina eluting with 3:1 hexane:chloroform gave 0.158 g (8%) of 55 as a mixture of syn and anti isomers. The major isomer was purified by successive washing of the mixture with ether, mp 315-317°C; ^1H NMR ($CDCl_3$) δ 1.90 (s, 12 H), 2.13 (s, 12 H), 6.63 (s, 4 H); mass spectrum, *m/e* (relative intensity) 396 (47), 370 (40), 353 (23), 344 (55), 327 (100), 310 (41), 43 (98). High resolution mass spectrum: Calcd. for $C_{28}H_{28}O_2$: 396.20893; Found: 396.21633.

19. 9,10-Dimethyl-1,4,5,8-tetrahydro-1,4;5,8-dimethanoanthracene (76)

A solution of tetrabromo-p-xylene (25) (4.22 g, 10 mmol) and freshly distilled cyclopentadiene (1.32 g, 20 mmol) in 100 mL of dry ether under argon was cooled to -78°C (most of **25** precipitated out). To this suspension 22 mmol of n-butyllithium in 100 mL of hexane was added dropwise for a period of 2 h. The mixture was allowed to gradually warm to room temperature. Reaction was quenched with methanol (1 mL) and the mixture was washed with water and dried ($MgSO_4$). After removal of the solvent (rotovap) the solid residue was washed on an alumina column with hexane to give 2.27 g (97%) of **76** as a mixture of two isomers, mp 105-107°C; ^1H NMR ($CDCl_3$) δ 2.13 (m, 4 H), 2.20 (s, 6 H), 3.8 (t, 4 H), 6.60 (t, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.73, 48.19, 70.02, 122.76, 143.31, 146.58; mass spectrum, *m/e* (relative intensity) 234 (69), 219 (100), 203 (24), 193 (51), 178 (36), 165 (26), 152 (17), 102 (19), 89 (18).

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74.
Found: C, 92.28; H, 7.84.

In this experiment when 40 mmol of n-butyllithium was used under otherwise similar conditions, the yield of bis-adduct **76** decreased to 37%.

This reaction was also repeated as follows: to a solution of cyclopentadiene (1.32 g, 20 mmol) in 100 mL of dry ether at 0°C under argon, 20 mmol of n-butyllithium was added (the cyclopentadiene anion precipitated). To this suspension tetrabromo-p-xylene (4.22 g, 10 mmol) was added. The reaction mixture was cooled to -78°C and then

20 mmol of n-butyllithium in 50 mL of hexane was added dropwise (2 h). After work-up similar to that mentioned for **76**, the reaction product contained cyclopentadiene dimer and some polymeric materials. No trace of bis-adduct **76** was observed.

20. 1,4,5,8-Tetrahydro-9,10-dimethyl-11,12-bis(1-methylethylidene)-1,4;5,8-dimethanoanthracene (**77**)

In a procedure similar to that used for **76**, reaction of **25** (4.22 g, 10 mmol) with **69**[100] (2.32 g, 20 mmol) in 150 mL of dry THF and 22 mmol of n-butyllithium in 100 mL of hexane gave a yellow solid residue which was chromatographed on activated alumina. Hexane first eluted 1.7 g of **77** as a single isomer, mp 270-272°C; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 12 H), 2.26 (s, 6 H), 4.33-4.43 (t, 2 H), 6.66-6.76 (t, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.74, 18.91, 48.62, 99.89, 121.38, 143.28, 145.44, 161.38; mass spectrum, m/e (relative intensity) 314 (100), 299 (25), 288 (16), 269 (14), 247 (45), 232 (15), 215 (21). High resolution mass spectrum: Calcd. for $C_{24}H_{26}$: 314.20346; Found: 314.20328.

Further elution with hexane resulted in 0.5 g more of **77** as a mixture of two isomers (total yield 70%).

21. 11,12-Bis(diphenylmethylene)-1,4,5,8-tetrahydro-9,10-dimethyl-1,4;5,8-dimethanoanthracene **78**

In a procedure similar to that used for **76**, reaction of **25** (4.22 g, 10 mmol) with **69**[100] (4.60 g, 20 mmol) in 300 mL of anhydrous THF and 22 mmol of n-butyllithium gave a white solid which was filtered and washed with water and dried to give 2 g (36%) of a pure isomer of **78**. The product did not melt below 350°C and did not dissolve in organic solvents suitable for an NMR spectrum; mass spectrum, m/e (relative intensity) 567 (77), 371 (56), 227 (39), 178 (55), 165 (40), 152 (18), 191 (100). High resolution mass spectrum: Calcd. for $C_{44}H_{35}$: 562.26605; Found: 562.2670. Attempts to purify the other isomer were not successful.

22. 1',4',5',8'-Tetrahydro-9',10'-dimethyldispiro[cyclopropane-1,11'-[1,4;5,8]dimethanoanthracene-12',11"-cyclopropane] **79**

In a procedure similar to that used for **76**, reaction of **25**, (4.22 g, 10 mmol) with diene **70**[101] (2.3 g, 25 mmol) in 100 mL of anhydrous toluene and n-butyllithium (22 mmol) gave a crude product mixture. This crude mixture was triturated with methanol (20 mL) and filtered to give 2.28 g (80%) of **79** as a mixture of two isomers. Recrystalization of this mixture from methanol/ethyl acetate gave 1.94 g (68%) of a pure isomer, mp 223-225°C; ^{1}H NMR ($CDCl_3$) δ 0.50 (m, 8 H), 2.16 (s, 6 H), 3.13-3.23 (t, 4 H), 6.60-6.76 (t, 4 H); ^{13}C NMR ($CDCl_3$) δ 8.96, 10.01, 14.75, 53.84, 65.13, 121.43, 142.72, 145.98; mass spectrum, m/e (relative intensity) 286 (100), 271 (27), 258 (76), 241

(30), 227 (43), 215 (53), 202 (44), 114 (47), 108 (37).

Anal. Calcd. for$C_{22}H_{18}$: C, 92.26; H, 7.74.
Found: C, 92.25; H, 7.77.

23. 1',4',5',8'-Tetrahydro-9',10'-dimethyldispiro [cyclopentane-1,11'-[1,4;5,8]dimethanoanthracene-12',1"-cyclopentane] 80

In a procedure similar to that used for 76, reaction of 25 (4.22 g, 10 mmol) with diene 71[102] (3.6 g, 30 mmol) in 100 mL of anhydrous THF and n-butyllithium (22 mmol) gave a crude product mixture. Column chromatography of this crude mixture on activated alumina, eluting with 4:1 hexane:methylene chloride, gave 1.992 g (58%) of 80 as a mixture of two isomers. Successive washing of this mixture with ether gave a pure sample of the major isomer, mp 222-225°C; ^1H NMR ($CDCl_3$) δ 1.00-1.73 (m, 16 H), 2.10 (s, 6 H), 3.33-3.43 (t, 4 H), 6.50-6.60 (t, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.76, 25,89, 25.89 (overlap), 33.75, 33.85, 56.98, 90.67, 123.04, 142.79, 146.24; mass spectrum, *m/e* (relative intensity) 342 (100), 327 (30), 259 (14), 215 (16),

Anal. Calcd. for $C_{26}H_{30}$: C, 91.17, H, 8.83.
Found: C, 91.07; H, 8.80.

24. 1,2-Dibromo-3,4,5,6-tetramethylbenzene (21)

This compound was prepared in nearly quantitative yield according to the Smith and Moyle method,[45] by bromination of prehnitene in carbon tetrachloride using iron powder as catalyst.

25. 5,6,7,8-Tetramethyl-1,4-dihydro-1,4-methanonaphthalene (**81**)

In a procedure similar to that used for **76**, reaction of **21** (5.8 g, 20 mmol) with cyclopentadiene (1.32 g, 20 mmol) in 200 mL of anhydrous ether and n-butyllithium (20 mmol) gave 3.86 g (97%) of **81** which was recrystalized from methanol; mp 50-52°C; ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 6 H), 2.13 (m, 2 H), 3.96 (t, 2 H), 6.63 (t, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.96, 16.22, 48.83, 68.23, 127.39, 130.52, 142.97, 167.87; mass spectrum; *m/e* (relative intensity) 198 (40), 183 (100), 172 (10), 168 (10), 165 (12), 157 (21), 153 (13), 141 (17), 128 (11), 115 (14), 91 (10).

Anal. Calcd. for $C_{15}H_{18}$: C, 90.85; H, 9.15.
Found: C, 90.98; H, 9.05.

26. 5,6,7,8-Tetramethyl-1,4-dihydro-9-(1-methylethylidene)-1,4-methanonaphthalene (**82**)

In a procedure similar to that used for **76**, reaction of **21** (2.92 g, 10 mmol) with **68** (1.06 g, 10 mmol) in 100 mL of THF and n-butyllithium (12 mmol) gave a yellow residue which was triturated with methanol (10 mL) to give 1.36 g (57%) of **82**, which was recrystalized from methanol, mp 96-98°C; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 6 H), 2.10 (s, 6 H), 2.23 (s, 6 H), 4.33-4.46 (t, 2 H), 6.60-6.20 (t, 2 H);

^{13}C NMR ($CDCl_3$) δ 16.01, 16.20, 18.99, 49.20, 101.21, 126.56, 130.90, 142.86, 145.79, 160.39; mass spectrum, *m/e* (relative intensity) 238 (100), 223 (27), 208 (13), 193 (11), 171 (17). High resolution mass spectrum: Calcd. for $C_{18}H_{22}$: 238.17215; Found: 238.17252.

27. *5,6,7,8-Tetramethyl-1,4-dihydro-9-(diphenylmethylene)-1,4-methanonaphthalene (**83**)*

In a procedure similar to that used for **76**, reaction of **21** (2.92 g, 10 mmol) with **69** (2.30 g, 10 mmol) in 150 mL of dry THF and 12 mmol of n-butyllithium gave a crude product which was triturated with methanol (20 mL) and filtered. Chromatography of the remaining solid on activated alumina, eluting with hexane, gave 2.3 g (62%) of **83**, mp 177-178°C; ^1H NMR ($CDCl_3$) δ 2.13 (s, 6 H), 2.20 (s, 6 H), 4.40-4.50 (t, 2 H), 6.76-6.86 (t, 2 H), 6.86-7.16 (m, 10 H); mass spectrum, *m/e* (relative intensity) 362 (45), 191 (75), 171 (100), 165 (60), 158 (88).

Anal. Calcd. for $C_{28}H_{26}$: C, 92.77; H, 7.22.
Found: C, 92.73; H, 7.21.

28. *5',6',7',8'-Tetramethyl-1',4'-dihydrospiro[cyclopropane-1,9'-[1,4]-methanonaphthalene] (**84**)*

In a procedure similar to that used for **76**, reaction of **21** (2.92 g, 10 mmol) with diene **70** (1.5 g, 16 mmol) in 100 mL of anhydrous toluene and n-butyllithium (12 mmol) gave a crude mixture which was chromatographed on activated alumina. Hexane first eluted some butylated compounds. Further elution with hexane gave 1.62 g (73%) of 84, which was recrystalized from methanol, mp 106-107°C; ^{1}H NMR (CDCl$_3$) δ 0.53 (m, 4 H), 2.10 (s, 6 H), 2.16 (s, 6 H), 3.30-3.40 (t, 2 H), 6.66-6.76 (t, 2 H). ^{13}C NMR (CDCl$_3$) δ 15.93, 16.16, 54.26, 63.25, 126.88, 130.28, 142.31, 146.55; mass spectrum, *m/e* (relative intensity) 224 (94), 209 (74), 196 (100), 181 (56), 165 (45), 149 (27).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99.
Found: C, 90.80; H, 9.08.

29. 5',6',7',8'-Tetramethyl-1'4'-dihydro-spiro[cyclopentane 1,9'-[1,4]-methanonaphthalene] (85)

In a procedure similar to that used for 76, reaction of 21 (2.92 g, 10 mmol) with diene 71 (1.8 g, 15 mmol) in 100 mL of THF and 12 mmol of n-butyllithium gave a crude product mixture. Chromatography of this crude mixture on activated alumina, eluting with 4:1 hexane: methylene chloride gave 1.32 g (52%) of 85, mp 95-97°C; ^{1}H NMR (CDCl$_3$) δ 1.10-1.70 (m, 8 H), 2.06 (s, 6 H), 2.16 (s, 6 H), 3.43-3.60 (t, 2 H), 6.43-6.60 (t, 2 H); ^{13}C NMR (CDCl$_3$) δ 16.00, 16.23, 25.60, 25.60 (overlap), 33.54, 33.80, 57.79, 88.37, 127.54, 130.11, 142.70, 164.99; mass spectrum, *m/e* (relative intensity) 252 (100), 237 (49), 223 (8), 208 (10).

Anal. Calcd. for $C_{19}H_{24}$: C, 90.41; H, 9.59.
Found: C, 90.28; H, 9.48.

30. 6,13-Dimethyl-5,7,12,14-tetrahydro-5,14[1',2']:7,12-[1",2"]-dibenzenopentacene 86 (R = CH_3)

To a stirred suspension of 2.11 g (5 mmol) of tetrabromo-p-xylene and 1.78 g (10 mmol) of anthracene in 250 mL of dry toluene under argon at -10° was added dropwise over 4 h 12 mmol of n-butyllithium in 100 mL of hexane. The mixture was allowed to gradually warm to room temperature. The reaction was quenched with methanol and the mixture was washed with water and dried ($MgSO_4$). After removal of the solvent (rotovap) the solid residue was chromatographed on silica gel. Hexane eluted the unreacted anthracene (1.07 g). Further elution with 9:1 hexane:methylene chloride gave 0.327 g (0.71 mmol, 35% based on consumed anthracene) of 86 (R = CH_3) which was recrystallized from chloroform, mp 460-462°C. ^1H NMR ($CDCl_3$) δ 2.65 (s, 6 H), 5.59 (s, 4 H), 6.90 (m, 8 H), 7.28 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 14.36, 50.84, 123.43, 124.32, 125.01, 140.48, 145.75; mass spectrum, m/e (relative intensity) 458 (88), 443 (41), 427 (30), 280 (100), 265 (34), 229 (80), 214 (66), 221 (49), 178 (53); UV (CH_3CN) λ_{max} 232 nm (log ε 4.66), 261 (3.75), 278 sh (3.66); IR (KBr) 3010, 3000, 1465, 1460, 750 cm^{-1}.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72;

Found: C, 94.16; H, 5.71.

31. 6,13-Dimethoxy-5,7,12,14-tetrahydro-5,14[1',2']:7,12-[1",2"]-dibenzenopentacene **86** (R = OCH_3)

The procedure and scale were identical to that used for **86** (R = CH_3). After recovery of the unreacted anthracene (0.88 g) by elution with hexane, further elution with 4:1 hexane:methylene chloride gave first 0.375 g (1.19 mmol, 21%) of 1,4-dimethoxytriptycene (**93**), mp 238-240°C (lit.[103] value 239-241°C); ^1H NMR ($CDCl_3$) δ 3.73 (s, 6H), 5.76 (s, 2 H), 6.33 (s, 2 H), 6.83 (m, 4 H), 7.20 (m, 4 H); mass spectrum, *m/e* (relative intensity) 314 (62), 283 (100), 252 (35), 239 (54), 149 (48), 142 (71), 85 (64), 83 (93). Continued elution with the same solvent gave 0.511 g (1.04 mmol, 37%) of **86** (R = OCH_3) which was recrystallized from acetonitrile, mp 400-402°C; ^1H NMR ($CDCl_3$) δ 3.76 (s, 6 H), 5.50 (s, 4 H), 6.73 (m, 8 H), 7.10 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 48.23, 62.85, 123.55, 125.23, 136.38, 145.34, 147.00; mass spectrum, *m/e* (relative intensity) 490 (19), 459 (9), 283 (100), 222 (22), 214 (14), 202 (12), 178 (15); UV (CH_3CN) λ_{max} 277 nm (log ε 3.71), 261 (3.93); IR (KBr) 2920, 2820, 1460, 1450, 1300, 1260, 1045, 755, 740 cm^{-1}.

Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.13; H, 5.34.

Found: C, 88.25; H, 5.36.

32. 6,13-Dihydroxy-5,7,12,14-tetrahydro-5,14[1',2']:7,12-[1",2"]dibenzenopentacene **86** (R = OH)

A solution containing 100 mg (0.20 mmol) of **86** (R = OCH_3) in 30 mL of glacial acetic acid and 10 mL of 47% hydrogen iodide was heated at reflux for 2 h. The cooled solution was extracted with chloroform and the combined organic layers were washed successively with water, aqueous sodium bisulfite, aqueous sodium bicarbonate, water and dried ($MgSO_4$). Removal of the solvent (rotovap) left 90 mg (97%) of **86** (R = OH) as a white solid which becomes gray at about 300°C and melts with decomposition at 427-430°C. ^1H NMR ($CDCl_3$) δ 4.40 (br s, 2 H), 5.50 (s, 4 H), 6.76 (m, 8 H), 7.20 (m, 8 H); in DMSO-d_6, δ 5.63 (s, 4 H), 6.66 (m, 8 H), 7.06 (m, 8 H), 8.40 (s, 2 H); UV (CH_3OH) λ_{max} 398 nm (log ε 4.61), 278 (4.82), 262 (4.92); mass spectrum *m/e* (relative intensity) 462 (74), 445 (39), 284 (32), 230 (42), 202 (100), 178 (80); IR (KBr) 3500, 1470, 1460, 1220, 750 cm^{-1}. The compound is not very stable in air and oxidizes slowly to the corresponding quinone.

33. 5,7,12,14-Tetrahydro-5,14[1',2']:7,12[1",2"]dibenzenopentacene-6,13-dione (**90**)

A solution containing 36 mg (0.078 mmol) of hydroquinone **86** (R = CH) and 0.5 g of ceric ammonium nitrate in 100 mL of acetonitrile was stirred at room temperature for 2 h. The solvent was removed (rotovap). The residue was extracted with chloroform and the organic layers were washed with water (3X) and dried ($MgSO_4$). Removal of the chloroform and recrystallization from the same solvent gave 31 mg (86%) of **90** which, upon heating, became gray at about 270°C and slowly turned black but did not melt up to 510°C. ^1H NMR ($CDCl_3$) δ 5.60 (s, 4 H), 6.76 (m, 8 H), 7.16 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 47.47, 124.31, 125.52, 143.77, 151.06, 180.02; UV (CH_3CN) λ_{max} 270 nm (log ε 4.76), 279 (4.73); mass spectrum, *m/e* (relative intensity) 460 (11), 230 (48), 202 (100), 178 (92); IR (KBr) 1650, 1475, 1460, 765, 755, 745 cm^{-1}.

Anal. Calcd. for $C_{34}H_{20}O_2$: C, 88.67; H, 4.38.

Found: C, 88.57; H, 4.49.

34. 6,7,14,15-Tetramethyl-5,8,13,16-tetrahydro-5,16-[1',2']:8,13[1",2"]dibenzenohexacene (**95**)

The procedure and scale were the same as with **86** (R = CH_3), but using **94** and anthracene. Chromatography of the crude product over silica gel and elution with hexane gave 0.41 g (2.08 mmol) of recovered anthracene. Further elution with 4:1 hexane:methylene chloride gave 1.607 g (3.0 mmol, 75%) of **95** which was recrystallized from methanol/chloroform, mp 358-360°C. ^1H NMR ($CDCl_3$) δ 2.66 (s, 12 H), 5.60 (s, 4 H), 6.76 (m, 8 H), 7.16 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 20.41, 50.57, 123.52, 125.25, 132.95, 140.69, 145.00 (2 C's); mass spectrum, *m/e* (relative intensity 536 (12), 253 (22), 246 (23), 238 (8), 83 (62), 57 (50), 44 (100); UV (CH_3CN) λ_{max} 277 nm (log ε 5.09), 273 (5.06), 259 (4.89); IR (KBr) 3000, 2900, 1460, 770, 750, 720 cm^{-1}. High resolution mass spectrum: Calcd. for $C_{42}H_{32}$: 536.24855; Found: 536.25041

35. 4,5-Dibromo-3,6-diiodo-o-xylene (**97**)

A solution of 16 g (0.0606 mol) of 4,5-dibromo-*o*-xylene[104] and 42 g of mercuric oxide in 160 mL of trifluoroacetic acid was heated at reflux for 4 h (a white precipitate was formed after about 2 h).[105] The solution was cooled, and the white solid was filtered and subjected directly to iodination without purification. A mixture of iodine (60 g), potassium iodide (40 g) and the crude 4,5-dibromo-3,6-di(trifluoroacetatomercuri)-*o*-xylene in 200 mL of water was heated to 70-75°C with stirring for 8 h, cooled and filtered. The solid product was dissolved in chloroform, washed successively with 10% aqueous sodium bisulfite, sodium bicarbonate and water, then dried ($MgSO_4$). Removal of the solvent (rotovap) and recrystallization from chloroform gave 25.5 g (81%) of 97, mp 239-240°C. ^1H NMR ($CDCl_3$) δ 2.66 (s); mass spectrum, *m/e* (relative intensity) 516 (2), 390 (17), 263 (15), 182 (20), 102 (100), 71 (61), 51 (64).

Anal. Calcd. for $C_8H_6Br_2I_2$: C, 18.62; H, 1.17.
Found: C, 18.72; H, 1.19.

36. 6,7-Dimethyl-5,8,13,14-tetrahydro-5,14[1',2']:8,13-[1",2"]dibenzenopentaphene 87 (R = CH_3)

The procedure and scale were the same as with 86 (R = CH_3) except that the reaction was carried out at -23°C. Reaction of 97 (2.56 g, 5 mmol) and anthracene (1.78 g, 10 mmol) with n-butyllithium gave a crude product. Chromatography of this crude product on silica gel and elution with hexane gave 1.13 g (6.34 mmol) of recovered anthracene. Further elution with 4:1 hexane:methylene chloride gave 0.322 g (0.70 mmol, 38%) of 87 (R = CH_3) which was recrystallized from methanol/chloroform, mp 382-384°C. ^1H NMR ($CDCl_3$) δ 2.33 (s, 6 H), 5.50 (s, 2 H), 5.83 (s, 2 H), 6.83 (m, 8 H), 7.23 (m, 8 H); ^{13}C NMR

($CDCl_3$) δ 15.32, 50.18, 50.93, 123.42, 123.61, 125.15, 125.21, 127.20, 136.31, 139.53, 145.52, 145.53; mass spectrum, m/e (relative intensity) 458 (97), 443 (5), 280 (100), 178 (52); IR (KBr) 2900-3050, 1445, 1380, 750, 720, 690, 620, 610 cm^{-1}; UV (CH_3CN) λ_{max} 227 nm (log ε 4.70) 262 sh (3.91), 269 sh (3.89), 277 sh (3.83). High resolution mass spectrum: Calcd. for $C_{36}H_{26}$: 458.20318; Found: 458.20346.

37. 11-Chloro-9,10-dihydro-9,10-ethenoanthracene (91)[106]

To a solution of potassium t-butoxide prepared from 3.9 g (0.1 mol) of potassium in 200 mL of t-butanol, under argon, was added 6.5 g (0.023 mol) of trans-11,12-dichloro-9,10-dihydro-9,10-ethenoanthracene[106] and the mixture was refluxed for 1 h. After cooling to room temperature 20 mL of water was added and the solvent was removed under reduced pressure (rotovap). The remaining solid was dissolved in 200 mL of ether, washed with water (3 X 50 mL) and dried ($MgSO_4$). Removal of the ether left 5.0 g (88%) of 91 which was recrystallized from methanol, mp 128°C (lit.[106] 127.5-128°C). ^1H NMR (CCl_4) δ 4.80 (d, C10-H, J = 3Hz), 4.96 (d, C9-H, J = 7.5 Hz), 6.56 (dd, C12-H, J = 3.75 Hz), 6.66-7.20 (m, 8 H); mass spectrum, m/e (relative intensity) 240 (8), 238 (24), 203 (100), 149 (16), 101 (22).

38. 11-Chloro-12-deuterio-9,10-dihydro-9,10-ethenoanthracene (**100**)

To a solution of **91** (0.5 g, 2.1 mmol) in anhydrous THF (50 mL) at -42°C under argon was added 2 mL (2.5 mmol) of *t*-butyllithium (1.3 M in pentane). The mixture was stirred for 2 h then warmed to 0°C. CH_3OD (1 mL) was added. The solvent was removed on a rotary evaporator and the residue was taken up in ether, washed with water and dried ($MgSO_4$). The ether solution was concentrated to give 0.5 g of **100**, mp 128-129°C (from methanol); NMR (CCl_4) δ 4.86 (s, C10-H), 4.93 (s, C9-H), 6.60-7.33 (m, 8 H); mass spectrum, *m/e*, (relative intensity) 241 (10), 239 (32), 204 (100).

39. 12-Chloro-9,10-dihydro-9,10-ethenoanthracene-11-carboxylic acid (**99**)

Metalation of **91** in a similar manner and on the same scale as for **100** followed by pouring the resulting **98** over a slush of dry ice and 100 mL of anhydrous ether gave, on workup by extraction with 10% sodium hydroxide and acidification to pH 2, 0.3 g (50%) of the known chloroacid **99**, mp 259-260°C (lit.[59,107] 260-261°C).

40. 11-Chloro-12-methyl-9,10-dihydro-9,10-ethenoanthracene (**101**)

Metalation of **91** as for **100** was followed by cooling the resulting solution of **98** to -78°C and the addition of methyl iodide (1 mL). After the mixture was quickly warmed to room temperature the solvent was removed (rotovap), and the residue was taken up in ether, washed with water and dried ($MgSO_4$). The ether solution was concentrated to give 0.53 g (100%) of **101** which was recrystallized from methanol, mp 204-205°C (lit.[108] 206-208°C). ^1H NMR (CCl_4) δ 1.90 (s, 3 H, methyl), 4.63 (s, 1 H, bridgehead), 4.76 (s, 1 H, bridgehead), 6.66-7.20 (m, 8 H, aromatic); mass spectrum, _m/e_ (relative intensity) 252 (32), 217 (100), 202 (33).

41. 11-Bromo-12-chloro-9,10-dihydro-9,10-ethenoanthracene (**102**)

The procedure described for **101** was followed but with 1 mL of 1,2-dibromoethane in place of methyl iodide, to give after similar workup 0.48 g (72%) of **102** after recrystallization from methanol, mp 173-175°C; ^1H NMR (CCl_4) δ 4.86 (s, 1 H), 4.90 (s, 1 H), 6.60-7.23 (m, 8 H); mass spectrum, _m/e_ (relative intensity) 318 (2), 281 (10), 237 (66), 202 (100); High resolution mass spectrum: Calcd. for $C_{16}H_{10}BrCl$: 315.96715; Found: 315.96550.

42. 5,6,11,12,17,18-Hexahydro-5,18[1',2']:6,11[1",2"]:12,17[1‴,2‴]tribenzenotrinaphthylene (**88**)

To a solution of **91** (1.0 g, 4.2 mmol) in anhydrous

THF (70 mL) at -42°C under argon was added 4 mL (5 mmol) of *t*-butyllithium (1.3 M in pentane). The mixture was stirred at -42°C for 2 h, then quickly warmed to room temperature and heated at reflux for 2 h. The mixture was cooled to room temperature and quenched with methanol (2 mL). The resulting white precipitate was filtered, washed with water and dried to give 0.169 g (20%) of **88**. ^{1}H NMR ($CDCl_3$) δ 6.18 (s, 6 H, bridgehead protons), 6.92 (m, 12 H), 7.45 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 48.64, 123.42, 125.01, 135.33, 145.36; mass spectrum, *m/e* (relative intensity) 606 (100), 428 (82), 256 (4), 178 (19).

The filtrate after removal of **88** was concentrated on a rotary evaporator. The resulting brown solid was taken up in chloroform, washed with water and dried ($MgSO_4$). The residue which remained after removing the chloroform was chromatographed on alumina with a 3:1 hexane:chloroform eluent to give 0.36 g (39%) of **103** mp 266-268°C (lit.[59] 268°C).

43. 9,10[1',2']-Benzeno-1,4-dimethyl-1,4-epoxy-1,4,9,10-tetrahydroanthracene (**105**)

To a solution of **98** (1.0 g, 4.2 mmol) in anhydrous THF (50 mL) at -42°C under argon was added 4 mL (5 mmol) of *t*-butyllithium (1.3 M in pentane) and the mixture was stirred for 2 h. This solution was transferred by syringe to a dropping funnel equipped with a cooling jacket (at -42°C), and was added dropwise over 1 h under argon to a refluxing solution containing 5 g of 2,5-dimethylfuran in 100 mL of anhydrous THF. After 1 h of additional reflux, the solution was cooled and quenched with methanol (2 mL). The solvent was removed on the rotary evaporator and the residue was taken up in ether, washed with water and dried ($MgSO_4$). The ether was removed to give a yellow solid which was chromatographed over alumina (using first hexane, then 4:1 hexane:chloroform as eluent) to give 0.50 g (40%) of **105**, mp 179-180°C; ^1H NMR (CCl_4) δ 1.63 (s, 6 H, methyls), 4.70 (s, 2 H, bridgehead), 6.00 (s, 2 H, vinyl), 6.40-7.16 (m, 8 H, arom); ^{13}C NMR ($CDCl_3$) δ 15.84, 50.93, 91.74, 123.03, 123.32, 124.34, 124.86, 145.01, 145.25, 145.57, 168.59; mass spectrum, *m/e* (relative intensity) 298 (100), 283 (68), 272 (36), 255 (87), 239 (67), 229 (36), 215 (23), 202 (40), 178 (50). High resolution mass spectrum: Calcd. for $C_{22}H_{18}O$: 298.13577; Found: 298.13630.

44. 6,11[1',2']-Benzeno-5,12-diphenyl-5,12-epoxy-5,6-11,12-tetrahydronaphthacene (**106**)

The same procedure used for **105** was followed, but using 1,3-diphenylisobenzofuran (1.13 g, 4.2 mmol) as the trapping agent. Chromatography of the crude product on alumina with hexane as eluent gave 0.32 g of unreacted 1,3-diphenylisobenzofuran. Further elutin with 3:1

hexane:chloroform gave 1.21 g (61%) of **106**, mp 208-209°C. ^{1}H NMR (CCl_4) δ 5.00 (s, 2 H, bridgehead), 6.20-7.60 (m, 22 H, arom); ^{13}C NMR ($CDCl_3$) δ 51.86, 94.35, 120.82, 123.06, 123.42, 124.44, 125.08, 128.82, 128.97, 134.53, 144.65, 145.43, 150.46, 167.75 (four peaks are overlapped); mass spectrum, m/e (relative intensity) 472 (100), 395 (15), 265 (20), 178 (21); High resolution mass spectrum: Calcd. for $C_{36}H_{24}O$: 472.18272; Found: 472.17913.

45. 9,10[1',2']-Benzeno-11,11-dimethoxy-1,2,3,4-tetrachloro-1,4-methano-1,4,9,10-tetrahydroanthracene (**107**)

The same procedure used for **105** was followed, but using 5,5-dimethoxytetrachlorocyclopentadiene (1.10 g, 4.2 mmol) as the trapping agent. Chromatography of the crude product on alumina with hexane as eluent removed the unreacted diene (0.2 g). Further elution with 3:1 hexane:chloroform gave 0.82 g (42%) of **107** as a yellow oil. Further purification by preparative tlc on alumina gave pure **107**, mp 141-142°C; ^{1}H NMR (CCl_4) δ 3.16 (s, 3 H, methoxyl), 3.36 (s, 3 H, methoxyl), 4.95 (s, 2 H, bridgehead), 6.66-7.30 (m, 8 H, arom); ^{13}C NMR ($CDCl_3$) δ 51.65, 55.28, 59.38, 105.39, 123.40, 123.68, 125.16, 125.57, 134.23, 143.73, 144.39, 146.50, mass spectrum, m/e (relative intensity) 466 (6), 429 (2), 393 (2), 264 (15), 229 (35), 203 (70), 178 (100), 101 (15); High resolution mass spectrum: Calcd. for $C_{23}H_{16}Cl_4O_2$: 463.99135; Found: 463.99045.

46. 9,10-Dimethyl-1,4,5,8-tetrahydrophenanthrene-1,4;5,8-bis-endoxide **127**

To a stirred suspension of 4,5-dibromo-3,6-diiodo-*o*-xylene **97** (2.16 g, 5 mmol) and furan (2 g, excess) in dry toluene (100 mL) under argon at -78°C was added dropwise over 4 h 12 mmol of n-butyllithium in 100 mL of hexane. The mixture was allowed to gradually warm to room temperature. The reaction was quenched with methanol (1 mL) and the mixture was washed with water and dried ($MgSO_4$). After removal of the solvent (rotovap) the solid residue was chromatographed on alumina, eluting with 1:1 hexane:chloroform,to give 0.854 g (71%) of **127** as a mixture of syn and anti isomers, mp 260-262°C. ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 6 H), 5.60 (broad s, 4 H), 6.80 (broad s, 4 H); mass spectrum *m/e* (relative intensity) 238 (27), 181 (46), 167 (100), 165 (85), 152 (41), 115 (46).

47. Hydrogenation of **127**

A solution of **127** (1.19 g, 5 mmol) in 100 mL of ethyl acetate was hydrogenated for 1 h over 0.5 g of 10% palladium on charcoal at room temperature and 45 p.s.i. of hydrogen.

The catalyst was filtered and the solvent was removed (rotary evaporator). The remaining oil was crystallized from hexane to give 1.075 g (89%) of 128, mp 162-164°C. ^{1}H NMR ($CDCl_3$) δ 1.16-1.43 (m, 8 H), 2.13 (broad s, 6 H), 5.33 (m, 4 H); mass spectrum, *m/e*, (relative intensity) 242 (6), 214 (27), 185 (100), 128 (7); with chemical ionization, $(M + 1)^+ = 243$.

48. 9,10-Dimethylphenanthrene (129)

A solution of 128 (1.07 g, 4.4 mmol) in 100 mL of absolute ethanol was saturated with HCl (hydrogen chloride was bubbled through the solution for 10 minutes). The mixture was heated at reflux for 2 h. After cooling to room temperature the solvent was removed (rotovap). The residue was taken up in chloroform (100 mL) and washed with a 10% aqueous sodium bicarbonate and water and dried ($MgSO_4$). Removal of the chloroform left a residue which was washed through a silica gel column. Elution with hexane gave 0.854 g (95%) of 129. Recrystallization of 129 from methanol gave a sample with mp 140°C (lit.[79] 140.5°C). ^{1}H NMR ($CDCl_3$) δ 2.66 (s, 6 H), 7.50 (m, 4 H), 8.0 (m, 2 H), 8.53 (m, 2 H); mass spectrum, *m/e* (relative intensity) 206 (100), 191 (82), 178 (12), 165 (32); ^{13}C NMR ($CDCl_3$) 15.86, 122.75, 124.54, 125.38, 126.51, 129.24, 129.43, 132.21.

49. 1,4,5,8,9,10-Hexamethyl-1,4,5,8-tetrahydrophenanthrene-1,4;5,8-bis-endoxide **130**

The same procedure and scale was followed as for **129** but 2,5-dimethylfuran (2 g, excess) was used as the diene. Chromatography of the crude product on alumina eluting with 1:1 hexane:chloroform resulted in separation of the syn and anti isomers. The first fraction (**130a**), 0.3 g (20%), was the major isomer, mp 167-168°C. ^{1}H NMR ($CDCl_3$) δ 1.86 (s, 6 H), 1.90 (s, 6 H), 2.13 (s, 6 H), 6.50 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.30, 19.15, 20.27, 88.51, 89.31, 125.94, 140.95, 146.27, 146.53, 147.01; mass spectrum, *m/e* (relative intensity) 294 (4), 268 (14), 251 (86), 242 (25), 225 (43), 208 (100), 193 (23), 178 (21).

The second fraction (**130b**), 0.204 g (14%), mp 166-168°C; ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 6 H), 2.00 (s, 6 H), 2.13 (s, 6 H), 6.43 (dd, *J* = 12, 4 Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.48, 19.04, 19.19, 89.94, 89.35, 126.12, 141.02, 145.18, 145.49, 146.18; mass spectrum, *m/e* (relative intensity) 294 (3), 268 (6), 251 (45), 242 (16), 225 (26), 209 (100), 193 (21), 178 (15).

50. Hydrogenation of **130b** (**131**)

A solution of **130b** (100 mg) in 100 mL of ethyl acetate was hydrogenated for 0.5 h over 100 mg of 10% palladium on charcoal at room temperature and 45 p.s.i. of hydrogen.

The catalyst was filtered and the solvent was removed (rotovap). The remaining oil was crystallized from methanol to give 90 mg (89%) of 131, mp 134-135°C. ^{1}H NMR ($CDCl_3$) δ 1.20-1.73 (m, 8 H), 1.86 (s, 6 H), 1.90 (s, 6 H), 2.23 (s, 6 H); mass spectrum, m/e (relative intensity 298 (1.4), 270 (19), 242 (100); with chemical ionization, $(M + 1)^+$ = 299.

51. Bis(N-dimethylamino)-1,4,5,8,9,10-hexamethyl-1,4,5,8-tetrahydrophenanthrene-1,4;5,8-bis-imine (136)

The same procedure and scale was followed as for 127, but using pyrrole 134 (1.38 g, 10 mmol) as the diene. The crude product was triturated with hexane (20 mL) to give 0.45 g (24%) of 136 (single isomer), mp 147-149°C. ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 6 H), 1.83 (s, 6 H), 2.16 (s, 6 H), 2.28 (broad s, 12 H), 6.43 (broad s, 4 H); ^{13}C NMR ($CDCl_3$) δ 14.93, 18.72, 19.43, 45.69, 74.71, 76.15, 126.44, 145.75, 146.00, 146.52, 146.75; mass spectrum, m/e (relative intensity) 321 (54), 276 (92), 262 (100), 116 (32); with chemical ionization $(M + 1)^+$ = 379.

The oily residue remaining from concentration of the hexane solution was chromatographed on alumina. Hexane eluted the unreacted pyrrole. Further elution with chloroform gave 0.432 g (22%) of 136 as a mixture of isomers (total yield 46%).

52. Bis(N-dimethylamino)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5,8-tetrahydrophenanthrene-1,4;5,8-bis-imine (137)

The same procedure and scale was followed as for 127 but pyrrole 135 (1.9 g, 10 mmol) was used as the diene. The crude product was triturated with hexane (20 mL) to give 0.35 g (16%) of 137 (single isomer), mp 174-175°C. ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 6 H), 1.60 (s, 6 H), 1.76 (s, 6 H), 1.80 (s, 6 H), 2.16 (s, 6 H), 2.43 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 10.50, 11.38, 14.77, 17.63, 18.69, 76.12, 76.30, 45.83, 125.68, 141.50, 145.16, 145.95, 148.21; mass spectrum, m/e (relative intensity) 318 (100), 304 (9), 288 (13); with chemical ionization $(M + 1)^{+}$ = 435.

The oily residue remaining from concentration of the hexane solution was chromatographed on alumina. Hexane eluted the unreacted pyrrole 135. Further elution with chloroform gave 0.614 g (28%) of 137 as a mixture of isomers (total yield 44%).

53. 1,4,5,8,9,10-Hexamethylphenanthrene (132)

Bis-adduct 136 (50 mg) was sealed under vacuum (0.1 torr) in a small tube. The tube was heated in an oil bath at 150°C for 1 h. After the tube was cooled to room temperature the residue was washed on alumina with hexane to give 31 mg (90%) of 132, which was recrystallized from methanol, mp 85-86°C. ^{1}H NMR ($CDCl_3$) δ 2.449 (s, 6 H), 2.631 (s, 6 H), 2.817 (s, 6 H), 7.171 (AB quartet, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.79, 22.02, 25.47, 126.08, 129.69, 130.11, 130.59, 131.58, 132.93, 134.64; mass spectrum, *m/e* (relative intensity) 262 (100), 247 (13), 232 (23), 217 (10); IR (KBr) 2850, 2900, 1450, 1360, 800, 790 cm^{-1}; UV (heptane) λ_{max} 324 nm (log ε 4.43), 266 (4.90), 241 (4.64).

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45.
Found: C, 91.65; H, 8.46.

54. Decamethylphenanthrene (138)

Pyrolysis of 137 (100 mg) at 170-180°C for 2 h (using the same procedure as for 132) gave a crude residue. This residue was washed on alumina with hexane to give 64 mg (97%) of 138 which was recrystallized from methanol/chloroform, mp 165-167°C. ^{1}H NMR ($CDCl_3$) δ 2.33 (broad s, 18 H), 2.46 (s, 6 H), 2.53 (s, 6 H); in C_6D_6 at 180 M Hz δ 2.227 (s, 12 H), 2.356 (s, 6 H), 2.368 (s, 6 H), 2.491 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 16.57, 20.88, 21.08, 21.96, 128.15, 128.98, 130.06, 131.73, 133.73, 134.38 (two methyls and two sp^2 carbons are overlapped); mass spectrum, *m/e* (relative intensity) 318 (100), 303 (7), 228 (17), 273 (14); UV (heptane) λ_{max} 325 (log ε 4.14), 277 (4.73).

Anal. Calcd. for $C_{24}H_{30}$: C, 90.50; H, 9.50.
Found: C, 90.69; H, 9.50.

55. Reaction of **131** or **132** with HCl

A solution of **131** (100 mg) in 50 mL of absolute ethanol was saturated with HCl gas. This solution was heated at reflux for 2 h. After similar work-up as for **129**, 65 mg of a viscous oil remained. Preparative GLC (10% SE-30 on chromosorb w, 200°C) gave two main fractions. The first fraction (25%) was hexamethylphenanthrene **132**. The second fraction (75%) was the rearranged product **133**. ^{1}H NMR ($CDCl_3$) δ 0.88 (d, *J* = 8 Hz, 3 H), 2.23 (s, 6 H), 2.33 (s, 3 H), 2.40 (s, 3 H), 3.43 (d, *J* = 8, 2 Hz, 1 H), 4.93 (d, *J* = 2 Hz, 1 H), 5.20 (d, *J* = 2 Hz, 1 H), 6.86 (s, 2 H), 7.00 (s, 2 H); mass spectrum, *m/e* (relative intensity) 262 (trace), 220 (35), 205 (100), 145 (10); with chemical ionization, $(M + 1)^+$ = 263.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45.
Found: C, 91.56; H, 8.49.

In a procedure similar to that described above, when 100 mg of **132** was treated with HCl in 50 mL of ethanol at reflux (2 h), GLC analysis of the crude reaction mixture showed 24% of **132** remained unreacted and 76% of **133** was formed.

56. 6,13-Dimethyl-5,7,12,14-tetraphenyl-5,6,12,14-tetrahydropentacene-5,14;7,12-bis-endoxide **149** ($R = CH_3$)

A solution of **25** (2.11 g, 5 mmol) and **148** (2.7 g, 10 mmol) in 200 mL of anhydrous toluene was cooled to

-78°C under argon (most of the **25** precipitated out). To this suspension n-butyllithium (12 mmol) in 50 mL of hexane was added dropwise over a 2 h period. After the reaction mixture was stirred for an additional 2 h at -78°C, it was allowed to warm to room temperature. Methanol (1 mL) was added. Toluene was removed on a rotary evaporator, the remaining solid was dissolved in methylene chloride (100 mL) and was washed with water, dried ($MgSO_4$) and evaporated under vacuum. The remaining residue was triturated with methanol (50 mL) and filtered to give 0.7 g (22%) of one pure isomer of **149** (R = CH_3); mp above 360°C; ^1H NMR ($CDCl_3$) δ 1.40 (s, 6 H), 6.73-7.83 (m, 28 H); ^{13}C NMR ($CDCl_3$) 17.43, 91.67, 122.01, 124.65, 126.46, 128.80, 128.59, 129.01, 129.63, 129.63, 134.95, 150.31, 150.53, 150.92; mass spectrum, m/e (relative intensity) 642 (11), 537 (21), 432 (82), 340 (15), 105 (100). High resolution mass spectrum: Calcd. for $C_{48}H_{34}O_2$: 642.2617; Found: 642.2607.

The remaining solid from concentration of the methanol solution was chromatographed on silica gel. Elution with hexane removed 0.56 g of unreacted **148**. Further elution with 3:1 hexane:methylene chloride removed 1.06 g (33%) of **149** (R = CH_3) as a mixture of two isomers (total yield 67% based on consumed diphenylisobenzofuran).

57. 6,13-Dimethoxy-5,7,12,14-tetraphenyl-5,6,12,14-tetrahydropentacene-5,14;7,12-bis-endoxide 149 (R = OCH_3)

In a procedure similar to that used for 149 (R = CH_3), reaction of 92 (2.27 g, 5 mmol) and 129 (2.70 g, 10 mmol) in 200 mL of anhydrous toluene with n-butyllithium (12 mmol) at -78°C gave a crude product mixture. Trituration of this crude mixture with 50 mL of hexane and filtration gave 1.85 g of a yellow solid which was chromatographed on silica gel. Elution with hexane removed 0.45 g of unreacted 1,3-diphenylisobenzofuran 148. Further elution with 3:1 hexane:methylene chloride first resulted in 1.02 g (30%) of 149 (R = OCH_3) as a mixture of isomers. The second fraction (0.38 g, 12%) was a pure isomer of 149, mp 355-357°C; ^1H NMR ($CDCl_3$) δ 2.66 (s, 6 H), 6.9-8.0 (m, 28 H); ^{13}C NMR ($CDCl_3$) δ 60.93, 91.37, 121.64, 125.64, 128.05, 128.38, 128.61, 129.14, 129.39, 134.34, 144.22, 145.41, 150.91; mass spectrum chemical ionization (M^+ + 1) = 676, (M^+ + 29) = 703. High resolution mass spectrum: Calcd. for $C_{41}H_{29}O_3(M^+-C_7H_5O)$: 569.21167; Found: 569.20545.

58. 9,10-Dimethyl-1,4,5,8-tetraphenyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-endoxide 150 (R = CH_3)

In a procedure similar to that used for 149, reaction of 25 (2.11 g, 5 mmol) and 147 (2.2 g, 10 mmol) in 100 mL of anhydrous toluene with n-butyllithium (12 mmol) at 0°C gave a crude product mixture. Trituration of this crude mixture with methanol (20 mL) gave 0.43 g (16%) of a pure isomer of **150** (R = CH_3), mp 320-321°C (dec.); ^1H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 7.16 (s, 4 H), 7.17-7.66 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 14.67, 94.29, 124.10, 127.96, 128.29, 128.53, 137.13, 144.47, 150.66; mass spectrum, *m/e* (relative intensity) 542 (trace), 527 (trace), 437 (2), 105 (100), 77 (12). High resolution mass spectrum: Calcd. for $C_{40}H_{30}O_2$: 542.2245; Found: 542.2247.

The remaining solid from concentration of the methanol solution was chromatographed on activated alumina. Elution with 4:1 hexane:methylene chloride first removed 0.45 g of unreacted **147**. The second fraction gave 0.69 g (25%) of **150** (R = CH_3) as a mixture of two isomers, (total yield 52% based on consumed 2,5-diphenylfuran).

59. 9,10-Dimethoxy-1,4,5,8-tetraphenyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-endoxide **150** (R = OCH_3)

In a procedure similar to that used for **149**, reaction of **92** (2.77 g, 5 mmol) and **147** (2.20 g, 10 mmol) in 250 mL of anhydrous toluene at 0°C with n-butyllithium (12 mmol) gave a mixture of crude products. Trituration of this crude mixture with hexane (50 mL) and filtration gave 0.16 g (6%) of a pure isomer of **150** (R = OCH_3); mp 303-305°C (dec.); ^1H NMR ($CDCl_3$) δ 1.96 (s, 6 H), 7.0-7.6 (m, 22 H); mass spectrum, *m/e* (relative intensity) 574 (trace), 469 (42), 443 (14), 364 (8), 105 (100). High resolution mass spectrum: Calcd. for $C_{33}H_{25}O_3(M^+ - C_7H_5O)$: 469.18037; Found: 469.17839.

The remaining solid from concentration of the hexane solution was chromatographed on activated alumina. Elution with 95:5 hexane:chloroform first removed 1.56 g of unreacted diphenylfuran **147**. The second fraction resulted in 0.156 g (9%) of mono-adduct **151**, mp 182-184°C; ^1H NMR ($CDCl_3$) δ 3.33 (s, 6 H), 6.40 (s, 2 H), 7.03-7.66 (m, 12 H); mass spectrum, *m/e* (relative intensity) 356 (13), 330 (13), 307 (8), 299 (9), 251 (100), 165 (13), 149 (33), 105 (78). High resolution mass spectrum: Calcd. for $C_{24}H_{20}O_3$: 356.14125; Found: 356.13757.

Further elution with 50:50 hexane:chloroform gave 0.365 g (13%) of a mixture of two bis-adduct isomers (50% total yield of bis-adducts based on diphenylfuran used.)

60. *6,7,14,15-Tetramethyl-5,8,13,16-tetraphenyl-5,8,13-16-tetrahydrohexacene-5,16;8,13-bis-endoxide* **152**

In a procedure similar to that used for **149**, reaction of **94** (2.5 g, 5 mmol) and **148** (2.7 g, 10 mmol) in 200 mL of anhydrous toluene with n-butyllithium (12 mmol) gave a yellow solid which was chromatographed on silica gel.

Elution with hexane removed a trace of unreacted 149. Further elution with 3:1 hexane:chloroform gave as the first fraction 1.23 g (34%) of a pure isomer of 152; mp 357-358°C; ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 12 H), 6.9-7.8 (m, 28 H); ^{13}C NMR ($CDCl_3$) δ 22.97, 92.29, 121.63, 125.98, 127.67, 127.95, 128.74, 129.01, 129.69, 135.21, 149.43, 149.66 (two peaks are missing, possibly overlapped); mass spectrum, m/e (relative intensity) 720 (3), 615 (8), 600 (2), 510 (5), 105 (100), 77 (23). High resolution mass spectrum: Calcd. for $C_{54}H_{46}O_2$: 720.30284; Found: 720.30082.

The second fraction gave 1.73 g (48%) of 152 as a mixture of two isomers.

61. Reaction of 149 (R = CH_3) with n-butyllithium in the presence of ferric chloride

To a suspension of anhydrous ferric chloride (0.487 g, 3 mmol) in 25 mL of anhydrous THF at -78°C under argon, was added dropwise n-butyllithium (9 mmol). The reaction mixture was kept at -78°C for 2 h. To this suspension was added dropwise a solution of bis-adduct 149 (R = CH_3) (0.642 g, 1 mmol) in 25 mL of anhydrous THF. Later the reaction mixture was allowed to warm to room temperature and filtered. 50 mL of ether and 10 mL of water were added to the filtrate. The organic layer was separated, dried ($MgSO_4$) and concentrated to give 0.64 g (100%) of the unreacted starting material 149 (R = CH_3).

62. Reaction of 149 (R = CH_3) with Zinc in Acetic Acid, (154)

A suspension of bis-adduct 149 (R = CH_3) (200 mg) and zinc dust (4 g) in 100 mL of glacial acetic acid was heated at reflux for 6 h. After cooling the reaction mixture to room temperature the solvent was removed (rotovap) and the organic product was taken up in 100 mL of chloroform. The chloroform solution was washed with water and dried ($MgSO_4$). Concentration of the chloroform gave 190 mg (100%) of 154. This compound starts to sublime at about 240°C and finally melts at 270-272°C upon rapid heating. ^1H NMR ($CDCL_3$) δ 4.86 (s, 4 H), 7.0-7.40 (m, 28 H); mass spectrum, m/e (relative intensity) 608 (80), 571 (15), 265 (57), 257 (52), 226 (58), 91 (37), 43 (100). High resolution mass spectrum: Calcd. for $C_{48}H_{32}$: 608.25041; Found: 608.24766.

63. Reaction of 149 (R = OCH_3) with Zinc in Acetic Acid (155)

A suspension of 149 (R = OCH_3) (100 mg) and zinc dust (2 g) in 80 mL of glacial acetic acid was heated at reflux under argon and in the dark. After 2 h the reaction mixture was cooled to room temperature and 50 mL of oxygen-free water was added to the solution. A greenish-blue solid which formed was filtered under argon and washed with oxygen-free water to give 80 mg (84%) of the crude pentacene 155, which melts at 285-290°C upon rapid heating; ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 6 H), 6.90-7.30 (m, 28 H); mass spectrum, m/e (relative intensity) 642 (3), 584 (30), 303 (16), 291 (37), 253 (100), 214 (31). High resolution mass spectrum: Calcd. for $C_{48}H_{38}O_2$: 642.25589; Found 642.25492.

64. Reaction of 25 with n-butyllithium in the presence of dipyrrole 155 (n = 3)

In a procedure similar to that used for 29, reaction of 25 (4.22 g, 10 mmol) with 155 (n = 3) (2.3 g, 10 mmol) in 150 mL of dry toluene and 12 mmol of n-butyllithium at -78°C gave 4.75 g of a yellow residue which was chromatographed on activated alumina. Elution with hexane first removed 0.175 g of unreacted 25 and 0.67 g of unreacted 155 (n = 3). Further elution with 4:1 hexane:ethyl acetate gave as the first fraction, 2.44 g (51%) of 1:1 adduct 157 (n = 3), mp 158-159°C; ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 6 H), 2.10-2.15 (m, 2 H), 2.13 (s, 6 H), 2.43 (s, 6 H), 3.43-3.76 (m, 4 H), 5.63 (s, 2 H), 6.50 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.47, 18.44, 20.63, 32.46, 32.46, (overlap), 42.07, 42.51, 77.37, 105.13, 126.25, 127.11, 132.88, 147.42, 150.26; mass spectrum, m/e (relative intensity) 492 (1.5), 150 (66), 149 (95), 120 (37), 108 (100), 95 (36). High resolution mass spectrum: Calcd. for $C_{23}H_{28}Br_2N_2$: 492.06006; Found: 492.05920.

The second fraction gave 1.003 g (21%) of 2:1 adduct 158 (n = 3), mp 122-125°C (gas evolved); ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 12 H), 2.40 (s, 12 H), 1.73-240 (m, 6 H), 6.50 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.59, 20.61, 33.06, 43.89, 77.35, 126.70, 132.33, 147.64, 150.29; mass spectrum, *m/e* (relative intensity) 754 (M^+, trace), 384 (8), 342 (30), 153 (18), 97 (27), 94 (100), 70 (45).

Anal. Calcd. for $C_{31}H_{34}Br_4N_2$: C, 49.39; H, 4.54; N, 3.71;
Found: C, 49.50; H, 4.53; N, 3.75.

65. Reaction of 25 with n-butyllithium in the presence of dipyrrole 155 (n = 4)

In a procedure similar to that used for 29, reaction of 25 (4.22 g, 10 mmol) with 155 (n = 4) (2.44 g, 10 mmol) in 150 mL of dry toluene and 12 mmol of n-butyllithium at -78°C gave 4.77 g of a crude product mixture which was chromatographed on activated alumina. Hexane first eluted 0.65 g of unreacted dipyrrole 155 (n = 4). Further elution with 4:1 hexane:ethyl acetate, gave as the first fraction 0.667 g (15%) of 1:1 adduct of 157 (n = 4), as a viscous oil; ^{1}H NMR ($CDCl_3$) δ 1.30-1.66 (m, 4 H), 1.76 (s, 6 H), 2.13 (s, 6 H), 2.40 (s, 6 H), 3.36-3.66 (m, 4 H), 5.56 (s, 2 H), 6.50 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.57, 18.49, 20.66, 29.00, 30.28, 43.52, 45.17, 77.41, 105.14, 126.33, 127.23, 132.39, 147.61, 150.33; mass spectrum, *m/e* (relative intensity) 506 (5), 163 (42), 150 (100), 120 (33), 108 (94), 94 (56). High resolution mass spectrum: Calcd. for $C_{24}H_{30}Br_2N_2$: 506.07572; Found: 506.07153.

The second fraction gave 2.24 g (47%) of 2:1 adduct **158** (n = 4), mp 218-219°C; ^{1}H NMR ($CDCl_3$) δ 1.50-1.66 (m, 4 H), 1.76 (s, 12 H), 1.90-2.33 (m, 4 H), 2.40 (s, 12 H), 6.53 (s, 4 H); ^{13}C NMR (CCl_4, CD_3CN) δ 18.26, 20.51, 29.63, 44.89, 77,30, 125.67, 131.95, 147.30, 151.20; mass spectrum, *m/e* (relative intensity) 768 (M^+, trace) 399 (35), 364 (15), 342 (100), 262 (12), 236 (16), 70 (21), 42 (42).

Anal. Calcd. for $C_{32}H_{36}Br_4N_2$: C, 50.03, H, 4.72; N, 3.65;

Found: C, 49.91; H, 4.72; N, 3.65.

66. Reaction of **25** and n-butyllithium in the presence of dipyrrole **155** (n = 5)

In a procedure similar to that used for **29**, reaction of **25** (4.22 g, 10 mmol) with **155** (n = 5) (2.58 g, 10 mmol) in 150 mL of dry toluene with 12 mmol of n-butyllithium at -78°C gave 5.37 g of a crude product mixture which was chromatographed on activated alumina. Hexane first eluted 0.4 g of unreacted **25** and 1.72 g of unreacted **155** (n = 5). Further elution with 4:1 hexane:ethyl acetate, gave as the first fraction 0.86 g (16%) of 1:1 adduct **157** (n = 5), mp 106-107°C; ^{1}H NMR ($CDCl_3$) δ 1.03-1.66 (m, 6 H), 1.76 (s, 6 H), 2.16 (s, 6 H), 2.46 (s, 6 H), 3.43-3.83 (m, 4 H), 5.65 (s, 2 H), 6.53 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.47, 18.41, 20.60, 25.29, 30.91, 31.58, 43.49, 45.30, 77.39, 105.05, 126.21, 127.13, 132.30, 147.54, 150.39; mass spectrum, m/e (relative intensity) 520 (7), 342 (2), 178 (21), 164 (100), 108 (63). High resolution mass spectrum: Calcd. for $C_{25}H_{32}Br_2N_2$: ; Found: .

The second fraction gave 2.20 g (41%) of 2:1 adduct 158 (n = 5), mp 230-231°C; ^{1}H NMR ($CDCl_3$) δ 1.0-1.60 (m, 6 H), 1.76 (s, 12 H), 1.76-2.16 (m, 4 H), 2.43 (s, 12 H), 6.50 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 18.42, 20.62, 26.09, 31.71, 45.37, 77.40, 126.14, 132.28, 147.57, 150.48; mass spectrum, m/e (relative intensity) 782 (M^+, trace) 384 (8), 370 (5), 342 (30), 165 (12), 97 (28), 94 (100) 70 (46).

Anal. Calcd. for $C_{33}H_{38}Br_4N_2$: C, 50.66; H, 4.90; N, 3.58;
Found: C, 50.57, H, 4.99; N, 3.61.

67. Reaction of 25 with dipyrrole 155 (n = 5) and n-butyllithium (attempted synthesis of 156)

A solution of 25 (4.22 g, 10 mmol) and 155 (n = 5) (2.58 g, 10 mmol) in 250 mL of dry toluene was cooled to -78°C under argon (most of the 25 precipitated out). To this suspension n-butyllithium (22 mmol) in 100 mL of hexane was added dropwise over 4 h. The reaction mixture was allowed to gradually warm to room temperature. Methanol was added (1 mL) and the toluene solution was washed with water and dried ($MgSO_4$). Concentration of the solvent gave 3.7 g of a yellow solid. Careful column chromatography of this solid on activated alumina failed to give any basket-type compound 156. The product had a broad band on TLC, did not melt below 300°C and did not show any conclusive NMR or mass spectral data.

68. Reaction of 157 (n = 5) and butyllithium (attempted synthesis of 156)

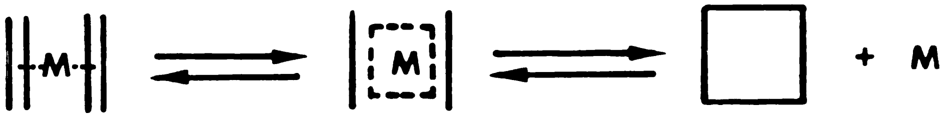
Solutions of 157 (n = 5) (0.8 g, 1.5 mmol) in 100 mL of dry toluene and of n-butyllithium (3 mmol) in 100 mL of hexane were added dropwise simultaneously at the same rate to 250 mL of dry toluene at -78°C under argon over a period of 4 h. The reaction mixture was allowed to gradually warm to room temperature. After work-up 0.6 g of a viscous oil remained. Column chromatography of this oil on activated alumina did not give any 156; rather, some butylated product along with polymeric material was obtained.

PART II

METALLACYCLOPENTANES AS CATALYSTS FOR THE LINEAR AND CYCLODIMERIZATION OF OLEFINS

INTRODUCTION

Conflicting explanations have been advanced to account for the observation that certain transition metals catalyze reactions which are thermally "forbidden" by the Woodward-Hoffman conservation of orbital symmetry rules,[109] e.g., as in the [2+2] cycloaddition of alkenes to form a cyclobutane moiety or the corresponding cycloreversion reactions. On the one hand it has been proposed that the new C-C bonds are formed simultaneously,[110] (eq. 1) and



(eq. 1)

that the function of the metal is to act merely as a template[111] which provides d orbitals of suitable symmetry

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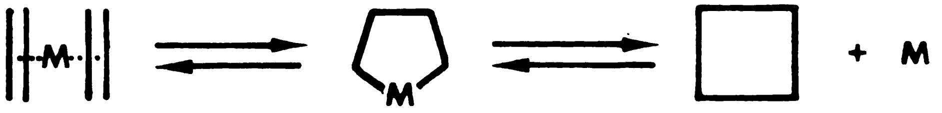
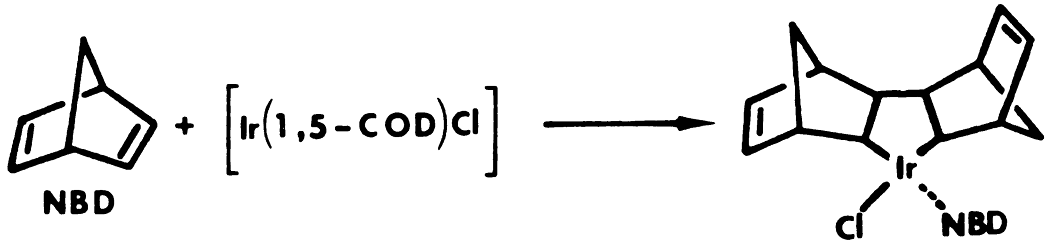
[*] This part of my research was done under the supervision of Professor R. Grubbs while he was at Michigan State University. My contribution to this subject, combined with that of others under Dr. Grubb's supervision, led to a communication to the Editor, J. Am. Chem. Soc., 100 7416 (1978) which failed to mention my name. In this part I will try to explicitly describe my contribution and also mention other authors' work in order to present the wide scope of this subject.

to mix with the orbitals of the organic species, thereby rendering the reaction symmetry "allowed."[112] An alternative interpretation[113] is a nonconcerted mechanism involving the stepwise formation of an M-carbon σ-bonded intermediate followed by reductive elimination of the hydrocarbon, as shown in eq. 2.



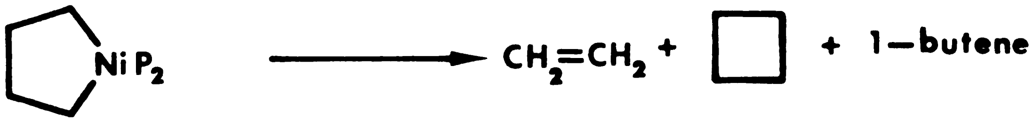
(eq. 2)

Such intermediates have been implicated in catalytic processes involving olefin metathesis,[113a] valence isomerization of cubane to syn-tricyclooctadienes,[113b] and cycloaddition reactions of norbornadienes.[114] Osborn et al.[115] reported the isolation of a stable metallacycle **159** from the dimerization of norbornadiene.



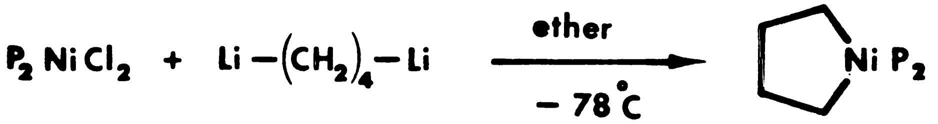
159

Since then a variety of metallocycles have been prepared.[116] Grubbs and coworkers[117] reported in 1977 the preparation and reactions of a series of phosphine nickelacyclopentanes (**162**) which undergo a competitive β-carbon cleavage, the reverse of the first step of the [2+2] cycloaddition reaction, reductive elimination, the required second step of the [2+2] cycloaddition reaction, and β-hydride transfer, the normal reaction of metal alkyl complexes.[118]



162a

The complexes were prepared by addition of 1,4-dillithiobutane (**161**)[119] to the appropriate dichlorobisphosphinenickel (II) complex (**160**) in ether at -78°C. The temperature was slowly raised to -20°C and the resulting yellow solid formed at this temperature was isolated by filtration.



160 **161** **162 (a, b, c)**

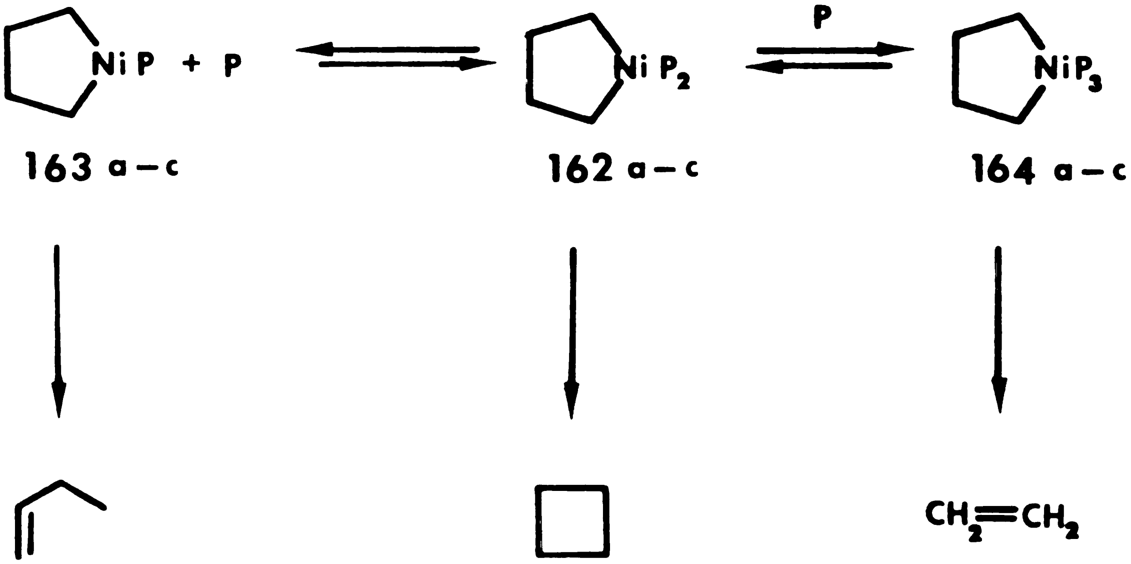
a, P_2: (Ph_3P)

b, P_2: [(cyclohexyl)$_3$P]$_2$

c, P_2: diphos.

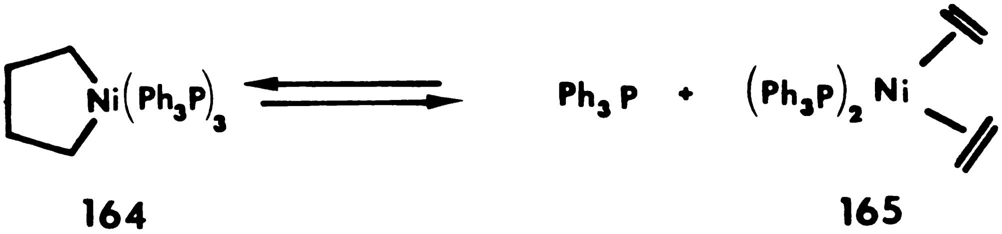
When a toluene solution of **162** was treated with an excess of Ph_3P at -10°C, the bright yellow solution gave golden crystals of **164a**. ^1H NMR and ^{31}P NMR spectra and the molecular weight information were consistent with the following equilibration for the phosphine complexes (Scheme 10).

Scheme 10

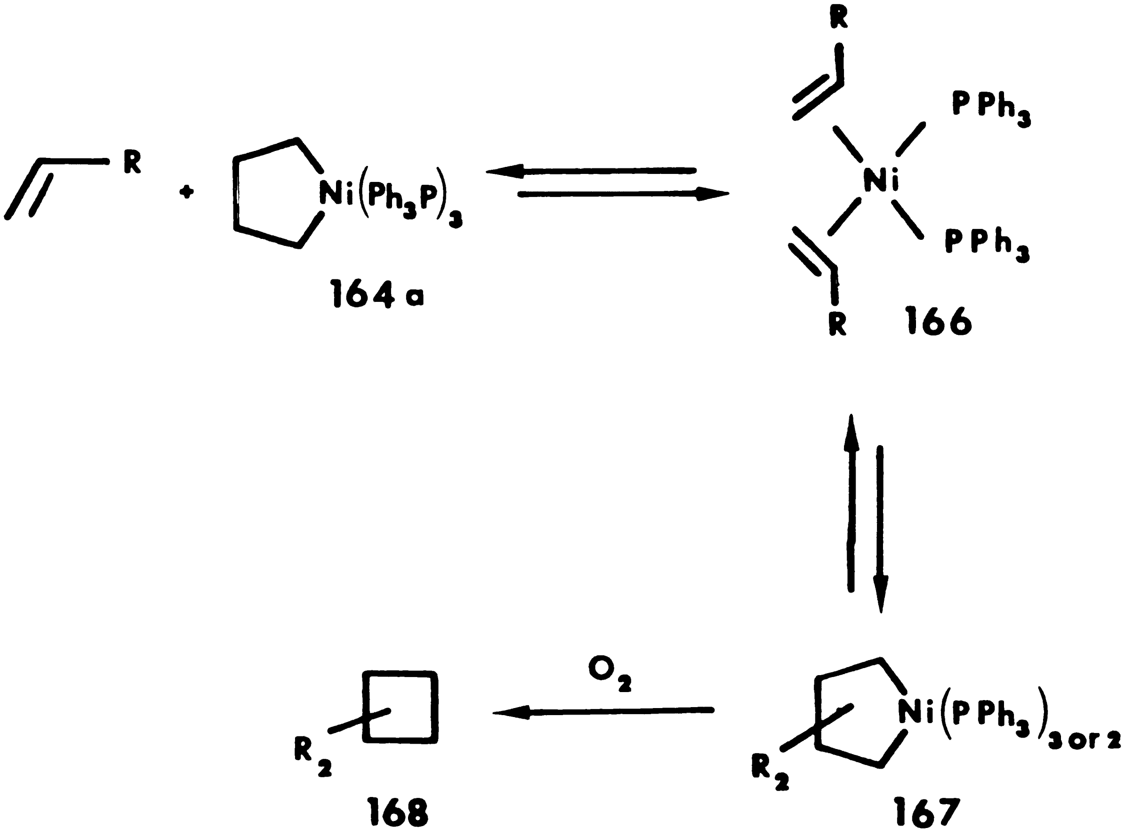


These phosphine-nickelacyclopentanes decomposed by reductive elimination, β-hydride elimination, or C-C bond cleavage depending on the coordination number of the complex (see Scheme 10).

Grubbs and coworkers[120] designed a deuterium labeling experiment in order to determine the relationship between metallacyclopentanes and bis-(olefin)-metal complexes. Their results suggest that there is an equilibrium between bis (olefin) complexes (165) and metallacyclopentanes and this may be a key reaction in a number of metal-catalyzed reactions of olefins.



Metallacyclopentanes were then tested as a catalyst. Our approach was to react different olefins with tris(triphenylphosphine)nickel complex 164a. The reaction



product is expected to be bis (olefin) complex 166 in equilibrium with disubstituted metallacyclopentane 167 which upon oxygen decomposition would produce disubstituted cyclobutanes (168).

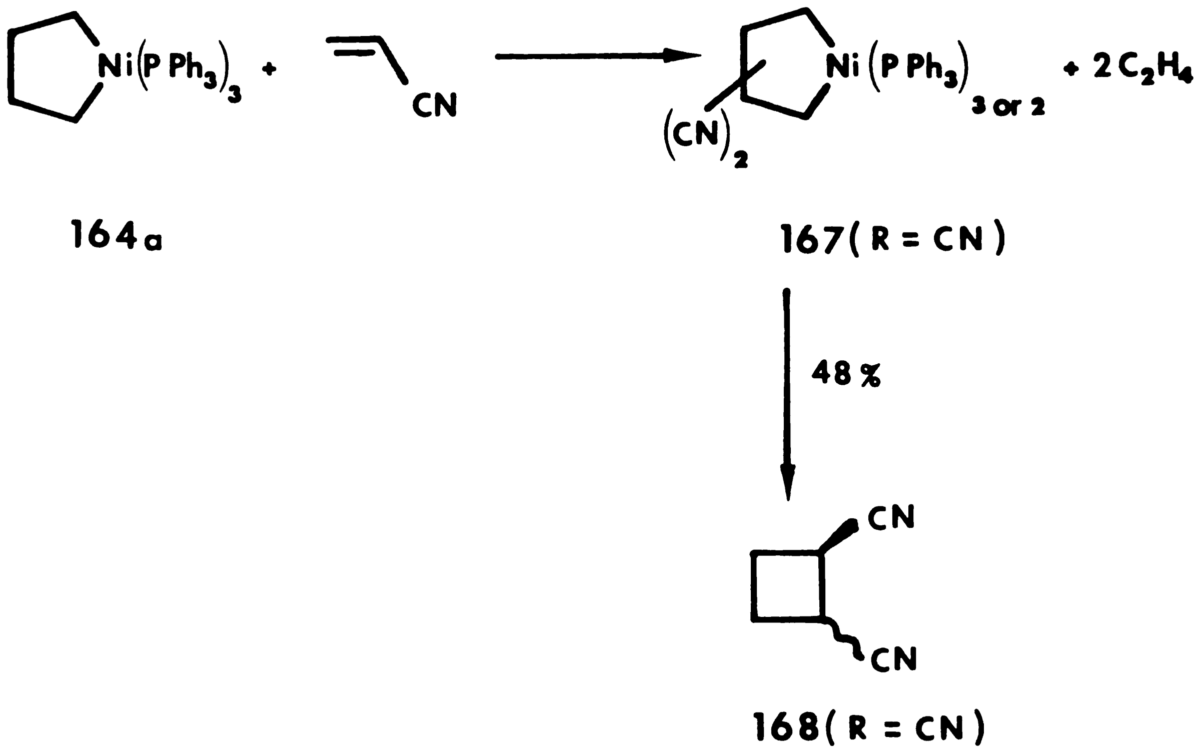
Disubstituted cyclobutanes are commercially important materials. We expected to synthesize a variety of these disubstituted cyclobutanes by using cyclodimerization of the corresponding olefins and metallocycles as catalysts.

RESULTS AND DISCUSSION

In an experiment designed to cyclodimerize acrylonitrile in the presence of tris(triphenylphosphine) tetramethylene Ni(II) **164a** as catalyst, a solution of **164a** in acrylonitrile at -20°C under argon was kept for 0.5 h; a bright yellow solid came out of solution. The reaction mixture was gradually warmed to room temperature. Introduction of pure oxygen to this solution at -78°C quickly destroyed the yellow complex. The resulting dark brown oil left after removal of the excess acrylonitrile was analyzed by GC. This crude reaction product contained a 48% yield of 1,2-dicyanocyclobutane (**168**) (calculated from amount of the **164a** initially used). The yellow precipitate in this reaction is presumably the dicyano substituted metallacycle **167** (R = CN), but it was not characterized.

Although this cyclodimerization was not catalytic, it showed that cyclodimerization is possible, and that more study is needed in order to find the right conditions to make the reaction catalytic.

In a similar reaction, bis(triphenylphosphine) tetramethylene Ni(II) (**162a**) was also used as a catalyst for cyclodimerization of acrylonitrile. Only an 8% yield of 1,2-dicyanocyclobutane was obtained. Thus **164a** is a more reactive catalyst than **162a**.

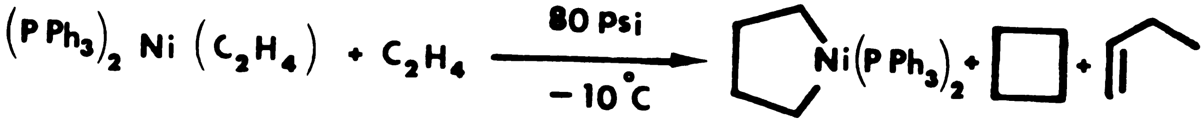


164a

167(R = CN)

168(R = CN)

Grubbs and coworkers[121] successfully used 164a in the catalytic dimerization of ethylene. In order for the reaction to be catalytic in nickel, the ethylene complex of nickel[122] must revert to metallacycles under ethylene pressure. Consequently, nickel-phosphine complexes of ethylene were examined. It was found that the reaction of bis(triphenylphosphine)ethylenenickel (0) 169 (-10°C, 72 h), with 80 psi of ethylene produced a 25% isolated yield of the metallacycle 162a. Cyclobutane (20%) and 1-butene were also produced in this reaction.

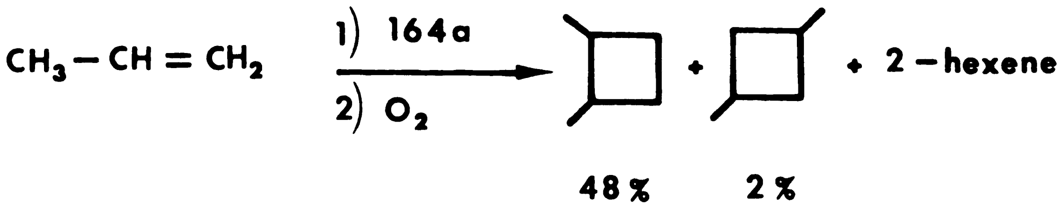


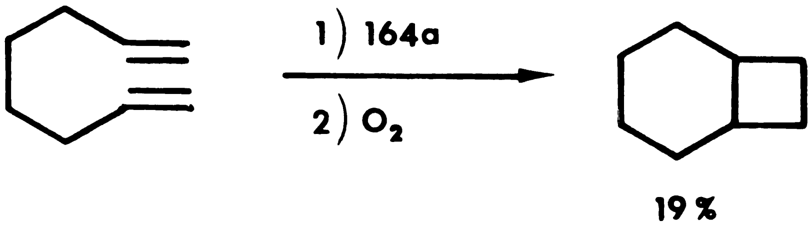
169

162a

As a result, when **164a** was dissolved in toluene and treated with ethylene (80 psi), cyclobutane and butenes were formed. The product ratio depended upon different factors (i.e. temperature, solvent and concentration of the catalyst). Solvents such as toluene resulted in the production of cyclobutane while chlorobenzene produced a very active catalyst for the linear dimerization of ethylene to 1-butene.

Propylene and 1,7-octadiene were also cyclodimerized using **164a** as a catalyst. This catalyst did not require an aluminum alkyl cocatalyst as do the more standard nickel oligomerization catalysts.[123]





Conclusion: This work, combined with that of others, demonstrates that metallacycles can play a major role in the dimerization of olefins to produce products normally not obtained by the usual metal hydride catalysts.

EXPERIMENTAL

1. Bis(triphenylphosphine)nickel (II) dichloride (160a)

This compound was prepared according to the literature method:[124] a solution of triphenylphosphine (52.6 g, 0.201 mol) in 500 mL of glacial acetic acid was heated on steam bath in a one-liter r.b. flask under argon until all the PPh_3 was dissolved. In another flask $NiCl_2$, $6H_2O$ (23.8 g, 0.1 mol) and 40 mL of water were stirred until most of $NiCl_2$ was dissolved, then 250 mL of glacial acetic acid was added and the mixture was heated on the steam bath. Both solutions were degassed by bubbling argon through while they were warm.

The $NiCl_2$ solution was added to PPh_3 solution while it was stirring on a steam bath. A blue-green microcrystalline precipitate immediately formed. The steam was turned off and the reaction mixture was stirred under argon at room temperature for 10 h. The blue crystals were filtered under vacuum and washed with acetic acid (2 × 10 mL) and then dried under vacuum for 20 h to give 48.6 g (74%) of 160a.

2. 1,4-dilithiobutane (161)

This compound was prepared according to the literature[125] as follows: in a 500-mL 3-necked flask equipped with an argon line and a 250-mL addition funnel, were put

5 g (excess) of cut-up lithium ribbon and 200 mL of dry ether. To this suspension at 0°C a solution of 1,4-dibromobutane (41 g, 0.19 mol) in 100 mL of dry ether was added dropwise over 3 h. After 0.5 h additional stirring, the solution was stored in the refrigerator overnight. A bluish-gray solid (LiBr) settled out, which was separated by filtration under argon. The concentration of 1,4-dilithiobutane in the ethereal solution was determined by reaction of 10 mL of this solution with trimethylsilyl chloride (2 mL) under argon. The concentration of the resulting 1,4-bis(trimethylsilyl)butane in solution was determined by GLC (5% DC-550 on chromosorb G; 6', ¼", 95°C) using durene as an internal standard. Thus a concentration of 0.185 molar with respect to 1,4-dilithiobutane **161** was obtained.

3. Bis(triphenylphosphine)tetramethylenenickel (II) (**162a**)

This compound was prepared according to Grubbs et al. as follows:[117] An ether solution of 1,4-dilithiobutane (**161**) (63 mL, 12.8 mmol) was added slowly to a suspension of bis(triphenylphosphine)dichloride (II) (**160**) (5 g, 7.5 mmol) in 100 mL of ether. The mixture was maintained at -50°C during the addition and then slowly warmed to 0°C. A bright yellow solid appeared at -10°C to 0°C and was collected by filtration (-10°C). The yellow solid was dissolved in oxygen-free toluene and filtered (at -15°C) to remove lithium chloride and starting material. After partial concentration (-15°C) of the toluene solution, hexane was added. Bright yellow crystals (1.73 g, 36% yield) of 162a were formed overnight at dry ice temperature. A portion of the complex was decomposed with sulfuric acid at -30°C. A 98% yield of n-butane, which is characteristic of this complex, was produced. The analysis was done by GLC on a Varian series 1400 instrument equipped with a flame ionization detector, using a Duropak (20 ft) paraffin wax-5% $AgNO_3$ on Al_2O_3 (13 ft) column.

4. Tris(triphenylphosphine)tetramethylene Ni(II) (164a)

This compound was prepared according to Grubbs et al.[117] as follows: an ethereal solution of 1,4-dilithiobutane (161), 6.88 mmol, was added slowly to a suspension of bis(triphenylphosphine)dichloride Ni(II) (160a) (3 g, 4.58 mmol), in 90 mL of dry ether at -60°C under purified argon. The mixture was kept at -60°C for 0.5 h, then slowly warmed. At -30°C a yellow solid appeared which disappeared to give a clear brown solution when the reaction mixture was warmed to 0°C. This solution was cooled to -10°C and 6 g of triphenylphosphine was added. The color of the solution quickly turned deep brown and a gold-brown solid precipitated.

This solution was stirred for 6 h at 5°C to 0°C and then the solid was filtered under argon. For purification the solid was taken up in 20 mL of oxygen-free toluene at -30°C, warmed to zero degrees and filtered (164a is soluble in toluene whereas lithium halides are not). The toluene solution was stored in a dry ice box overnight and the gold-brown solid was filtered to give 1.7 g (51%) of a pure sample of 164a. A small sample of 164a was decomposed with H_2SO_4 under argon at room temperature. A mixture of ethylene, 1-butene and 2-butene and cyclobutane, which is characteristic of this complex, was formed. The mixture of gases was analyzed by gas chromatography on a Varian series 1400 instrument equipped with flame ionization detectors, using a Duropak (20 ft) and a paraffin wax -5% $AgNO_3$ on Al_2O_3 (13 ft) column.

5. Cyclodimerization of acrylonitrile

A solution of 164a (0.928 g) in acrylonitrile (5 mL) at -20°C under argon was kept for 0.5 h; a bright yellow solid came out. The reaction mixture was gradually warmed to zero degrees (some of the complex decomposed), then it was left to warm to room temperature and kept for 6 h. The flask was then cooled to -78°C, evacuated and filled with O_2. After connection to a bubbler, the flask was warmed slowly to room temperature. The product was purified by GLC (DC 550, 120°C) to give a 48% yield of 1,2-dicyanocyclobutane **168** (R = CN) (durene was used as an internal standard). The product was compared with an authentic sample of cis- and trans-1,2-dicyanocyclobutane obtained from Aldrich Chemical Co. The proton NMR spectrum showed peaks at δ 3.45 (m, 2 H), and 2.40 (broadened d of d, 4 H). The GLC trace was similar to that of the commercial isomer mixture.

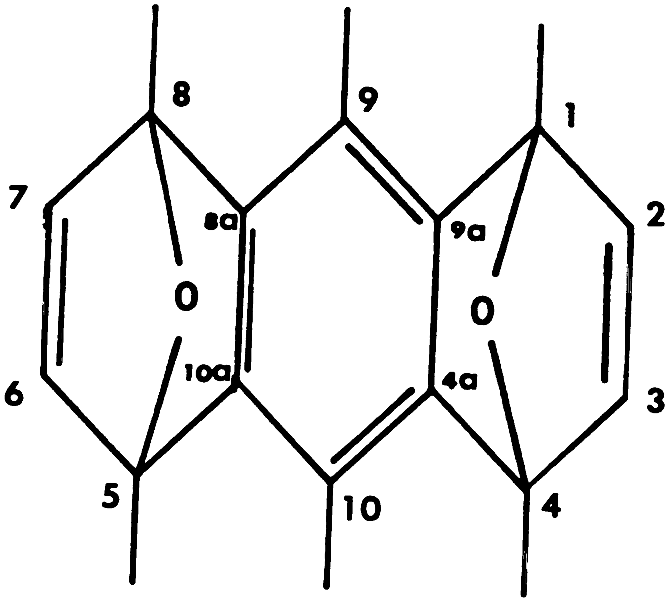
APPENDIXES

Appendix 1

Crystallographic Data for Compound 29b

Crystals of 29b, $C_{20}H_{22}O_2$, are monoclinic; space group $P2_1/n$; a = 9.697(5), b = 7.582(4), c = 11.185(6)Å, β = 111.17(4)°; Z = 2; M = 294.39; ρ_c = 1.275 g cm^{-3}. Lattice dimensions were determined using a Picker FACS-I diffractometer and $MoK\alpha_1$ (λ = 0.70926Å) radiation.

Intensity data were measured using MoKα radiation ($2\theta_{max}$ = 65°) yielding 2772 total unique data and, based on $I>2\sigma(I)$, 2297 observed data. The data were reduced;[126] the structures were solved by direct methods;[127] and the refinement was by full-matrix least-squares techniques.[128] The final R value was 0.048. The final difference Fourier map showed densities ranging from +0.37 to -0.30 with no indication of missing or incorrectly placed atoms. Bond lengths and bond angles are given in the following pages.



29b

Bond Distances (Å) for **29b**

atoms		distance
O(1)	-C(1)	1.451(1)
O(1)	-C(4)	1.453(1)
C(1)	-C(1M)	1.503(2)
C(1)	-C(2)	1.541(2)
C(1)	-C(9A)	1.548(1)
C(2)	-C(3)	1.317(2)
C(3)	-C(4)	1.539(2)
C(4)	-C(4A)	1.547(1)
C(4)	-C(4M)	1.503(2)
C(4A)	-C(9A)	1.399(1)
C(4A)	-C(10)	1.399(1)
C(9A)	-C(10)'	1.395(1)
C(10)	-C(10M)	1.507(2)
C(1M)	-H(1)	0.97(2)
C(1M)	-H(2)	1.01(2)
C(1M)	-H(3)	0.98(2)
C(4M)	-H(4)	0.99(2)
C(4M)	-H(5)	0.99(2)
C(4M)	-H(6)	0.97(2)
C(10M)	-H(7A)	1.01(3)
C(10M)	-H(8A)	1.02(3)
C(10M)	-H(9A)	0.99(3)
C(10M)	-H(7B)	1.01(5)
C(10M)	-H(8B)	1.01(3)
C(10M)	-H(9B)	1.05(5)
C(2)	-H(10)	1.02(2)
C(3)	-H(11)	1.00(1)

'designates an atom at -x,1-y,1-z

Bond Angles (°) for 29b.

atoms			angle
C(1)	-O(1)	-C(4)	97.2(1)
O(1)	-C(1)	-C(1M)	109.6(1)
O(1)	-C(1)	-C(2)	99.7(1)
O(1)	-C(1)	-C(9A)	98.9(1)
C(1M)	-C(1)	-C(2)	117.3(1)
C(1M)	-C(1)	-C(9)	122.0(1)
C(2)	-C(1)	-C(9)	105.6(1)
C(1)	-C(2)	-C(3)	105.7(1)
C(2)	-C(3)	-C(4)	106.7(1)
O(1)	-C(4)	-C(3)	99.4(1)
O(1)	-C(4)	-C(4A)	98.6(1)
O(1)	-C(4)	-C(4M)	110.7(1)
C(3)	-C(4)	-C(4A)	105.9(1)
C(3)	-C(4)	-C(4M)	116.2(1)
C(4A)	-C(4)	-C(4M)	122.4(1)
C(4)	-C(4A)	-C(9A)	104.5(1)
C(4)	-C(4A)	-C(10)	132.5(1)
C(9A)	-C(4A)	-C(10)	123.0(1)
C(1)	-C(9A)	-C(4A)	104.7(1)
C(1)	-C(9A)	-C(10)'	132.5(1)
C(4A)	-C(9A)	-C(10)'	122.7(1)
C(4A)	-C(10)	-C(9A)'	114.3(1)
C(4A)	-C(10)	-C(10M)	122.7(1)
C(9A)'	-C(10)	-C(10M)	123.0(1)
C(1)	-C(1M)	-H(1)	108.0(1)
C(1)	-C(1M)	-H(2)	112.0(1)
C(1)	-C(1M)	-H(3)	111.0(1)
H(1)	-C(1M)	-H(2)	105.0(2)
H(1)	-C(1M)	-H(3)	107.0(2)
H(2)	-C(1M)	-H(3)	113.0(2)
C(4)	-C(4M)	-H(4)	115.0(1)
C(4)	-C(4M)	-H(5)	109.0(1)
C(4)	-C(4M)	-H(6)	109.0(1)
H(4)	-C(4M)	-H(5)	106.0(2)
H(4)	-C(4M)	-H(6)	109.0(2)
H(5)	-C(4M)	-H(6)	108.0(2)
C(10)	-C(10M)	-H(7A)	107.0(1)
C(10)	-C(10M)	-H(8A)	110.0(1)

'indicates an atom at -x,1-y,1-z

Bond Angles (°) for **29b** Continued.

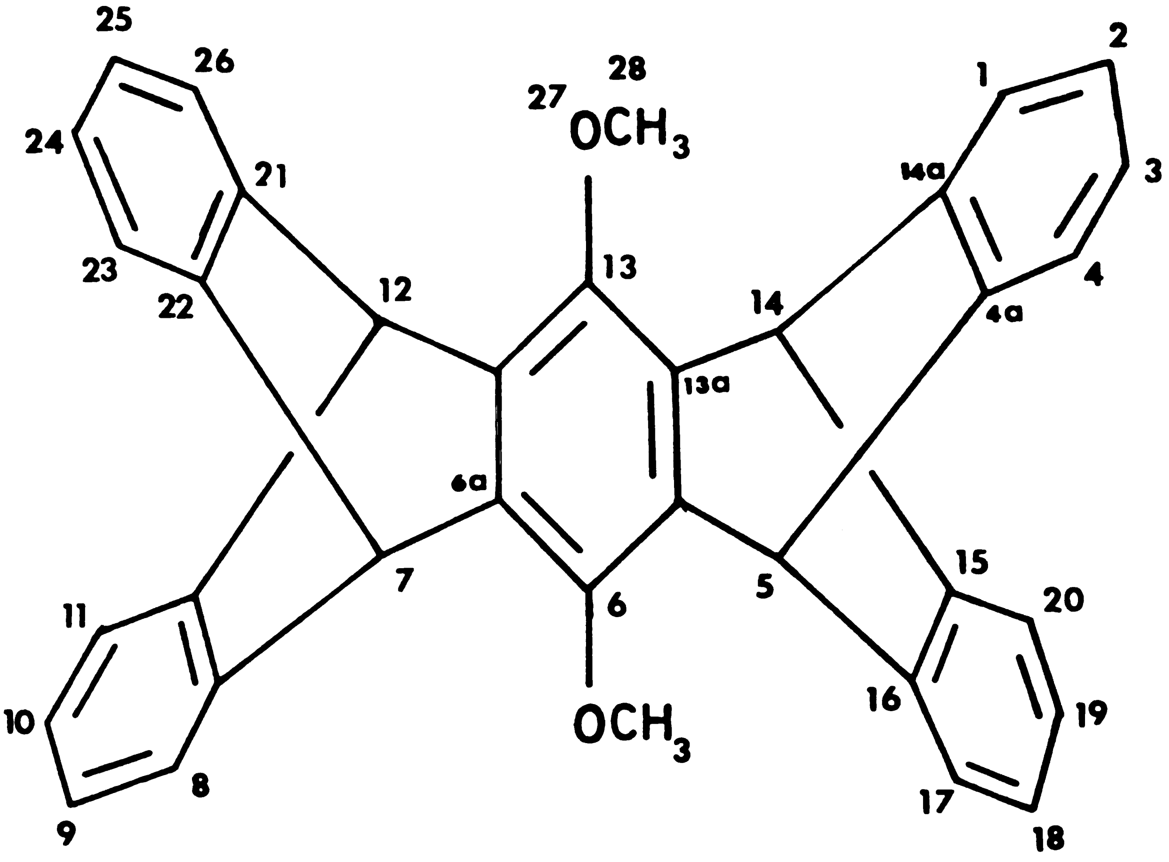
C(10)	-C(10M)	-H(9A)	109.0(2)
C(10)	-C(10M)	-H(7B)	118.0(3)
C(10)	-C(10M)	-H(8B)	115.0(2)
C(10)	-C(10M)	-H(9B)	112.0(2)
H(7A)	-C(10M)	-H(8A)	106.0(4)
H(7A)	-C(10M)	-H(9A)	125.0(4)
H(7A)	-C(10M)	-H(7B)	134.0(4)
H(7A)	-C(10M)	-H(8B)	73.0(3)
H(7A)	-C(10M)	-H(9B)	46.0(3)
H(8A)	-C(10M)	-H(9A)	99.0(3)
H(8A)	-C(10M)	-H(7B)	52.0(4)
H(8A)	-C(10M)	-H(8B)	133.0(3)
H(8A)	-C(10M)	-H(9B)	61.0(3)
H(9A)	-C(10M)	-H(7B)	47.0(4)
H(9A)	-C(10M)	-H(8B)	54.0(3)
H(9A)	-C(10M)	-H(9B)	138.0(4)
H(7B)	-C(10M)	-H(8B)	93.0(5)
H(7B)	-C(10M)	-H(9B)	105.0(6)
H(8B)	-C(10M)	-H(9B)	111.0(4)
C(1)	-C(2)	-H(10)	122.0(1)
C(3)	-C(2)	-H(10)	132.0(1)
C(2)	-C(3)	-H(11)	130.0(1)
C(4)	-C(3)	-H(11)	123.0(1)

Appendix 2

Crystallographic Data for Compound 86 (R = OCH_3)

Crystals of 86 (R = OCH_3), $C_{36}H_{26}O_2$, are monoclinic; space group $P2_1/c$; a = 8.228(3), b = 18.797(9), c = 16.919(8)Å, β = 99.29(3)°; Z = 4; M = 490.60; ρ_c = 1.262 g cm^{-3}. Lattice dimensions were determined using a Picker FACS-I diffractometer and $MoK\alpha_1$ (λ = 0.70926Å) radiation.

Intensity data were measured using MoKα radiation ($2\theta_{max}$ = 50°) yielding 4569 total unique data and, based on $I>2\sigma(I)$, 1965 observed data. The data were reduced;[126] the structures were solved by direct methods;[127] and the refinement was by full-matrix least-squares techniques.[128] The final R value was 0.055. The final difference Fourier map showed densities ranging from +.46 to -.52 with no indication of missing or incorrectly placed atoms.


1
2
3
4
4a
14a
5
6
6a
7
8
9
10
11
12
13
13a
14
15
16
17
18
19
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21
22
23
24
25
26
27
28
OCH3
OCH3

86 (R=OCH$_3$)

Bond Distances (Å) for **86** (R = OCH_3)

atoms		distance
C(A1)	-C(A2)	1.382(7)
C(A1)	-C(A14a)	1.376(6)
C(A2)	-C(A3)	1.367(7)
C(A3)	-C(A4)	1.396(7)
C(A4)	-C(A4a)	1.367(6)
C(A4a)	-C(A5)	1.521(6)
C(A4a)	-C(A14a)	1.396(6)
C(A5)	-C(A5a)	1.524(6)
C(A5)	-C(A16)	1.515(6)
C(A5a)	-C(A6)	1.378(6)
C(A5a)	-C(A13a)	1.402(5)
C(A6)	-C(A13a)'	1.375(6)
C(A6)	-O(A27)	1.394(4)
C(A13a)	-C(A14)	1.513(6)
C(A14)	-C(A14a)	1.527(6)
C(A14)	-C(A15)	1.518(6)
C(A15)	-C(A16)	1.396(6)
C(A15)	-C(A20)	1.377(6)
C(A16)	-C(A17)	1.382(6)
C(A17)	-C(A18)	1.392(7)
C(A18)	-C(A19)	1.369(7)
C(A19)	-C(A20)	1.381(6)
O(A27)	-C(A28)	1.431(6)
C(B1)	-C(B2)	1.393(8)
C(B1)	-C(B14a)	1.376(7)
C(B2)	-C(B3)	1.363(10)
C(B3)	-C(B4)	1.378(9)
C(B4)	-C(B4a)	1.383(7)
C(B4a)	-C(B5)	1.532(7)
C(B4a)	-C(B14a)	1.379(7)
C(B5)	-C(B5a)	1.521(6)
C(B5)	-C(B16)	1.534(6)
C(B5a)	-C(B6)	1.398(5)
C(B5a)	-C(B13a)	1.389(6)

'designates an atom at 2-x,-y,-z

Bond Distances (Å) for 86 (R = OCH_3) Continued.

atoms		distance
C(B6)	-C(B13a)"	1.393(6)
C(B6)	-O(B27)	1.377(5)
C(B13a)	-C(B14)	1.533(6)
C(B14)	-C(B14a)	1.519(6)
C(B14)	-C(B15)	1.534(6)
C(B15)	-C(B16)	1.390(6)
C(B15)	-C(B20)	1.384(6)
C(B16)	-C(B17)	1.369(7)
C(B17)	-C(B18)	1.381(8)
C(B18)	-C(B19)	1.366(8)
C(B19)	-C(B20)	1.393(7)
O(B27)	-C(B28)	1.432(7)

"designates an atom at 1-x,-y,1-z

Bond Angles (°) for **86** (R = OCH_3)

atoms			angle
C(A2)	-C(A1)	-C(A14a)	119.3(6)
C(A1)	-C(A2)	-C(A3)	120.8(5)
C(A2)	-C(A3)	-C(A4)	120.0(6)
C(A3)	-C(A4)	-C(A4a)	119.5(6)
C(A4)	-C(A4a)	-C(A5)	126.9(5)
C(A4)	-C(A4a)	-C(A14a)	120.2(5)
C(A5)	-C(A4a)	-C(A14a)	112.8(4)
C(A4a)	-C(A5)	-C(A5a)	105.4(4)
C(A4a)	-C(A5)	-C(A16)	106.4(4)
C(A5a)	-C(A5)	-C(A16)	105.5(4)
C(A5)	-C(A5a)	-C(A6)	126.9(4)
C(A5)	-C(A5a)	-C(A13a)	112.9(4)
C(A6)	-C(A5a)	-C(A13a)	120.2(5)
C(A5a)	-C(A6)	-C(A13a)'	119.4(5)
C(A5a)	-C(A6)	-O(A27)	120.7(4)
O(A27)	-C(A6)	-C(A13a)'	119.8(4)
C(A5a)	-C(A13a)	-C(A6)'	120.4(5)
C(A5a)	-C(A13a)	-C(A14)	112.8(4)
C(A14)	-C(A13a)	-C(A6)'	126.8(4)
C(A13a)	-C(A14)	-C(A14a)	104.9(4)
C(A13a)	-C(A14)	-C(A15)	106.6(4)
C(A14a)	-C(A14)	-C(A15)	105.9(4)
C(A1)	-C(A14a)	-C(A4a)	120.1(5)
C(A1)	-C(A14a)	-C(A14)	126.8(5)
C(A4a)	-C(A14a)	-C(A14)	113.0(4)
C(A14)	-C(A15)	-C(A16)	112.9(4)
C(A14)	-C(A15)	-C(A20)	127.2(5)
C(A16)	-C(A15)	-C(A20)	119.9(4)
C(A5)	-C(A16)	-C(A15)	113.2(4)
C(A5)	-C(A16)	-C(A17)	126.9(5)
C(A15)	-C(A16)	-C(A17)	119.9(5)
C(A16)	-C(A17)	-C(A18)	119.4(5)
C(A17)	-C(A18)	-C(A19)	120.4(5)
C(A18)	-C(A19)	-C(A20)	120.3(6)
C(A15)	-C(A20)	-C(A19)	120.0(5)
C(A6)	-O(A27)	-C(A28)	112.7(4)

'designates an atom at 2-x,-6,-z

Bond Angles (°) for **86** (R = OCH_3) Continued.

atoms			angle
C(B2)	-C(B1)	-C(B14a)	118.2(8)
C(B1)	-C(B2)	-C(B3)	120.4(6)
C(B2)	-C(B3)	-C(B4)	121.1(7)
C(B3)	-C(B4)	-C(B4a)	119.0(8)
C(B4)	-C(B4a)	-C(B5)	126.9(6)
C(B4)	-C(B4a)	-C(B14a)	119.4(7)
C(B5)	-C(B4a)	-C(B14a)	113.5(5)
C(B4a)	-C(B5)	-C(B5a)	106.0(4)
C(B4a)	-C(B5)	-C(B16)	105.2(4)
C(B5a)	-C(B5)	-C(B16)	105.3(4)
C(B5)	-C(B5a)	-C(B6)	126.8(5)
C(B5)	-C(B5a)	-C(B13a)	113.4(4)
C(B6)	-C(B5a)	-C(B13a)	119.8(5)
C(B5a)	-C(B6)	-C(B13a)"	119.2(5)
C(B5a)	-C(B6)	-O(B27)	120.6(4)
O(B27)	-C(B6)	-C(B13a)"	120.2(4)
C(B5a)	-C(B13a)	-C(B6)"	121.0(5)
C(B5a)	-C(B13a)	-C(B14)	112.8(4)
C(B14)	-C(B13a)	-C(B6)"	126.2(5)
C(B13a)	-C(B14)	-C(B14a)	105.4(4)
C(B13a)	-C(B14)	-C(B15)	105.9(4)
C(B14a)	-C(B14)	-C(B15)	105.6(4)
C(B1)	-C(B14a)	-C(B4a)	121.5(6)
C(B1)	-C(B14a)	-C(B14)	125.4(6)
C(B4a)	-C(B14a)	-C(B14)	113.2(5)
C(B14)	-C(B15)	-C(B16)	113.1(4)
C(B14)	-C(B15)	-C(B20)	125.6(5)
C(B16)	-C(B15)	-C(B20)	121.3(5)
C(B5)	-C(B16)	-C(B15)	112.9(50
C(B5)	-C(B16)	-C(B17)	126.5(5)
C(B15)	-C(B16)	-C(B17)	120.7(5)
C(B16)	-C(B17)	-C(B18)	118.3(6)
C(B17)	-C(B18)	-C(B19)	121.4(6)
C(B18)	-C(B19)	-C(B20)	121.2(6)
C(B15)	-C(B20)	-C(B19)	117.2(6)
C(B6)	-O(B27)	-C(B28)	112.0(5)

"designates an atom at 1-x,-y,1-z

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