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Part I. Applications of Bis-Aryne Equivalents to Organic Synthesis

Part II. Attempted Synthesis of Thiophene or Furan Fused Radialene Analogues

presented by

Chung-Yin Lai

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of the requirements for

Ph. D. degree in Chemistry

Harold Hart

Major professor

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PART I

APPLICATIONS OF BIS-ARYNE EQUIVALENTS TO ORGANIC SYNTHESIS

PART II

ATTEMPTED SYNTHESIS OF THIOPHENE OR FURAN FUSED RADIALENE ANALOGUES

By

Chung Yin Lai

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ABSTRACT

PART I

APPLICATIONS OF BIS-ARYNE EQUIVALENTS TO ORGANIC SYNTHESIS

PART II

ATTEMPTED SYNTHESIS OF THIOPHENE OR FURAN FUSED RADIALENE ANALOGUES

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In Part I of this thesis, an efficient synthesis for per-substituted acenes was developed via bis-aryne equivalents (derived from the reaction of n-butyllithium with a tetrahaloarene such as tetrabromo-p-xylene, 21). These underwent addition to various pyrroles, and subsequent N-bridge extrusion gave the desired acenes.

A series of N and/or C substituted pyrroles were selected as dienes for the bis-annelation reaction. Bis-adduct formation was affected primarily by the electron density of the diene system but not by the bulkiness of the substituents on C-2 or C-5 of the pyrrole. Thus, adducts

having bulky substituents, as for example bis(N-methyl)-2,3,6,7,9,10-hexamethyl-1,4,5,8-tetraphenyl-1,4,5,8-tetrahydroanthracen-1,4; 5,8-bis-imine, were prepared without difficulty. Similarly, no change was found in the yield of bis-adducts with respect to the size of the substituents on the nitrogen of the pyrroles. Both N-iso-propyl-tetramethylpyrrole and N-phenyl-tetramethylpyrrole reacted with bis-aryne equivalents to give a good yield of bis-adducts.

Besides symmetric bis-adducts unsymmetric bis-adducts could also be prepared, by a stepwise process. When 21 was treated with one equivalent of n-BuLi and N-methyloctahydrocarbazole a mono-adduct was isolated which was subsequently reacted with another mole of n-BuLi and pentamethylpyrrole. An unsymmetric bis-adduct was thus prepared.

With the use of an N-(dimethylamino)-pyrrole as the diene, the bis-adduct obtained became an excellent precursor for per-substituted acenes. For instance in the presence of N-(dimethylamino)tetramethylpyrrole (83) the reaction of n-BuLi with p-dimethoxytetrabromobenzene or 2,3,6,7-tetrabromo-1,4,5,8-tetramethylnaphthalene provided bis-adducts which subsequently could be converted quantitatively by pyrolysis to 9,10-dimethoxyoctamethylanthracene or dodecamethylnaphthacene respectively. Octamethylnaphthalene and decamethylanthracene were similarly prepared. Due to various limitations which plagued known methods for aromatizing 7-aza-bicyclo[2.2.1]heptadienes, this two step

process for peracene synthesis represents the most successful preparation developed to date.

Cycloaddition of N-(dimethylamino)-octahydrocarbazole 110 with a bis-aryne equivalent provided a short synthesis of 2,3-difunctionalized triphenylenes. Reaction of 110 and 21 with one equivalent of n-BuLi gave a mono-adduct which was converted to 1,4-dimethyl-2,3-dibromotriphenylene by pyrolysis and dehydrogenation.

The preparation of an unsymmetric peracene via this sequence was also studied. Thus bis(tetrahydrobenzo-[1,2;3,4])-5,6,7,8,9,10-hexamethylanthracene was prepared in a stepwise manner from pyrrole 83 and octahydrocarbazole 110.

In Part II of this thesis, the synthesis of cyclobuta[1,2-c;3,4-c'] dithiophene 185 and its oxygen analog 184 was attempted. The first approach explored was the coupling of thiophene moieties by the Ullmann reaction. However, neither the direct coupling of 3,4-dibromothiophene nor the closure of 3,3'-dibromo-4,4'-bithienyl appeared suitable for this purpose. Therefore another approach, which started from an intermediate which already contained the four-membered ring, was planned. Thus cyclobuta[1,2-c;3,4-c']-octahydrodithiophene 219 and cyclobuta[1,2-c;3,4-c']-octahydrodifuran 217 or similar intermediates but with the sulfur oxidized to a sulfone group (e.g., tricyclo[5.3.0.$0^{2,6}$]-3,9-dithiadecane-3,3-dioxide 220 and tricyclo[5.3.0.$0^{2,6}$]-3-thia-9-oxodecane 223 became the intermediate synthetic targets.

Preparation of all the above mentioned intermediates has been accomplished. Preliminary results revealed that sulfone 220 and sulfide 219 could not be readily dehydrogenated, nor could they be chlorinated by N-chlorosuccinimide. Although the ultimate synthetic targets have not yet been achieved, it is hoped that other manipulations of the intermediates 217, 219, 220, or 223 may provide a route to difuran 184 and dithiophene 185.

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Professor Harold Hart for his enthusiastic assistance, encouragement and guidance throughout the course of this study.

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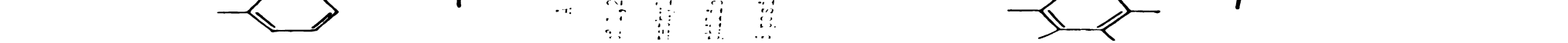
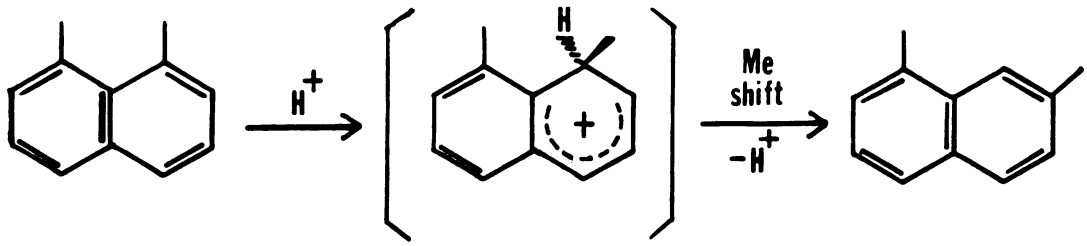
PART I

APPLICATIONS OF BIS-ARYNE EQUIVALENTS TO ORGANIC SYNTHESIS

INTRODUCTION

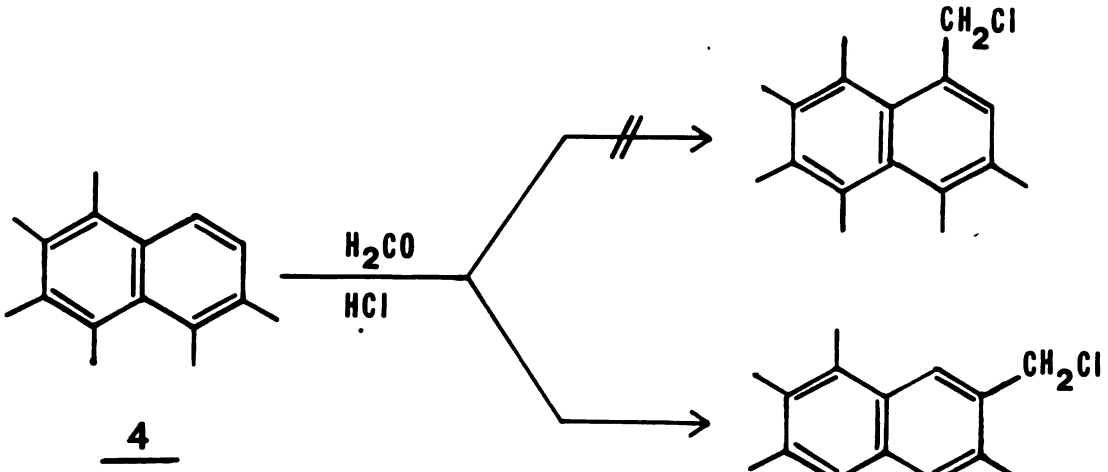
The preparation of polymethylarenes presents a synthetic challenge because the compounds may be highly strained. Except for hexamethylbenzene, which is planar,[1] the molecular geometry may be severely distorted from planarity to minimize the repulsion between peri substituents (in the naphthalene molecule, the 1- and 8- position are said to be "peri" to each other). Substituents located at peri positions are in much closer proximity than similar substituents located "ortho" to each other on a benzene ring. This close proximity is responsible for the appearance of several unique properties[2,3] and contributes to the instability of peri-substituted polyarenes. For instance, the isomerization of dimethylnaphthalene has been studied by Suld and Stuart.[2] Rearrangement is slow for all the isomers except 1,8-dimethylnaphthalene 1. With hydrogen fluoride as the catalyst, 1,8-dimethylnaphthalene 1 isomerized (98%) to the 1,7-isomer 3 in ten minutes at room temperature. This unusual ease of rearrangement was presumably due to relief of the "peri" interaction in the transition state leading to 2.





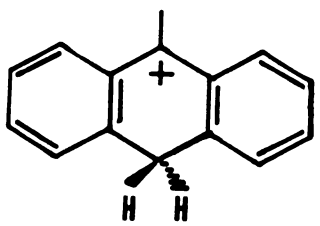
1 2 3

A similar argument[3] was also used to explain the failure of 1,2,3,4,5,6-hexamethylnaphthalene 4 to undergo chloromethylation at position 8. Contrary to the usual α-electrophilic substitution, chloromethylation took place at the β position to give 5.



4 5

In sharp contrast to the well known fact that 9-methylanthracene is protonated at C-10 to give the tertiary carbocation 6,[4] the peri-substituted 1,4,5,8,8-pentamethylanthracene 7 was found to be protonated in trifluoroacetic acid exclusively at C-9 to give the secondary carbocation 9.[5] Undoubtedly the carbocation 9, although secondary, is more stable than the tertiary ion 8 due to relief of the double peri-interaction as the carbon bearing the central methyl substituent becomes sp^3 hybridized.



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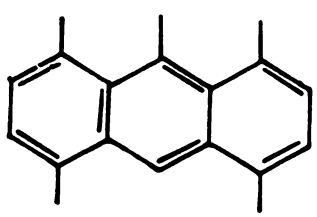

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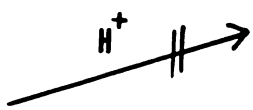

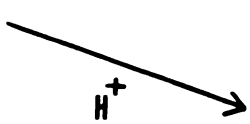

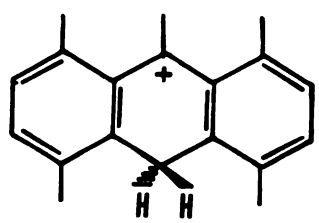

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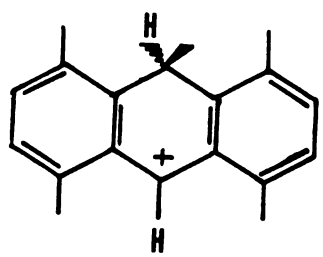
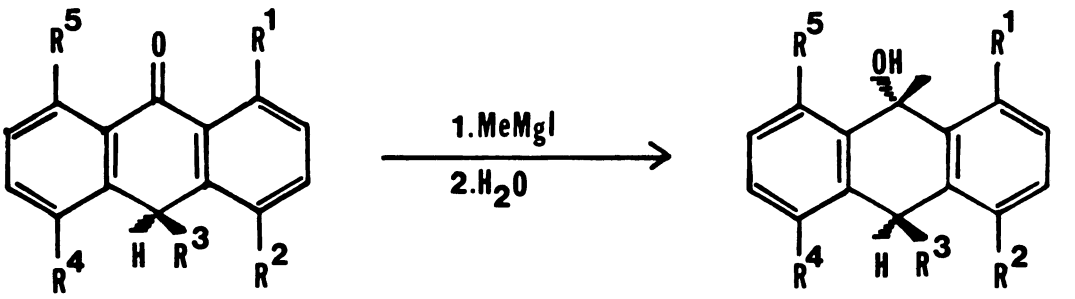


9

Because of the described unusual properties of highly substituted polyarenes, they are sometimes difficult to prepare. The compounds are sensitive to acidic and/or basic media. For instance, Cameron and Bowden[6,7] synthesized a series of methylated anthracenes starting from the substituted 9-anthrones **10** - **13**, by either 1,2-addition of methylmagnesium iodide or reduction with lithium aluminum hydride. The resulting alcohols were then dehydrated using p-toluenesulfonic acid or phosphoryl chloride in pyridine. The nature of the products differed with the degree of crowding. Those systems having no more than one peri methyl-methyl interaction, *e.g.*, the 1,4,9-trimethyl and 1,4,5,9-tetramethyl series (**10**,**11**) were obtained exclusively as anthracene tautomers. Those products which incorporated at least two peri interactions were obtained as the methylene-dihydroanthracene tautomers (**14**,**15**) in which the peri crowding was relieved by having a tetrahedral carbon at the 9- or 10- position.

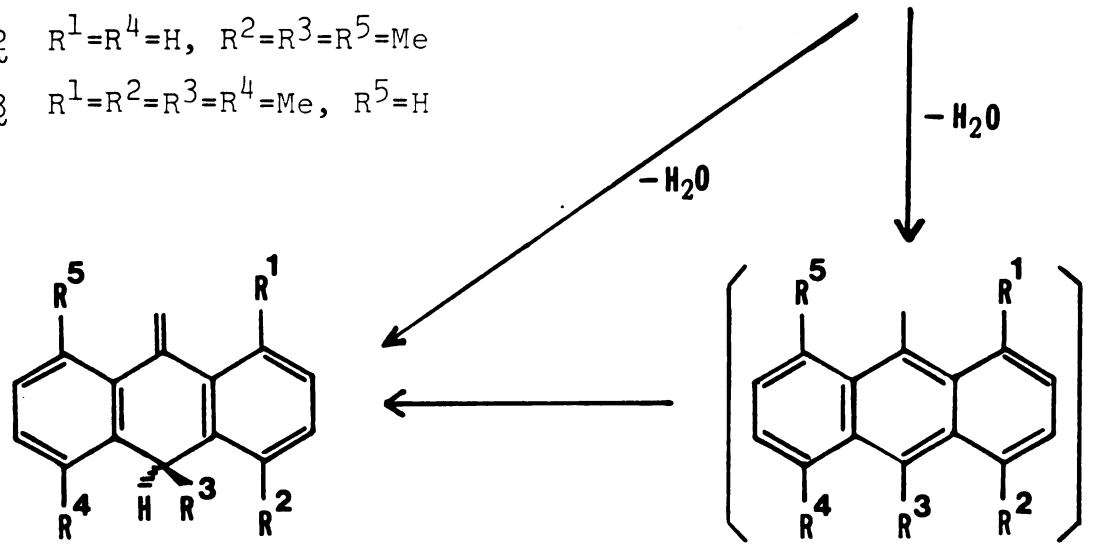


10 $R^1=R^2=Me$, $R^3=R^4=R^5=H$

11 $R^1=R^2=R^4=Me$, $R^3=R^5=H$

12 $R^1=R^4=H$, $R^2=R^3=R^5=Me$

13 $R^1=R^2=R^3=R^4=Me$, $R^5=H$

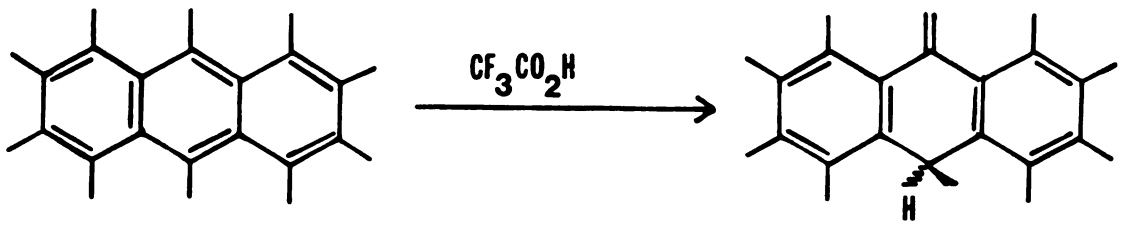


14 $R^1=R^4=H$, $R^2=R^3=R^5=Me$

15 $R^1=R^2=R^3=R^4=Me$, $R^5=H$

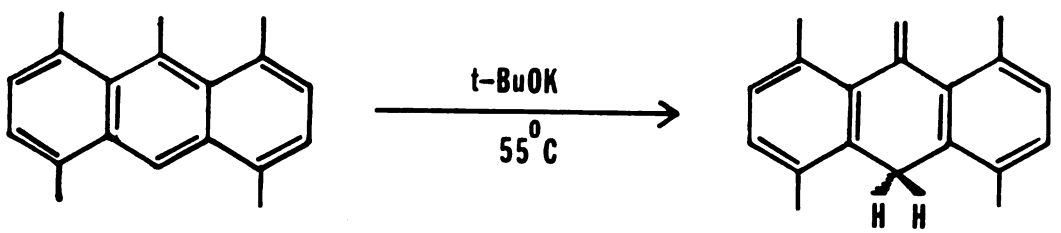
The isomerization of peri-substituted anthracenes to derivatives which are not aromatic in the central ring was also encountered when decamethylanthracene 16 was

treated with acid.[8]



16 89

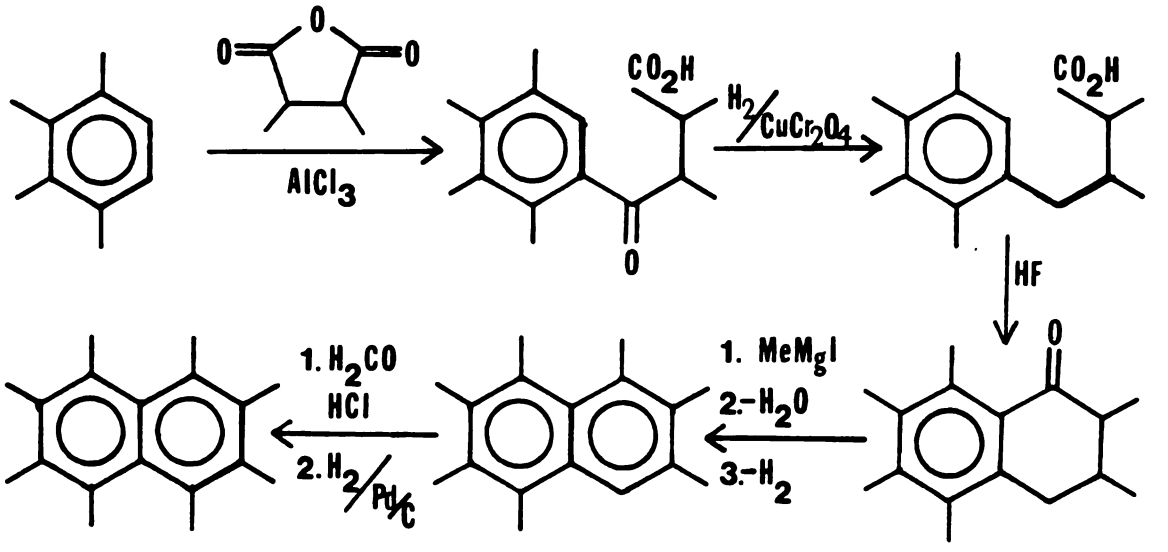
This type of tautomerization can also be accomplished by bases.[9] For examples, treatment of pentamethylanthracene 7 with t-BuOK in dimethyl sulfoxide (55°C, 2 h) gave a mixture of isomerization product 17 and the starting anthracene 7.



7 17

Therefore, the release of peri-crowding becomes an inevitable possible side reaction in synthetic approaches in which a catalytic dehydration either by bases or acid is involved.

The Haworth synthesis has been used for preparing naphthalene derivatives. Such syntheses usually involve two steps, cyclization to form a second ring from the parent



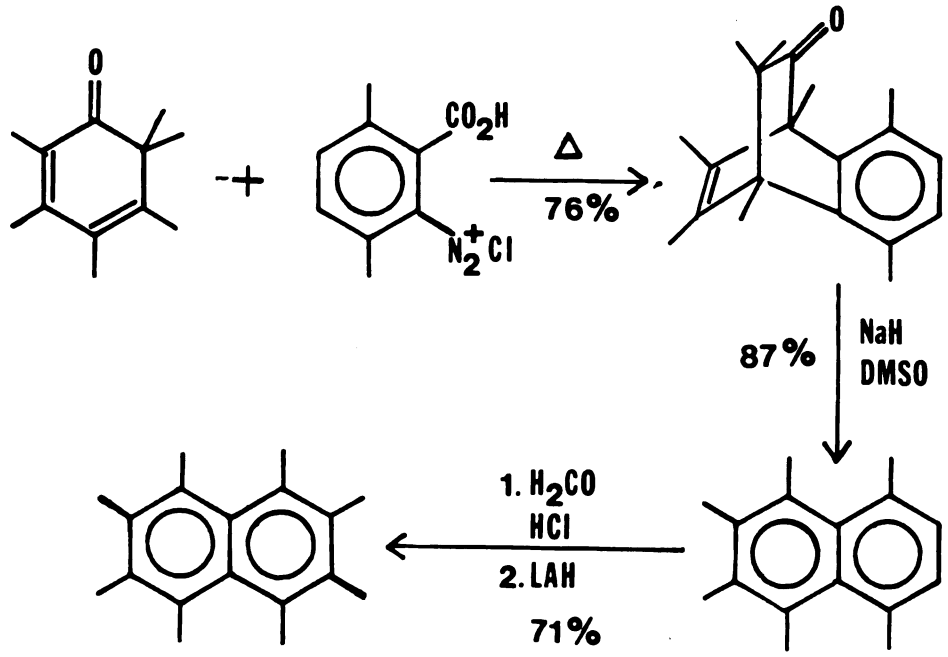
18

Scheme 1

benzenoid hydrocarbon and then dehydrogenation of the newly formed ring to an aromatic system. This sequence was adopted by Abadir, Cook and Gibson for the original preparation of octamethylnaphthalene 18.[3] For this purpose, dimethylsuccinic anhydride was chosen as the "building material". The synthesis consisted of ten steps with an overall yield of less than 1% (Scheme 1).

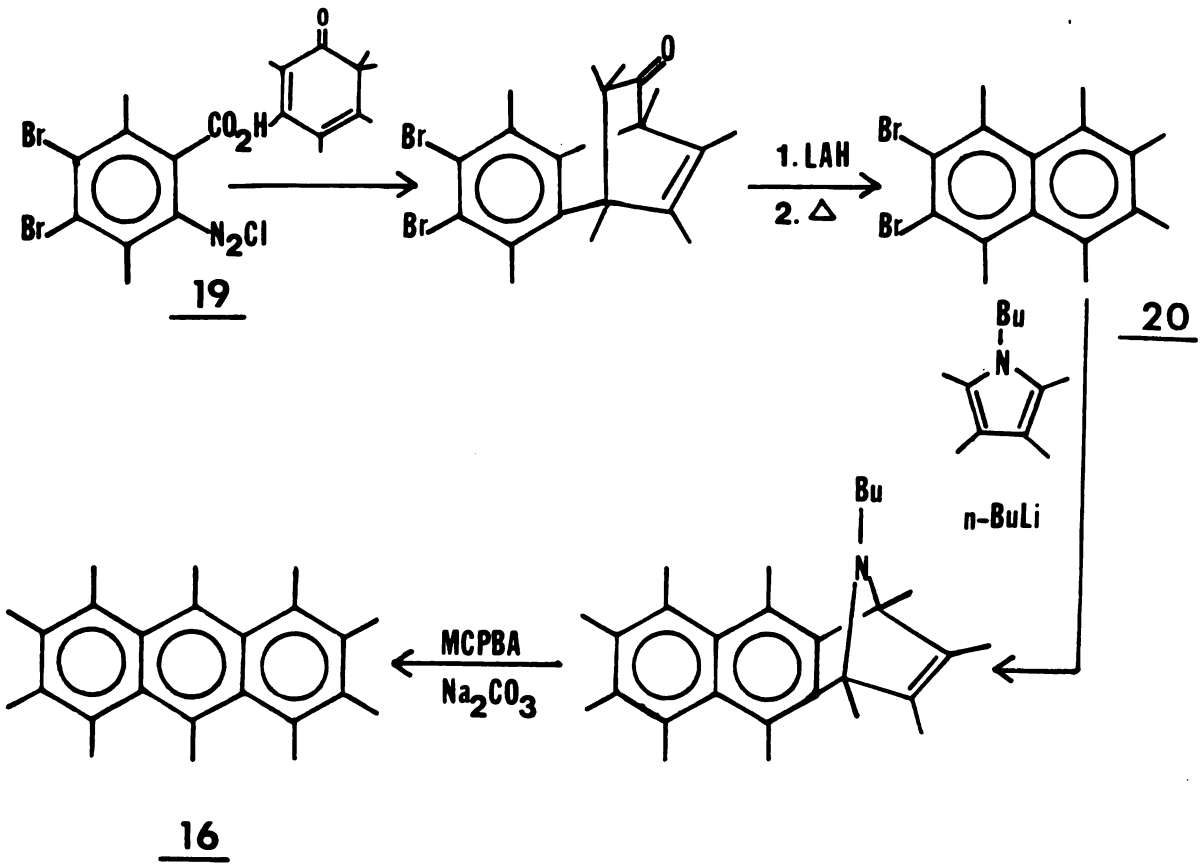
Compared to the original multistep synthesis, a

simpler synthesis was introduced by Hart and Oku[10] via a benzyne intermediate, as shown in Scheme 2.



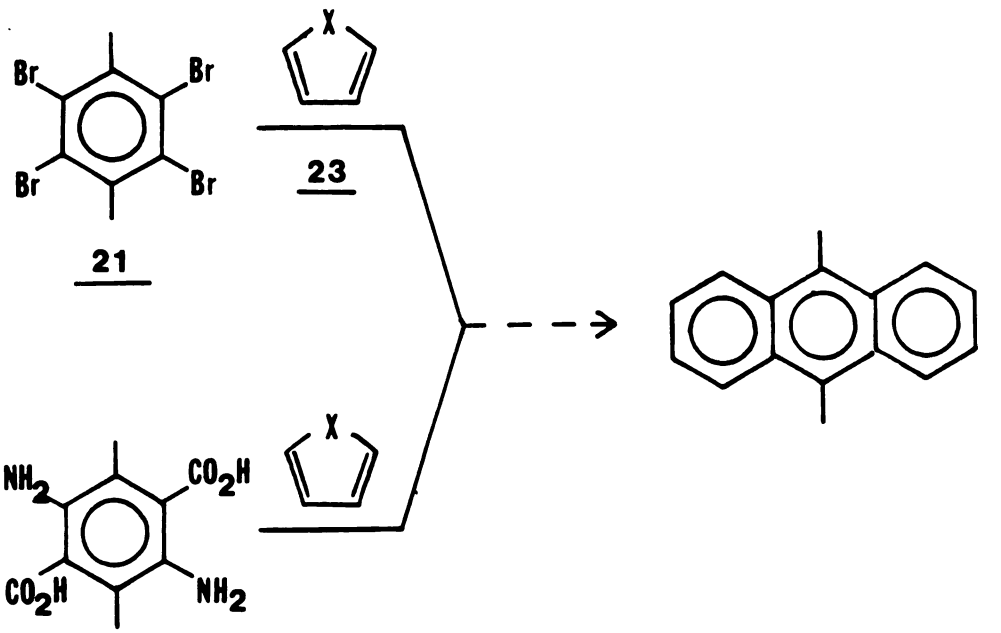
Scheme 2

This approach was successfully applied to the preparation of decamethylanthracene 16 through the use of two different benzyne precursors, 19 and 20. Compound 19 furnished the "central" ring of the product, and the two "outside" benzene rings were built up in the subsequent steps, eventually leading to decamethylanthracene 16 in fair yield (Scheme 3).[7]

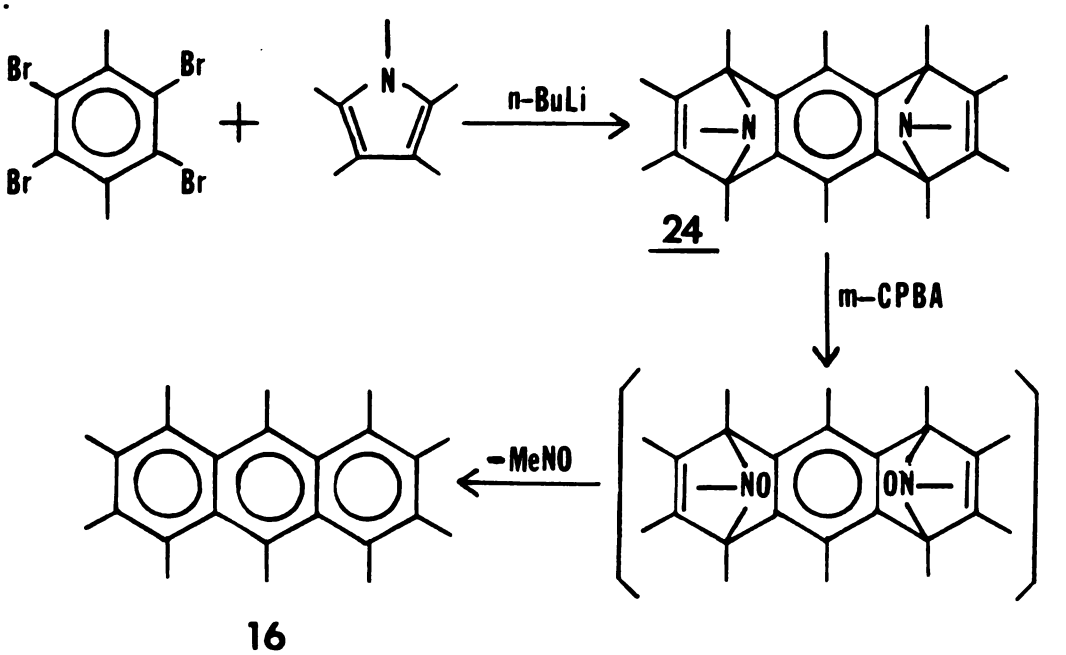


Scheme 3

In light of the above approach, it was reasoned that a benzene ring bearing two sets of functionalities which could be aryne precursors, such as 21 or 22, would serve as a more attractive starting point for synthesizing highly substituted polyarenes. Because the diene synthon 23 could provide two benzene equivalents simultaneously, after the Diels-Alder cycloaddition, the syntheses would obviously be shortened.

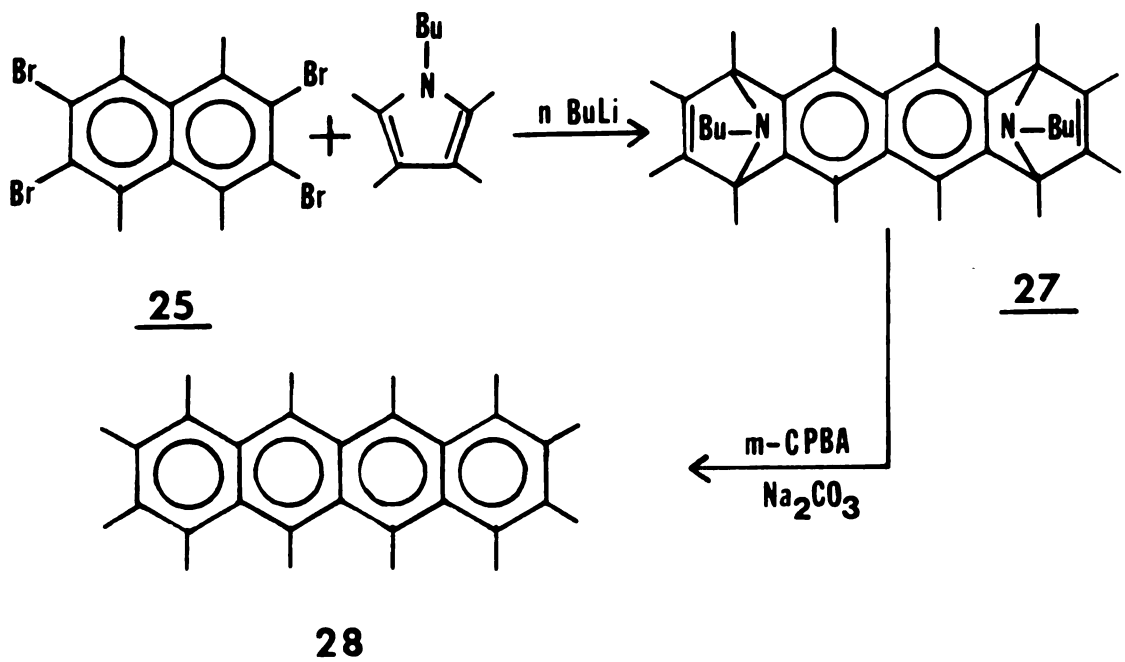


Some preliminary results using this strategy have been found in this laboratory.[11] For example, tetrabromo-p-xylene reacted with n-butyllithium in the presence of pentamethylpyrrole to give a mixture of syn and anti bis-adducts 24.



Elimination of the nitrogen bridge could be accomplished by oxidizing 24 with m-chloroperbenzoic acid (m-CPBA), followed by thermal elimination of nitrosomethane.[12] Decamethylanthracene 16 was thus prepared with an overall yield of 25%.

However, further application of this sequence to the preparation of dodecamethylnaphthacene 28 could be accomplished with only modest success. Treatment of a mixture of tetrabromonaphthalene 25 and N-butyltetramethylpyrrole with n-butyllithium gave two stereoisomeric bisadducts 27. The bridges then were removed in the same fashion as in the preceding example with m-chloroperbenzoic acid (m-CPBA), but in very poor yield (overall 8%).[13]



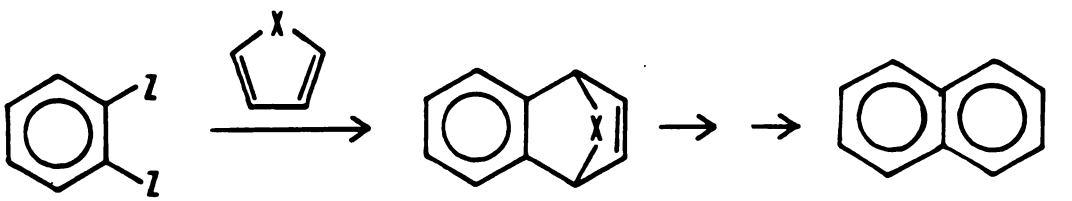
25 27 28

One possible reason for this unsatisfactory result may be the instability of the product toward acid. Although attempts were made to increase the yield by changing the reaction conditions, such as the amount of buffer reagents or solvent, and the reaction temperature, no improvement was observed. Therefore, it seemed worthwhile to search for a different bridge in the bis-adduct, one which could be eliminated without using acidic or basic reaction conditions.

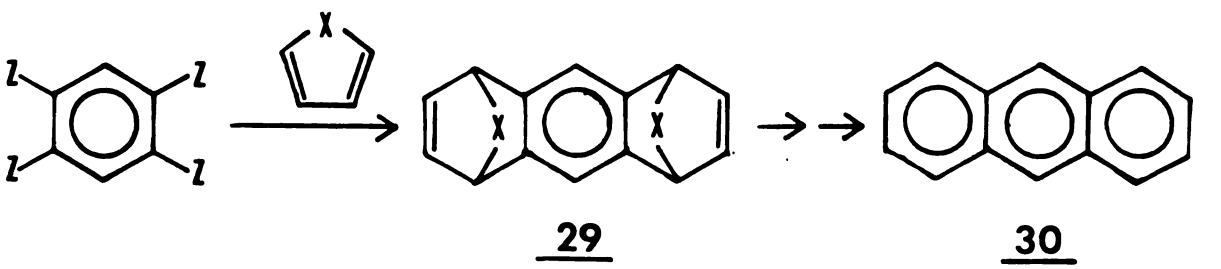
We have successfully used N-(dimethylamino)pyrroles as the diene component in bis-aryne equivalent cycloadditions, and found that the bridge can then be removed quantitatively in most of the cases by pyrolysis. It is the purpose of this part of the thesis to describe these studies and the applications of this approach to the preparation of highly substituted polyarenes.

RESULTS AND DISCUSSION

Many of the preceding methods for preparing highly methylated polyarenes begin by fusing a new benzene ring onto the starting hydrocarbon (as in Scheme 4).[7,10] Ideally, if the starting hydrocarbon were to possess two sets of functionalities capable of being manipulated to react with two building synthons, the resulting bis-adduct 29 might then be converted to a polyarene such as 30 by conventional methods (Scheme 5)



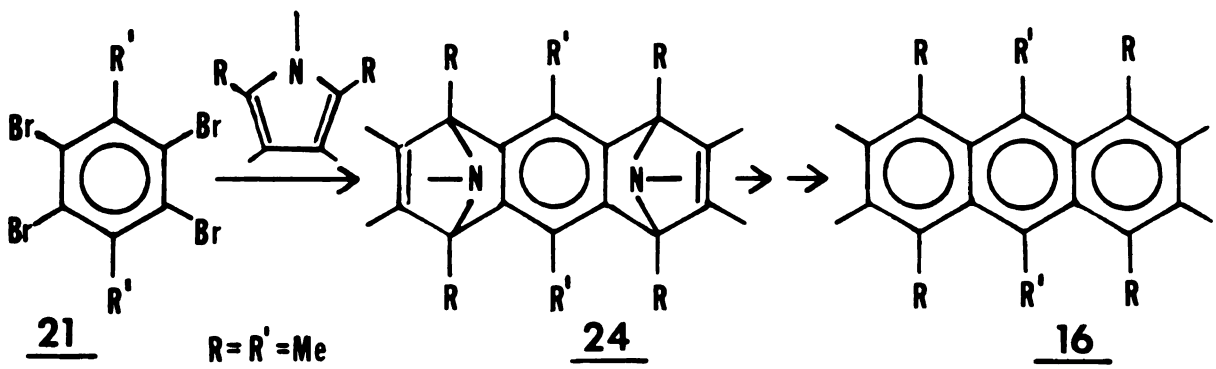
Scheme 4



29 30

Scheme 5

This synthetic plan was realized as follows. Tetrabromo-p-xylene 21, prepared in 90% yield by the bromination of p-xylene in carbon tetrachloride, reacted with two equivalents of n-butyllithium in the presence of a substituted pyrrole at -78°C in THF to give a mixture of syn and anti bis-annelated adducts 24 in good yield.



Scheme 6

This bis-annelation reaction via a bis-aryne equivalent could provide a successful strategy for the synthesis of highly methylated polyarenes if a subsequent bridge-removing process for converting 24 to 16 were available. This is an attractive strategy for the following reasons (see Scheme 6). The synthesis is designed to proceed with bis-adduct formation and aromatization as two separate stages. In the formation of bis-adduct, the arrangement of the substituents (R, R') is such that the steric interaction between them is minimized (Figure 1).

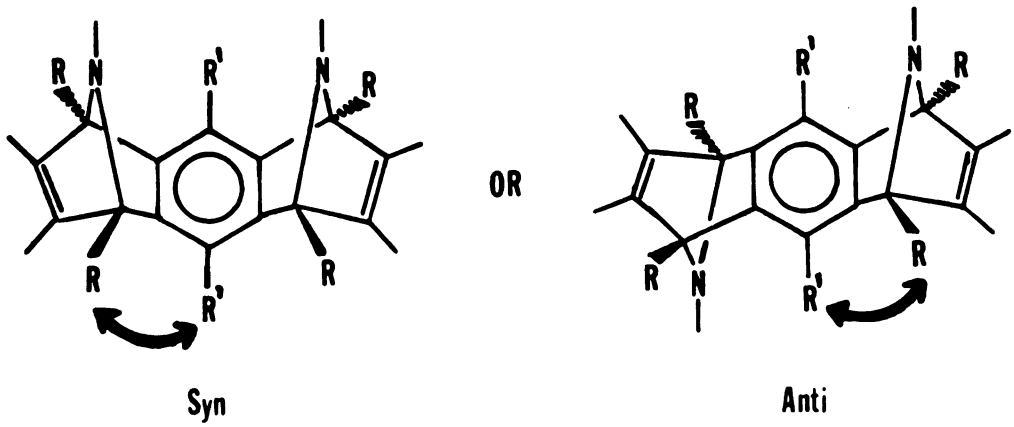
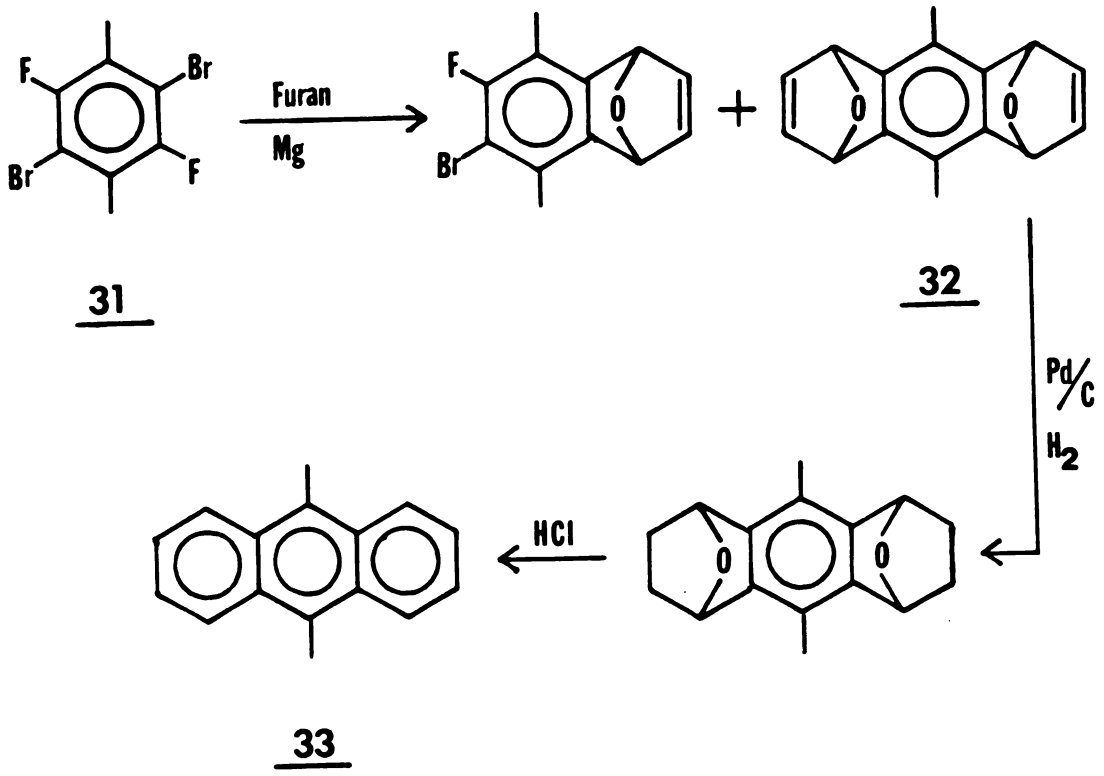


Figure 1. Structures of the syn and anti bis-adduct.

In other words, the crowdedness due to the substituents can be accommodated at this stage because of molecular distortion by the bridges. Furthermore, the reaction involved in forming the bis-adduct is highly exothermic, since it proceeds via a very reactive intermediate (i.e., aryne).

The peri interaction between R' and R is then introduced into the molecule when the bridges are removed. Nevertheless, this unfavorable strain energy is more than compensated by the energy obtained from aromatization. Therefore, this synthetic sequence enables the easy introduction of the substituents via the bis-adduct, and provides a driving force for the conversion of the bis-adduct to an arene.

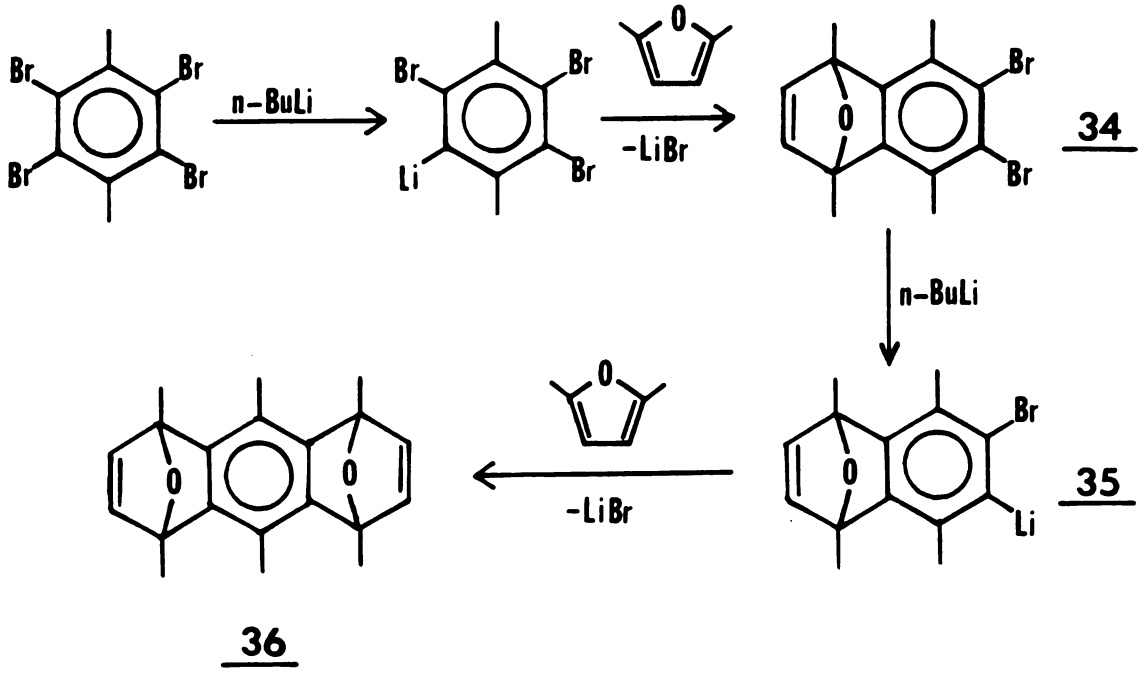
One similar bis-annelation was previously reported by Wittig and his co-worker.[14] 2,6-Difluoro-3,5-dibromo-p-xylene 31, when reacted with magnesium in the presence of furan, gave a low yield (5%) of bis-adduct 32, which was



31 32 33

then reduced with palladium on charcoal and dehydrated to give 9,10-dimethylanthracene 33 in unspecified yield (the overall yield must be less than 5%). In contrast to the unsatisfactory results of Wittig, we were able to optimize the reaction for bis-annelation and found that the following procedure provides a good yield of bis-adduct. A mixture of 10 mmole of bis-aryne equivalent and 20 mmole of pyrrole in 200 mL of anhydrous solvent is cooled to -78°C under argon atmosphere as 25 mmole of n-butyllithium (diluted 5-fold with hexane from the commercially available 2.4 M reagent) is added dropwise over a period of 2 hours. The mixture is allowed to warm slowly to room temperature and

is then quenched with methanol. The reaction was usually worked up by extraction of the adduct into methylene chloride and purification by chromatography and/or recrystallization.



The mechanism of this reaction, as demonstrated by Hart and co-workers,[15] is a stepwise process involving the initial formation of mono-adduct 34 via dibromodimethylbenzyne. Subsequent lithiation of the mono-adduct gives intermediate 35, which undergoes another Diels-Alder cycloaddition via an aryne, to give the bis-adduct 36.

1.

met

Ben

dam

bis

pro

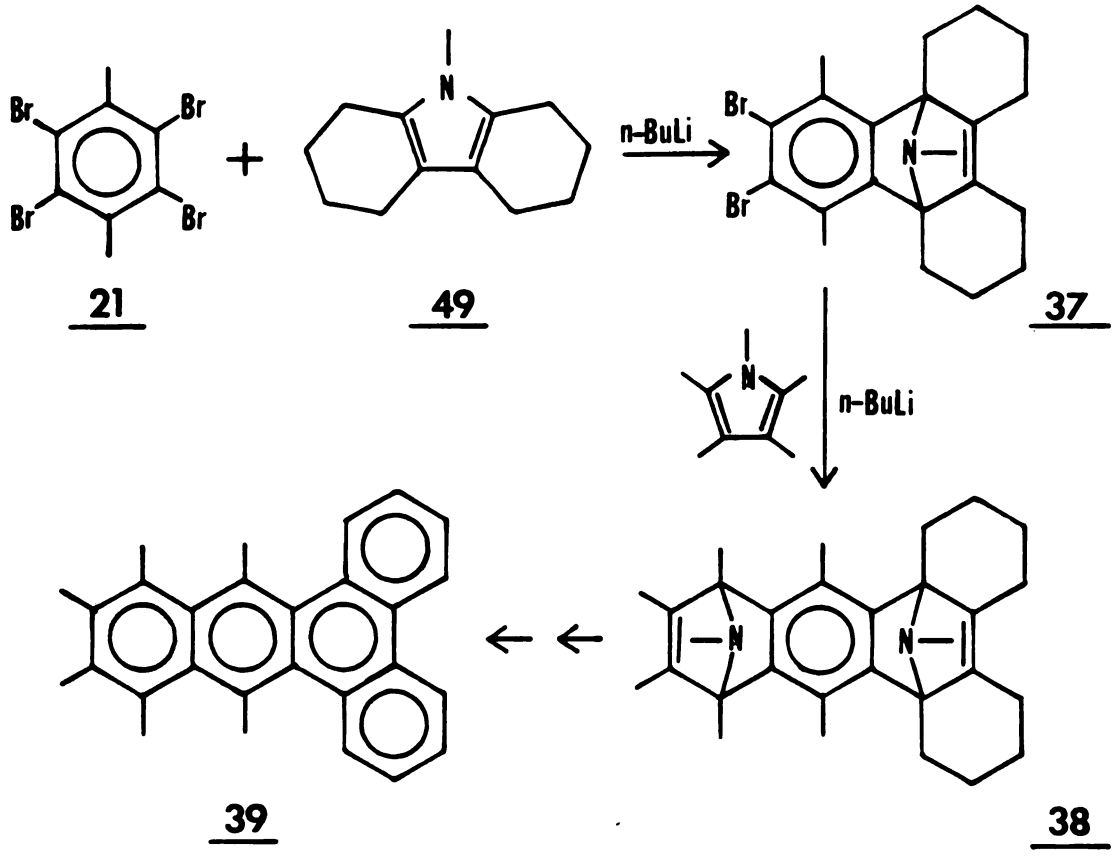
Ter

Br

Br

1. <u>The Preparation of Unsymmetric Bis-adduct</u>.

As indicated at the beginning of this section, symmetric bis-adducts were derived from the bis-aryne equivalent and 2 moles of pyrrole. This bis-annelation process can also be extended to the synthesis of a non-symmetric bis-adduct by taking advantage of the stepwise nature of the process. A representative example is described as follows. Tetrabromo-p-xylene was allowed to react with one equivalent

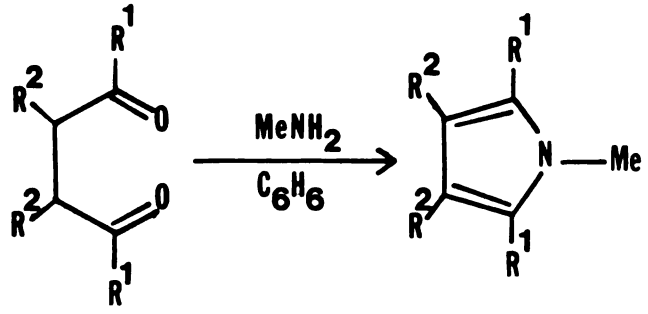


Scheme 7

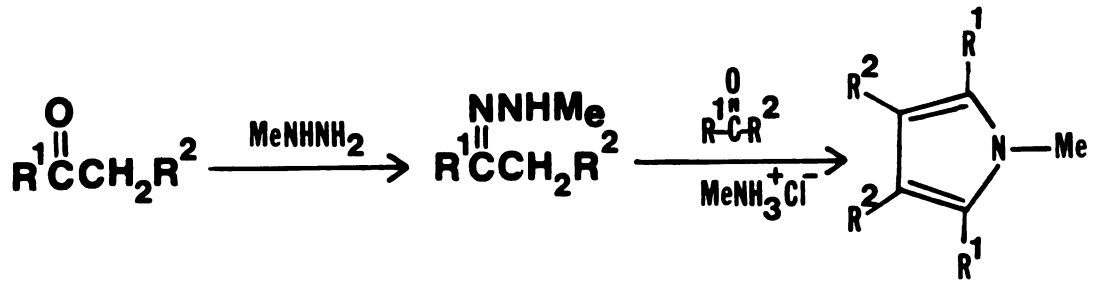
of n-butyllithium in the presence of N-methyloctahydrocarbazole in toluene at -78°C. The mono-adduct 37 was isolated in 73% yield. It was subsequently reacted with another equivalent of n-butyllithium and pentamethylpyrrole to give the bis-adduct 38 in 58% overall yield from 21. This example typifies the applicability of the process to the preparation of unsymmetric bis-adducts, and such adducts should eventually lead to a non-symmetric polyarenes with substituents at the desired positions, as illustrated in Scheme 7.

2. The Introduction of Substituents other than Methyl Groups.

In order to fully take advantage of the bis-aryne equivalent cycloaddition reaction, it was of interest to investigate the possibility of introducing different substituents other than methyl groups. Therefore, a series of pyrroles 44-49 was prepared using either the Paal-Knorr



40	R^1=Me, R^2=H	44	R^1=Me, R^2=H
41	R^1=R^2=Me	45	R^1=R^2=Me
42	R^1=Ph, R^2=H	46	R^1=Ph, R^2=H
43	R^1=Ph, R^2=Me	47	R^1=Ph, R^2=Me

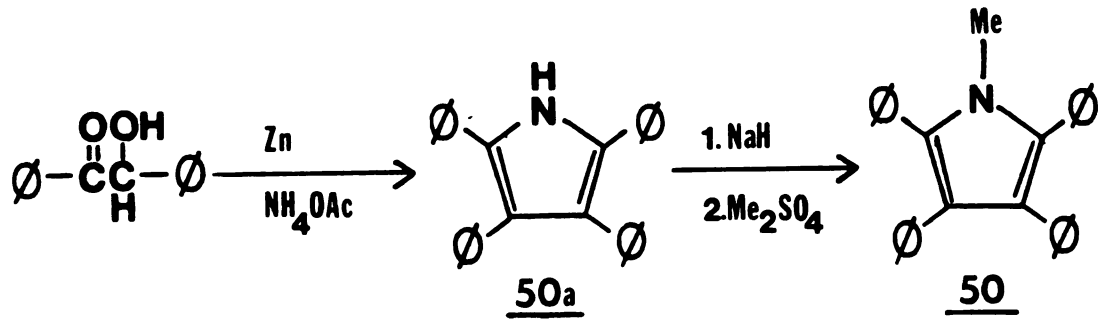


48 R^1=Me, R^2=Ph

49 R^1R^2=$(CH_2)_4$

pyrrole synthesis[16] (azeotropic distillation of the corresponding 1,4-diketone 40-43 with methylamine), or the procedure developed by Posvic (48, 49).[17]

Tetraphenyl-N-methylpyrrole 50 was prepared in an overall yield of 40% by the dehydrocyclization of benzoin with zinc and ammonium acetate,[18] followed by methylation of the pyrrole anion with dimethyl sulfate.

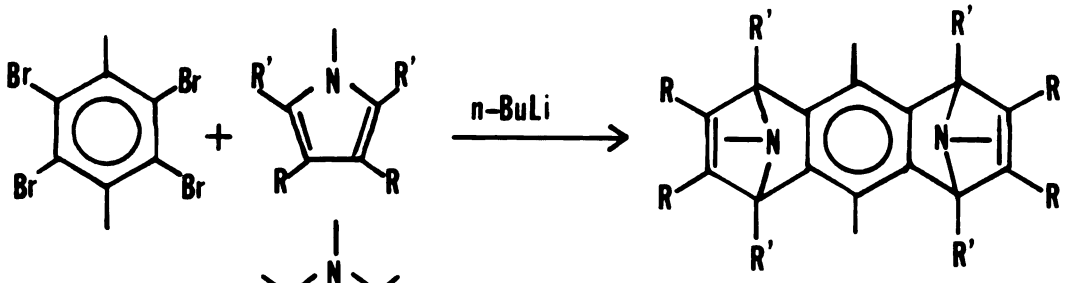


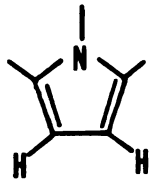
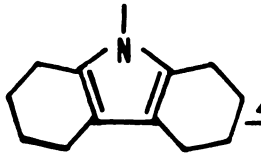
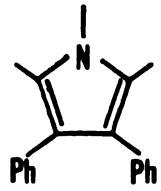
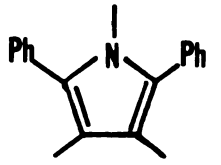
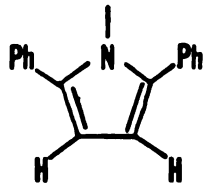
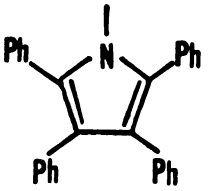
When the bis-annelation reaction was carried out with these pyrroles, the results showed that the bulkiness of the substituents on the pyrrole did not change the yield

of bis-adduct dramatically (see Table 1).

The results do suggest that the electronic factor may be much more important than the steric factor in these cycloadditions. For example, pyrroles 47, 48 were used because they have the same substituents, e.g., two methyl and two phenyl groups, but the substituents are arranged such that the pyrroles differ sterically at C-2 and C-5. Presumably, if the steric effect of the substituents at the point of bond formation (C-2, C-5) were predominant in cycloaddition, the yield of bis-adduct 54 should be appreciably less than that of bis-adduct 53 due to the tremendous change in steric hindrance at C-2 and C-5. However, the results show that the yields are about the same. On the other hand, in comparing 46, 47 and 50 in which the substituents on C-2 and C-5 of the pyrrole were the same, the cycloaddition was found to be unsuccessful if the methyl substituents on C-3 and C-4 were replaced by hydrogen atoms or phenyl groups. The failure of these cycloadditions might be ascribed to insufficient electron density in the diene system because of the inductive effect of the hydrogen and phenyl groups, which are electron-withdrawing relative to the methyl group. Unfortunately, the orientation of the phenyl groups in pyrroles 46, 47 and 50 is not known. Therefore this conclusion is based on the assumption that the phenyl groups are similarly oriented in all three pyrroles.

Table 1. The Cycloaddition of a Bis-aryne Equivalent with Substituted Pyrroles at -78°C.[a]



	44	51	73%
	45	24	79%
	49	52	76%
	48	53	59%
	47	54	57%
	46		0%
	50		0%

[a]The yields reported are the total isolated yield of syn and anti isomers.

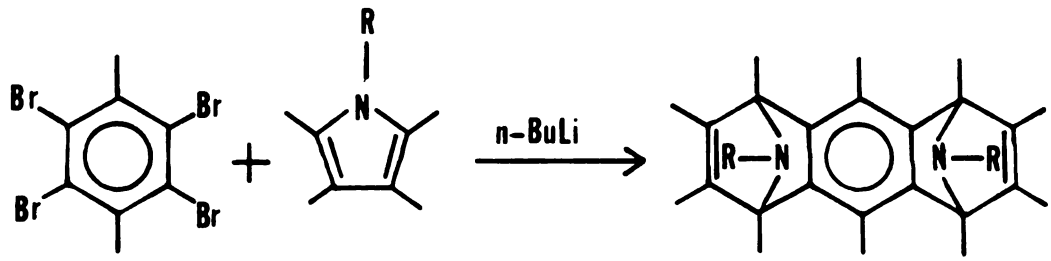
3. The Effect of the Size of Group Attached to the Pyrrole Nitrogen Atom.

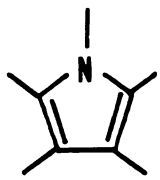
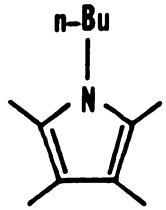
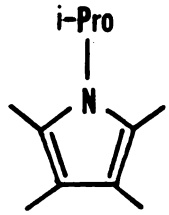
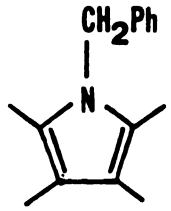
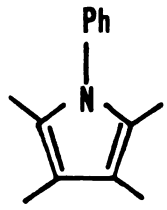
In the previous section, attention was focussed on the effect of the C-substituents on the pyrrole. Another question which can be raised is whether the yield of bis-adduct would be effected if the pyrrole had an N-substituent other than a methyl group. It might be suspected that the more bulky the N-substituent on the pyrrole the more difficult it would be to have effective orbital overlap for bis-adduct formation (the orbitals considered here are the active orbitals on the bis-aryne equivalent and those at the 2- and 5- position of the pyrrole). Therefore a study was planned to address this question. A series of pyrroles[19,20] with different bulky groups on the N-atom were prepared and reacted with a bis-aryne equivalent as described in the Table 2.

The results indicate that the bulkiness of the substituents on the N-atom of the pyrrole does not effect drastically the yield of bis-adduct. These observations are consistent with data obtained by Wolthuis and Boer[21] who found that when benzyne was reacted with N-substituted pyrroles 55-59, the yield of 1:1 adduct was not affected greatly by the bulkiness of the N-substituents.

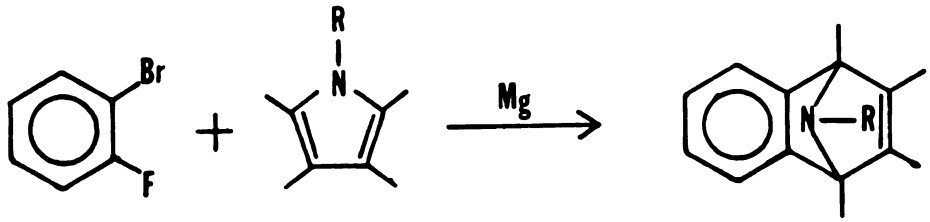
Apparently the formation of bis-adduct proceeds through a transition state according to the Alder rule, which

Table 2. The Cycloaddition of a Bis-aryne Equivalent with Different N-substituted Pyrroles at -78°C.[a]



	45	24	79%
	55	60	64%
	56	61	75%
	57	62	61%
	58	63	51%

[a]The yields reported are the total isolated yield of syn and anti isomers.



55	R=Bu	63%
57	R=CH_2Ph	50%
58	R=Ph	51%
59	R=cyclo-C_6H_{11}	59%

requires maximum π to π orbital overlap between the diene and dienophile. The overlap is achieved by approach of the benzyne and pyrrole moieties in two parallel planes rather than in a head to head fashion (as indicated by Figure 2).

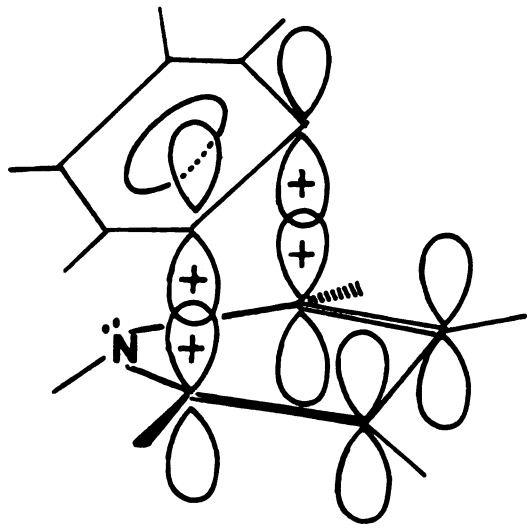


Figure 2. The transition state of cycloaddition with respect to basis set orbitals.

Consequently steric hindrance by the N-substituent is not important in the cycloaddition.

The results of the foregoing studies can be summarized as follows:

I) As described in Scheme 7, a particular bis-adduct having substituents at desired positions usually can be synthesized in a stepwise process with different predesigned pyrroles.

II) The annelation of pyrroles to benzynes is primarily controlled by the inductive effects of the substituents rather than by steric factors. The bis-adduct can usually be prepared from an electronically efficient pyrrole (i.e., one which contains electron-donating substituents) regardless of the size of the substituents.

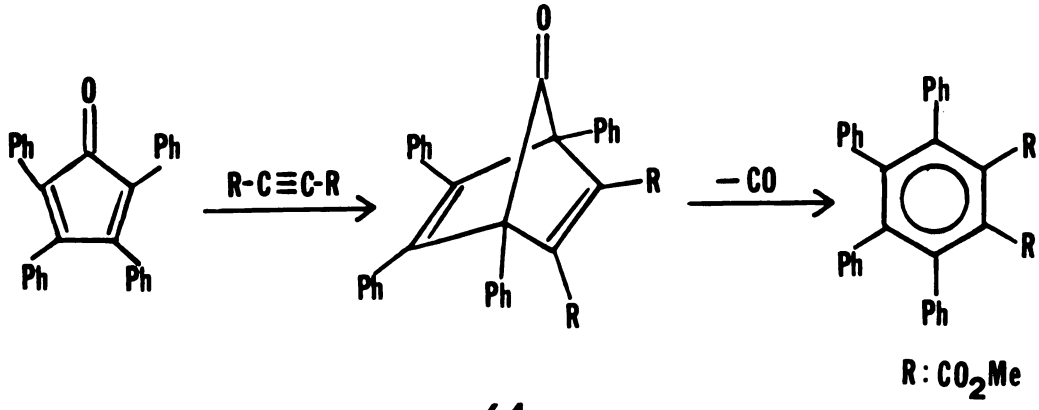
III) The applicability of pyrroles as dienes is also not limited by the bulkiness of the substituent on the N-atom.

Having arrived at these conclusions concerning factors which affect the bis-annelation, we now turn to the question of converting the bis-adducts to aromatic compounds.

4. Aromatization.

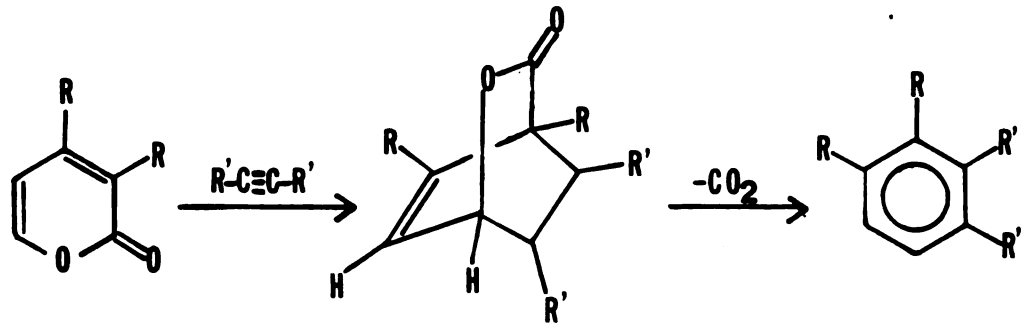
A variety of dienes have been employed in benzene ring construction based on the cycloaddition-extrusion sequence.[22,23] Some extrusions occur with only a little

effort. For example, the cycloaddition of dimethyl acetylene-dicarboxylate to tetracyclone gave the adduct 64 which spontaneously extruded carbon monoxide to give the tetraphenyl



64

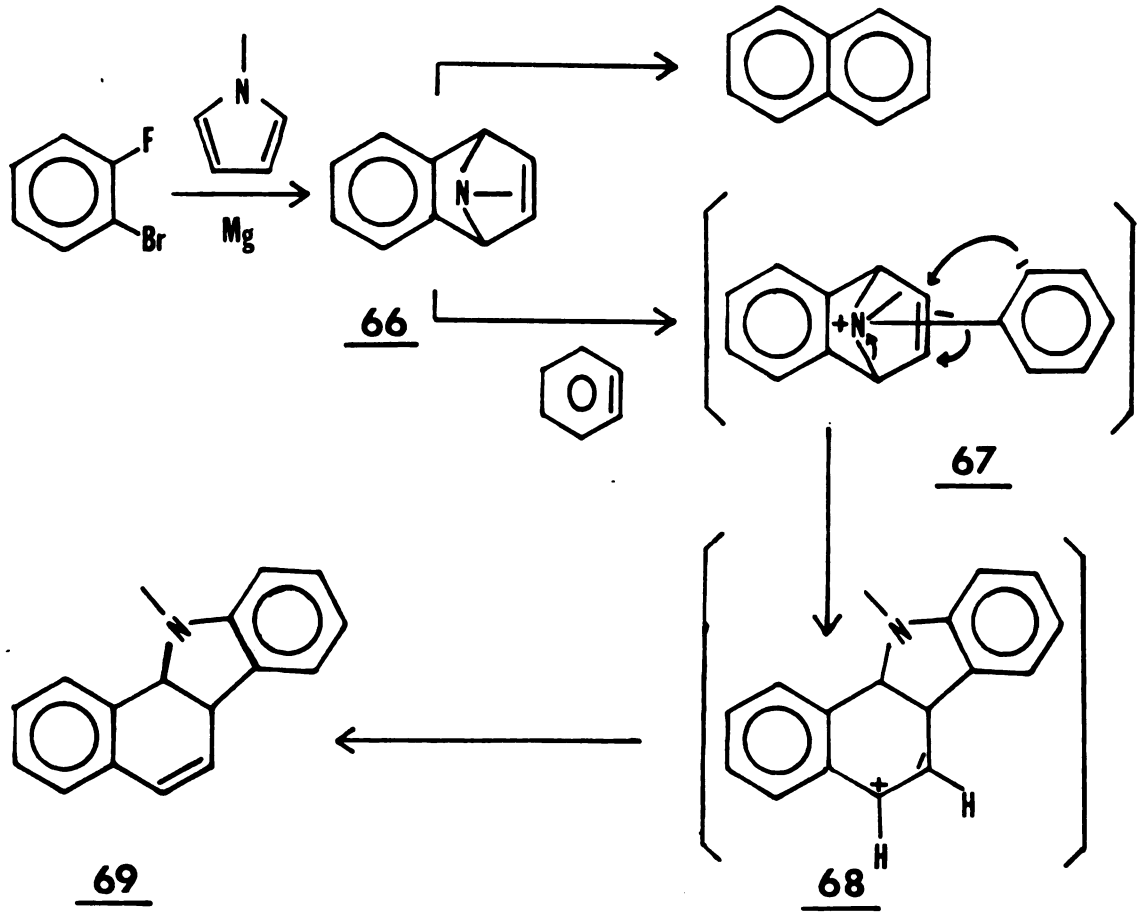
diester quantitatively.[22] Similarly, benzene derivatives have been prepared from 2-pyrone and acetylenes.[23] This is a typical Diels-Alder reaction which is followed by



65

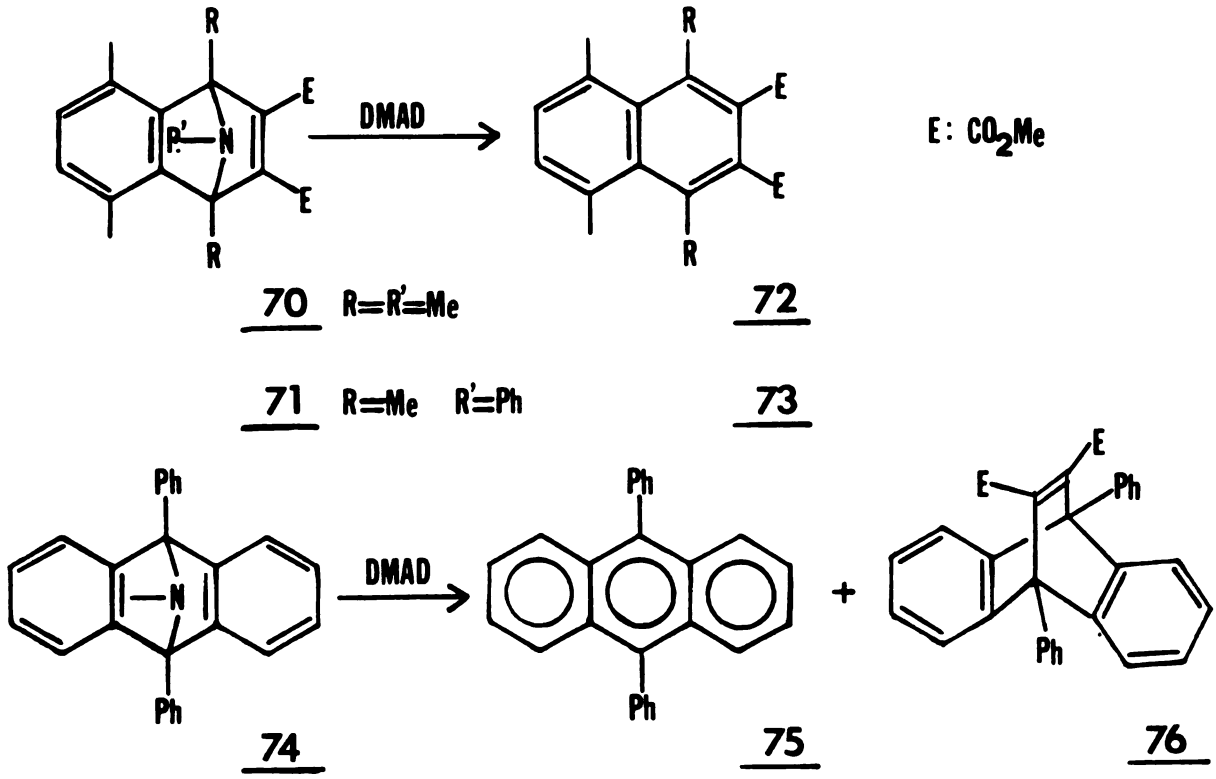
loss of carbon dioxide from the adduct 65 to provide the aromatic product. But the presence of a highly nucleophilic reagent which is also a strong base, i.e., n-butyllithium in our bis-adduct forming reaction does not permit the use of these carbonyl-containing dienes.

Although the utilization of pyrroles for adduct formation has been reported elsewhere, subsequent aromatization usually cannot be performed with ease, as exemplified by previous examples (this is especially true when trying to prepare highly strained arenes[8,13]).



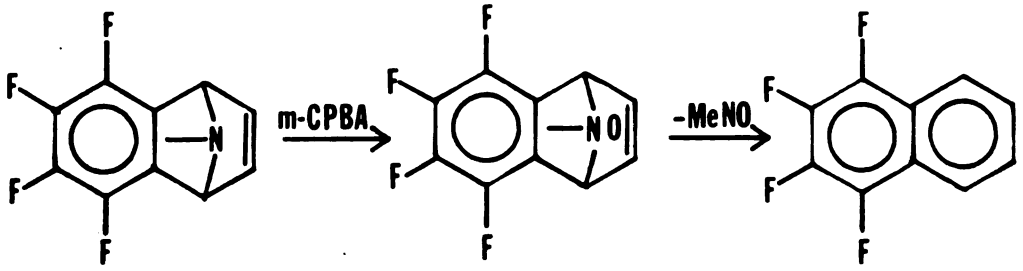
The formation of a small amount of naphthalene as a by-product in the reaction of benzyne with N-methyl-pyrrole was first noted by Wittig and Behnisch.[24] N-methyl-10,11-dihydro-1,2-benzocarbazole 69, the major product, presumably arose from the reaction of adduct 66 with another mole of benzyne to form an intermediate zwitterion 67, which then underwent ring closure to 69. The mechanism for obtaining the complementary product naphthalene was not explained.

The 1,4-dihydronaphthalene-1,4-imine-2,3-diesters 70 and 71, on heating with excess dimethyl acetylenedicarboxylate, also lead to the deaminated naphthalene diester



72 and 73, respectively.[25,26] Analogously compound 74 on heating at 180°C with acetylenic ester, gave some of the anthracene 75. But in none of these cases was the deamination product the major product. Furthermore, Diels-Alder reaction of the expected arene with excess dimethyl acetylenediester leads to a secondary product, such as 76, adding another disadvantage to this process.

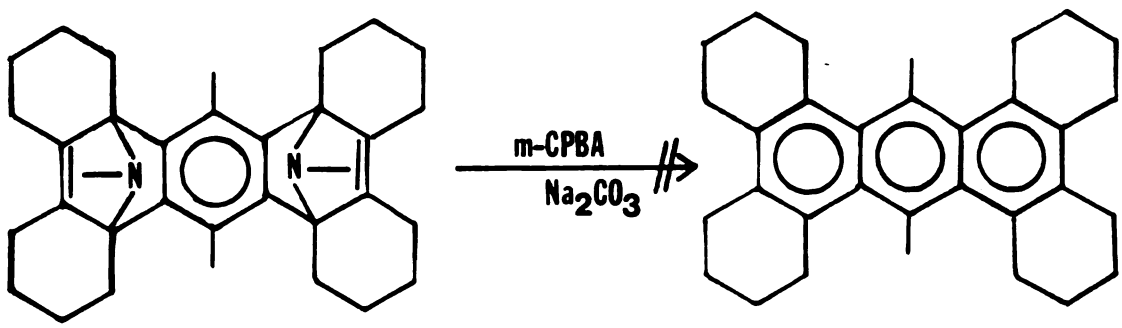
A successful method for aromatizing 1,4-naphthaleneimines was reported by Gribble and his co-workers.[12] The observation was made that peroxide or peracid oxidation of the 1,4-imine rapidly generated an N-oxide 77 and subsequently produced the aromatic hydrocarbon 78 with the elimination of nitrosoalkane. This method does afford a useful



77 78

synthetic approach to simple polyarenes. One competing reaction is oxidation of the carbon-carbon double bond. Also, the oxidation was carried out with a peracid which on reduction gives a carboxylic acid that may cause

isomerization of peri-substituted polyarenes. As a result of this anticipated disadvantage, we modified the reaction conditions for our systems by adding a weak base, such as Na_2CO_3 or $NaHCO_3$, along with m-CPBA during the oxidation. It was intended that the acid generated during the oxidation would be neutralized by the pre-added bases and reduce the chance of isomerizing the product. The modification did give a respectable improvement in yield for the preparation of decamethylanthracene,[8] but the yield was poor for dodecamethylnaphthacene,[13] and the reaction failed completely for the highly rigid anthracene derivative 79.

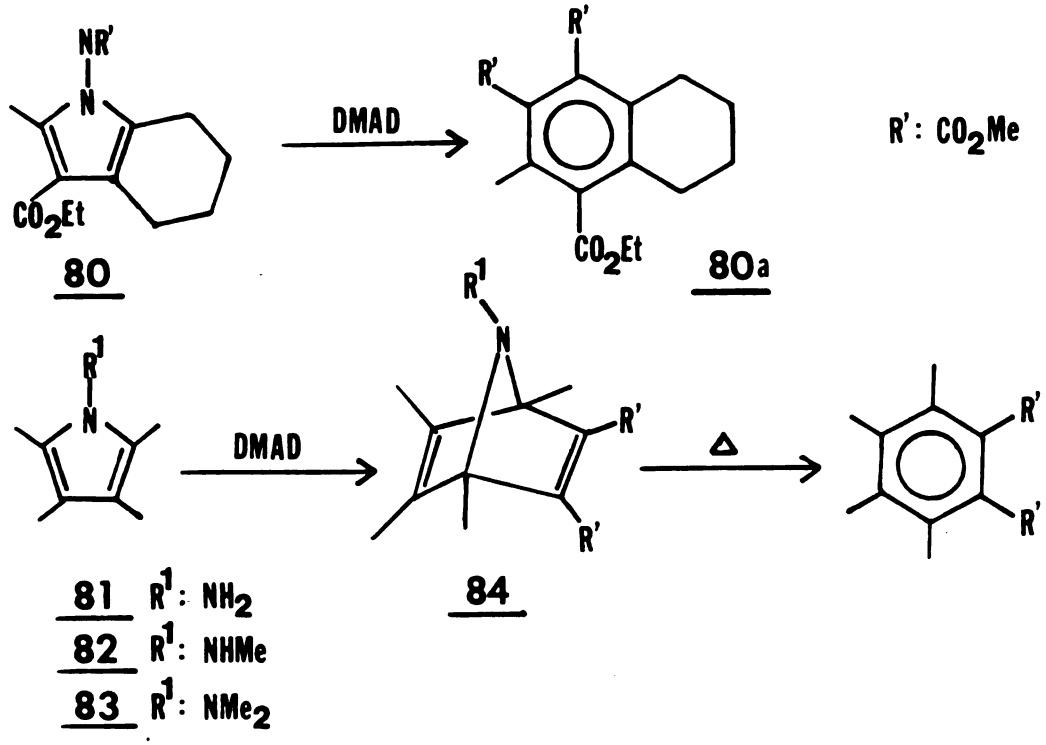


52 79

Several other modifications were tried, such as changing the solvent, reaction time, or using pyridine as a base. All the results turned out to be essentially the same, so an alternative method was sought.

Schultz[27] reported very recently that the reaction of N-carbomethoxyaminopyrrole 80 with excess dimethyl

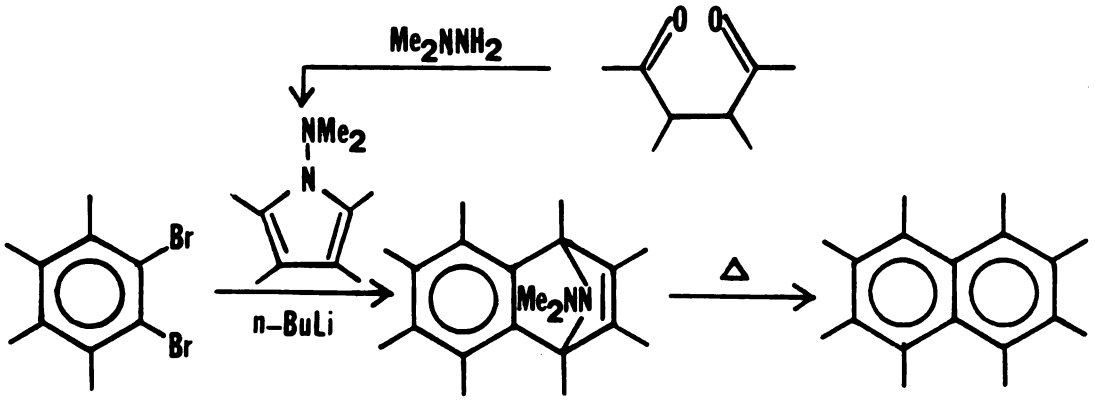
acetylenedicarboxylate in refluxing toluene (48 h) gave the tetralin 80a in 55% isolated yield. This simple method



for benzene ring construction also worked for the reaction of pyrroles 81 - 83 with DMAD on an NMR tube experimental scale. The thermal decomposition of adduct 84 to arenes seemed attractive for our purposes because no other reagents are involved in the transformation.

N-(dimethylamino)-2,3,4,5-tetramethylpyrrole 83 was easily obtained in 90% yield by azeotropic distillation from a mixture of 3,4-dimethyl-2,5-hexanedione and 1,1-dimethyl-hydrazine. The cycloaddition of pyrrole 83 was

first carried out at dry ice temperature in THF with dibromoprehnitene 85, and gave an 82% yield of N-(dimethylamino)-1,2,3,4,5,6,7,8-octamethyl-1,4-dihydronaphthalen-1,4-imine 86. The mass spectrum of adduct 86 shows a very weak parent at m/e 298 but a base peak at m/e 240, which corresponds to the fragment without the nitrogen bridge. The ^{1}H NMR spectrum of 86 in $CDCl_3$ consisted of five sharp equal intensity singlets at δ1.60, 1.93, 2.08, 2.21, 2.30.



85 86 18

Upon pyrolysis at 200°C, adduct 86 was converted to octamethylnaphthalene 18 quantitatively in 30 min. Attempts were made to investigate the volatile compounds from the pyrolysis, but the results from GC-Mass spectrometric analysis showed that the composition of the pyrolysate was not reproducible. The mixture was too complex to lead to

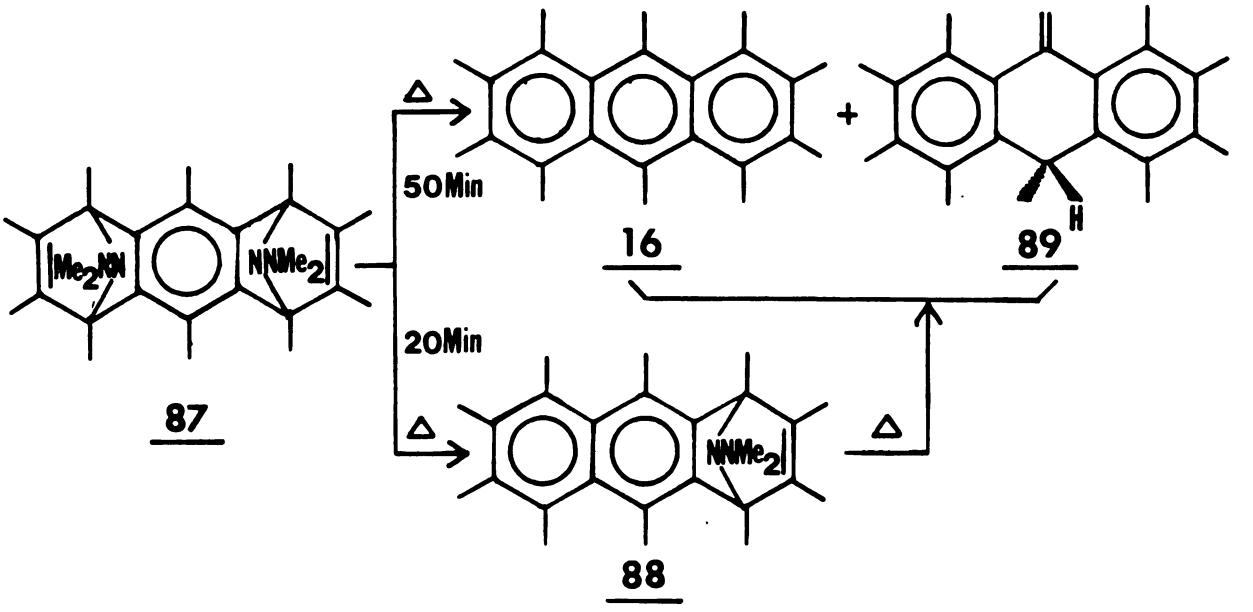
any conclusions. The pyrolysis may involve a nitrene extrusion as suggested by Schultz and Shen.[27] Alternatively, it might proceed via the elimination of nitrogen and ethane. The mechanism of the bridge removal is not clear at this point and requires further study.

5. The Applications of N-(Dimethylamino)pyrrole to the Preparation of Polyacenes.

N-(Dimethylamino)-tetramethylpyrrole 83 was used in a bis-cycloaddition with the bis-aryne equivalent derived from tetrabromo-p-xylene and n-butyllithium. A mixture of syn and anti bis-adducts 87 was obtained in 64% overall yield. The mixture could be resolved by column chromatography. However, no attempt was made to distinguish which isomer was which. In contrast to the smooth conversion of the naphthalene imine 86 to naphthalene 18, the pyrolysis of 87 was complex and the product composition depended on the pyrolysis time. When bis-adduct 87 was heated at 180°C for 30 min, decamethylanthracene 16 and its isomerization product 89 were isolated in 45% and 36% yield respectively. Prolonged pyrolysis only increased the amount of 89 at the expense of 16.

Compound 89 could be formed in several ways. Possibly the isomerization is induced by an active species such as a nitrene generated during pyrolysis. It might also be formed by a thermally allowed 1,5-H migration process on

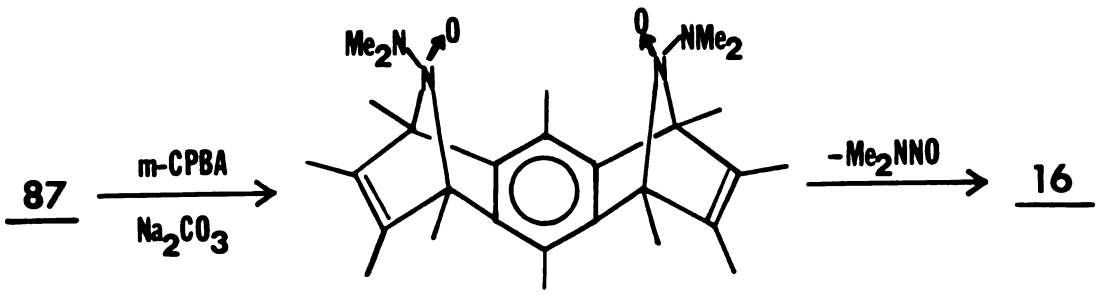
the central ring of the anthracene, to relieve the peri interactions of the methyl groups at the 1,4,5,8,9, and 10 positions. However, the latter explanation was ruled out by the complete recovery of decamethylanthracene after heating it under the same conditions used for the conversion of 87 to 16.



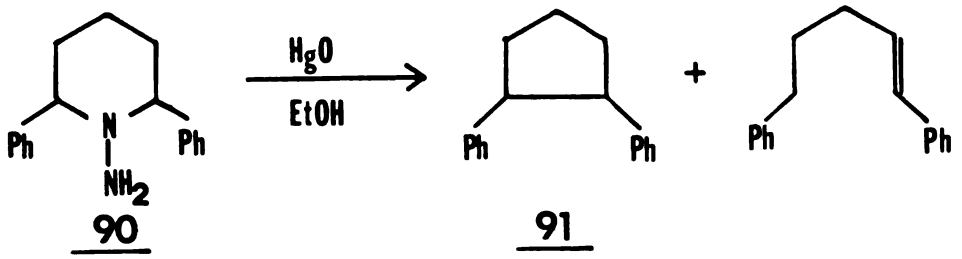
The double bridge removal occurs stepwise. Thus, by interrupting the pyrolysis at an earlier stage, some N-(dimethylamino)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4-dihydroanthracen-1,4-imine 88 was isolated, although most of the starting bis-adduct was recovered. However, stepwise bridge removal was not beneficial in increasing the yield of decamethylanthracene, because when the mono-imine 88 was

pyrolyzed at 200°C for 30 min, compound 16 and 89 were isolated in the same ratio as in the pyrolysis of bis-adduct 87.

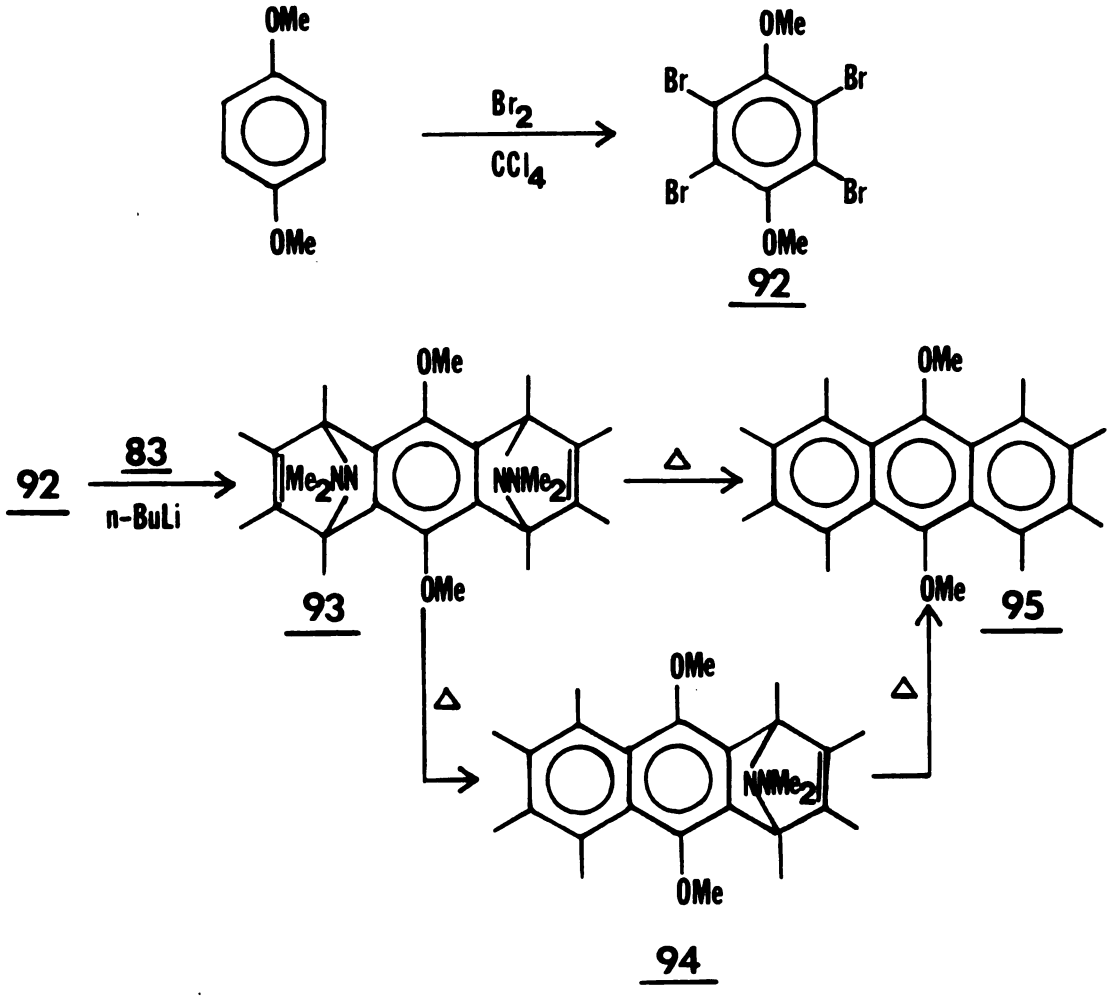
Surprisingly, when bis-adduct 87 was treated one equivalent of m-CPBA in the presence of Na_2CO_3 in refluxing $CHCl_3$, decamethylanthracene was isolated in 72% yield along with 12% of its tautomer 89. This improvement over



the result with 24 is reasonably explained because the reaction involves extrusion of nitrosodimethylamine, a thermodynamically more stable species than nitrosomethane. Oxidation of the bis-adduct with lead tetraacetate also gave 16 and 87, but in trace amounts. Whether the reaction went through a nitrene, as in the conversion of 90 to 91,[28] is not known.



To avoid the isomerization which occurs when the substituents at C-9 and C-10 are methyl groups, another bis-aryne equivalent with two blocking groups at the para positions was used. Tetrabromo-p-dimethoxybenzene 92 was prepared in 75% yield by the bromination of p-dimethoxybenzene. After carrying out the bis-annelation reaction, a mixture of syn and anti bis-adduct bis-N-(dimethylamino)-9,10-dimethoxy-1,2,3,4,5,6,7,8-octamethylanthracen-1,4; 5,8-bis-imine 93 was obtained in 69% yield.



Without resolution of the two isomers, the mixture was pyrolyzed at 150°C for 60 min, and gave 9,10-dimethoxy-1,2,3,4,5,6,7,8-octamethylanthracene 95 quantitatively as shiny yellow crystals. The ^{1}H NMR($CDCl_3$) spectrum showed only three singlets at δ2.38(12 H), 2.76(12 H), and 3.33 (6 H). The ultraviolet spectrum of 95 is similar to that of decamethylanthracene (Figure 3) but with an appreciable

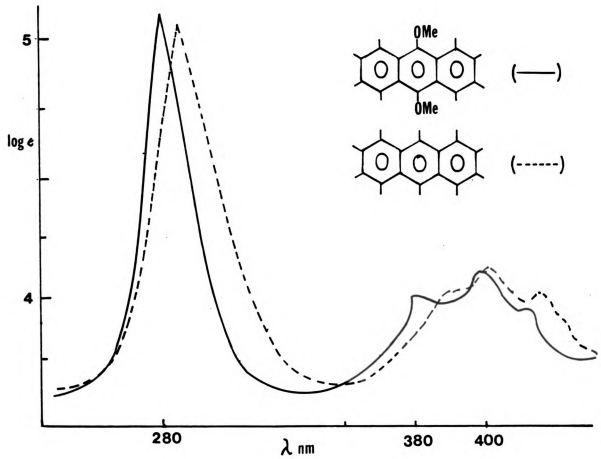


Figure 3. Ultraviolet absorption spectra of 16 and 95.

hypsochromic shift for all the principle absorption maxima.

The effect of steric strain on the ultraviolet absorption spectra of polycyclic aromatic molecules has been well documented. Data for polymethylated naphthalenes and anthracenes were collected.[29,30] In both series of compounds the band shifts could be correlated with the location

Table 3. Absorption Spectral Data of Substituted Anthracenes.[a]

Compound	nm	nm	nm	nm
Anthracene (A)	253	339	356	375
2-methyl A	255	340	358	377
2,3-dimethyl A	257	341	358	378
2,3,6-trimethyl A	259	342	360	379
2,3,5,6-tetramethyl A	261	343	359	379
2,3,9-trimethyl A	261	350	368	388
2,3,9,10-tetramethyl A	265	359	379	400
2,3,6,7,9,10-hexamethyl A	296	360	380	402
9,10-dimethoxy-1,2,3,4,5,6,7,8-octamethyl A	280	378	399	418
1,2,3,4,5,6,7,8,9,10-decamethyl A	288	---	403	427

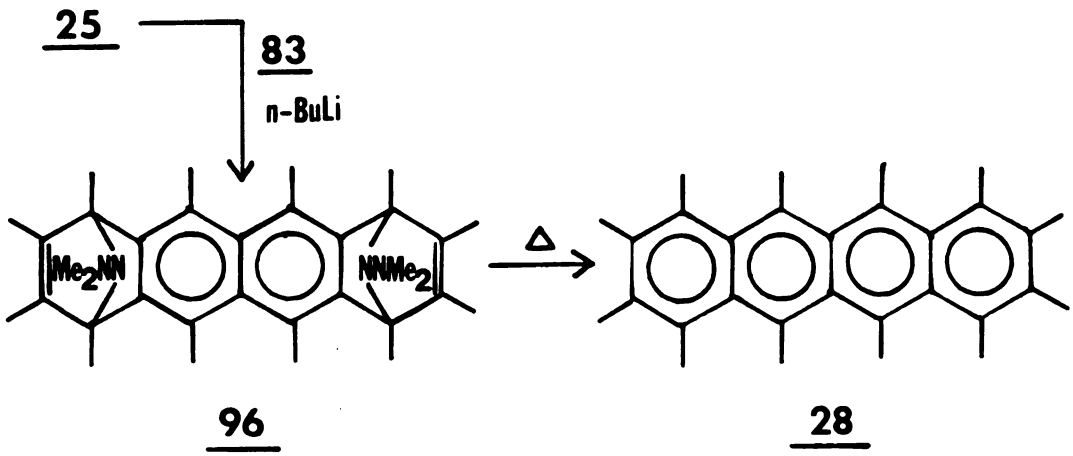
[a]Solvent: cyclohexane.

of the methyl groups. A nearly 2 nm bathochromic shift per "beta" methyl group on the shortest wavelength intense maximum of anthracene (253 nm) was reported. However, methyl substitution at the "peri" positions causes a more pronounced shift of about 4 nm. (See Table 3.)

Although this is an empirical conclusion, there is no doubt about a qualitative correspondence between the bathochromic shifts due to methyl substitution and the change of molecular structure caused by the overcrowding. The data clearly imply that the more crowded the substitution on the anthracene the larger the bathochromic shift which will be found. No adequate theoretical explanation of the observed shift is available, but it is generally assumed that this phenomenon is associated with the alignment of the substituent with respect to certain axes of the molecule. All the principal absorption maxima of 9,10-dimethoxy-octamethylanthracene 95 have a bathochromic shift relative to 2,3,6,7,9,10-hexamethylanthracene, but have a hypsochromic shift relative to decamethylanthracene. Therefore, the UV data support the conclusion that 9,10-dimethoxy substitution experiences less of a peri effect than 9,10-dimethyl substitution on the anthracene skeleton. In other words, 9,10-dimethoxy-octamethylanthracene might have a less distorted geometry than decamethylanthracene.

The new aromatization technique has been combined with bis-annelation to improve the preparation of dodecamethylnaphthacene 28. Tetrabromo-1,4,5,8-tetramethylnaphthalene

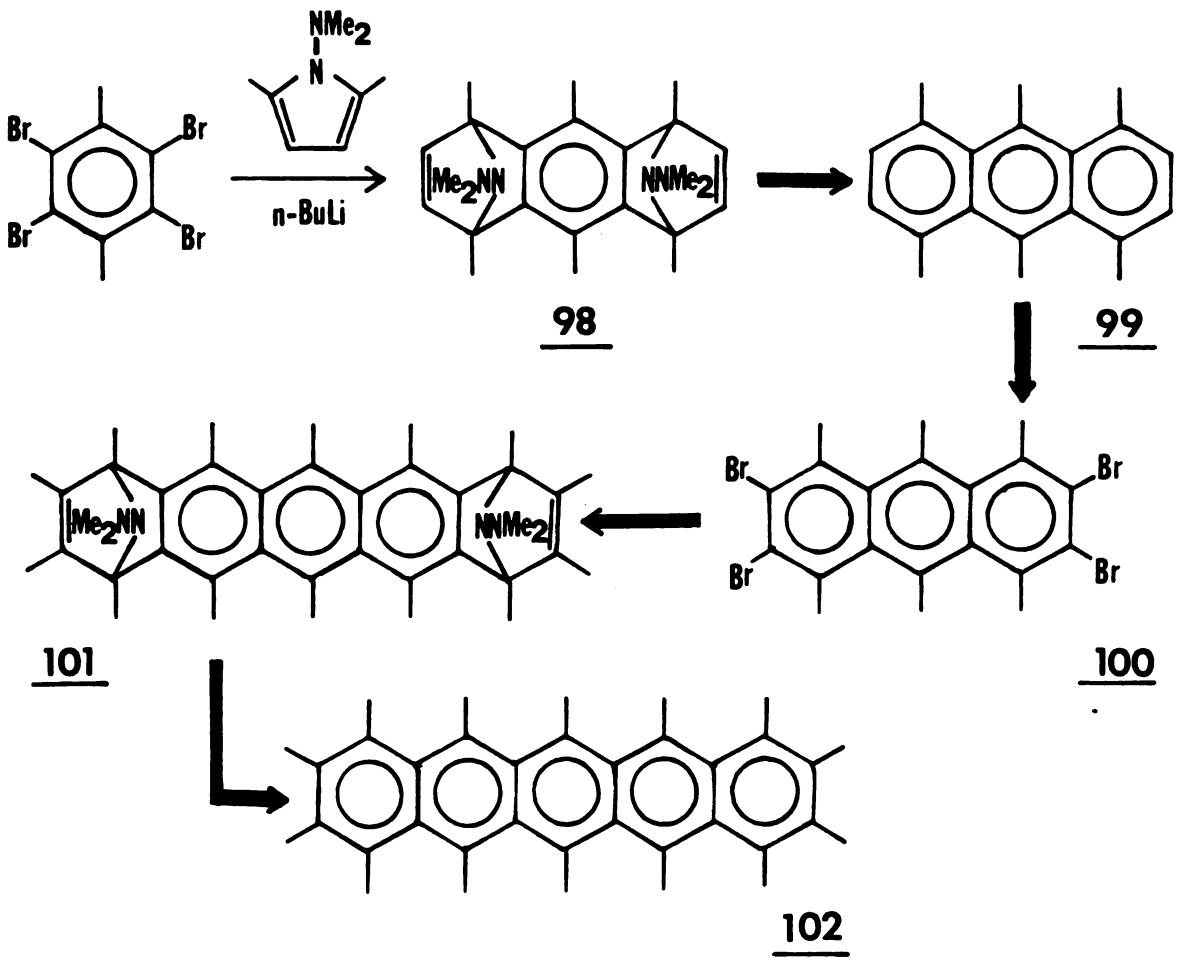
25 was prepared[13] and reacted with N-(dimethylamino)-tetramethylpyrrole 83 and n-butyllithium at -78°C, and gave a 62% total yield of two isomeric bis-adducts 96. The mixture of stereoisomeric bis-adduct 96 was pyrolyzed at 180°C, and the red crystalline dodecamethylnaphthacene 28 was obtained quantitatively. Compared to the previously reported work (8% overall yield from 25),[13] the utilization of N-(dimethylamino)-tetramethylpyrrole as a building block represents a dramatic success in this synthesis.



In general, the reactivity of acenes (naphthalene, anthracene, naphthacene, pentacene, hexacene) increases with increasing molecular weight. It was reported that heptacene is so unstable that all attempts to prepare the compound in a pure state failed.[31] A similar difficulty

was encountered in the preparation of tetradecamethylpentacene 102 by our methodology.

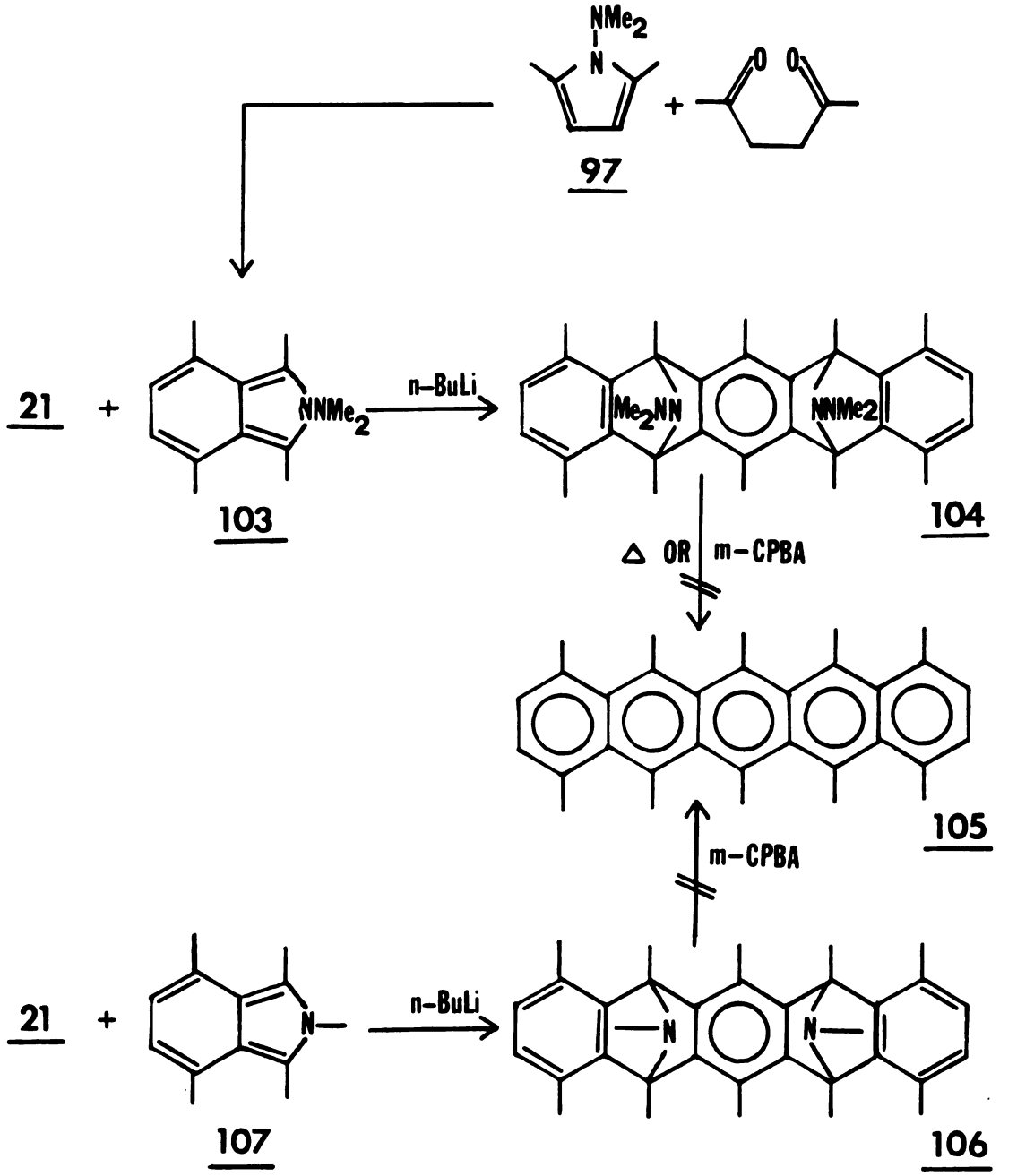
Two possible synthetic routes to pentacenes (102 or 105) are outlined in Schemes 8 and 9. The key feature for differentiating the better approach must reflect the nature of the peri-substituted arene. In Scheme 8, the difficulty lies in the preparation of 2,3,6,7-tetrabromo-1,4,5,8,9,10-hexamethylanthracene 100. It was hoped that 100 could be



Scheme 8

prepared by the bromination of 1,4,5,8,9,10-hexamethylanthracene 99. However, the preparation of 99 according to current method was not satisfactory. Treatment of tetrabromo-p-xylene 21 with n-butyllithium and N-(dimethylamino)-2,5-dimethylpyrrole 97 only provides 7% of the bis-adduct 98. Also anthracene 99, with quadruple peri-interactions, is predicted to be unstable under the acidic condition which prevail during bromination. Therefore, neither the pyrolysis of bis-adduct 98 to 99 nor the bromination of anthracene 99 was tried.

Alternatively, the synthesis shown in Scheme 9 was pursued. The required N-(dimethylamino)-1,3,4,7-tetramethylisoindole 103 was prepared using the procedure developed by Bonnett.[32] Reaction of 2,5-hexanedione and pyrrole 97 in refluxing benzene gave a 45% yield of isoindole 103 as an extremely unstable air-sensitive compound. Therefore, instead of isolating 103 pure, crude material was used directly in the bis-aryne equivalent cycloaddition. Bis-adduct 104 was obtained in 56% yield, and it gave a satisfactory elementary analysis. However, the ^{1}H NMR($CDCl_3$) spectrum only showed four singlets, at δ2.14, 2.34, 2.56, and 6.52, with relative intensities of 12:12:6:4. Similarly, one sp^3 carbon peak (NMe_2) was missing from the ^{13}C NMR ($CDCl_3$) spectrum δ150.75, 148.98, 128.47, 127.73, 122.06, 76.17, 19.48, 15.25, and 10.00. Also in contrast to the mass spectroscopic data of previous bis-adducts

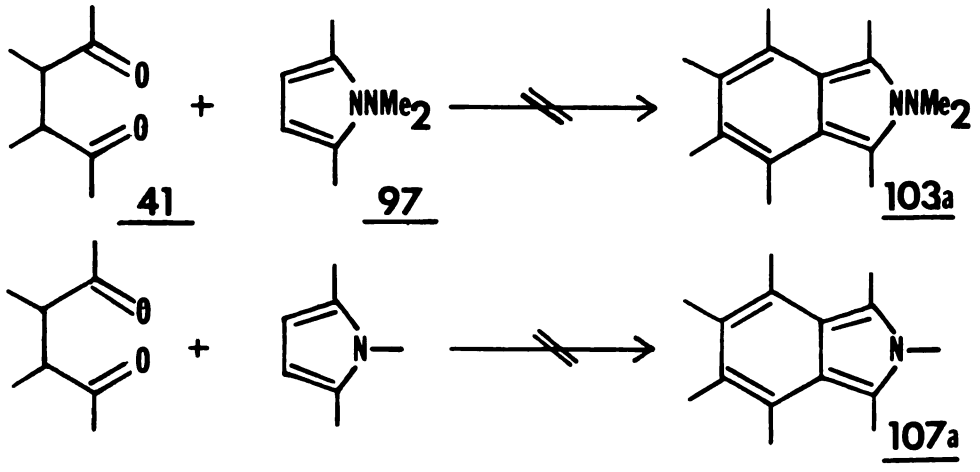


Scheme 9

such as 87, 93 and 98 (no parent peak was found), the mass spectrum of 104 reveals a noticeable parent peak at m/e 534.

The appearance of this parent peak implies that removing both bridges by thermolysis might be difficult. Indeed, the pyrolysis of 104 at a variety of temperatures was not successful. Attempts to oxidize bis-adducts 104 or 106 with m-CPBA yielded only intractable tars.

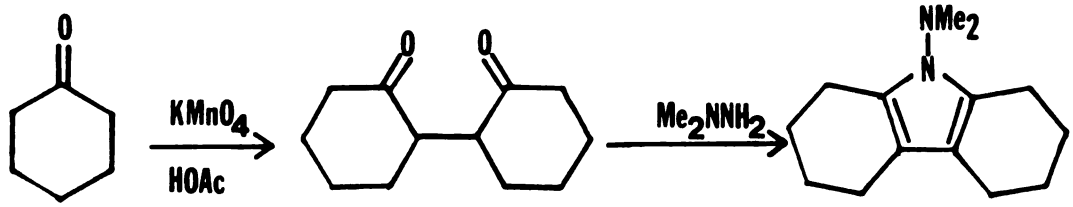
The preparation of fully methylated isoindole 103a was tried by the same procedure used for 107. No condensation product 103a could be isolated from the reaction mixture of 41 and 97. A similar failure for the preparation of 107a was observed by Bonnett.[32] With all the unsatisfactory results encountered above, no further attempts were made for the synthesis of tetradecamethylpentacene and hexadecamethylhexacene.



6. The Applications of N-(Dimethylamino)-octahydrocarbazole to Arene Synthesis.

The use of N-(dimethylamino)pyrrole as a diene with arynes has proved to provide a simple and effective process for preparing arenes. This success prompted us to study the utility of this process for synthesizing more strained systems. N-(dimethylamino)octahydrocarbazole 110 was chosen for this purpose, because the six-membered rings on the pyrrole could eventually be aromatized.

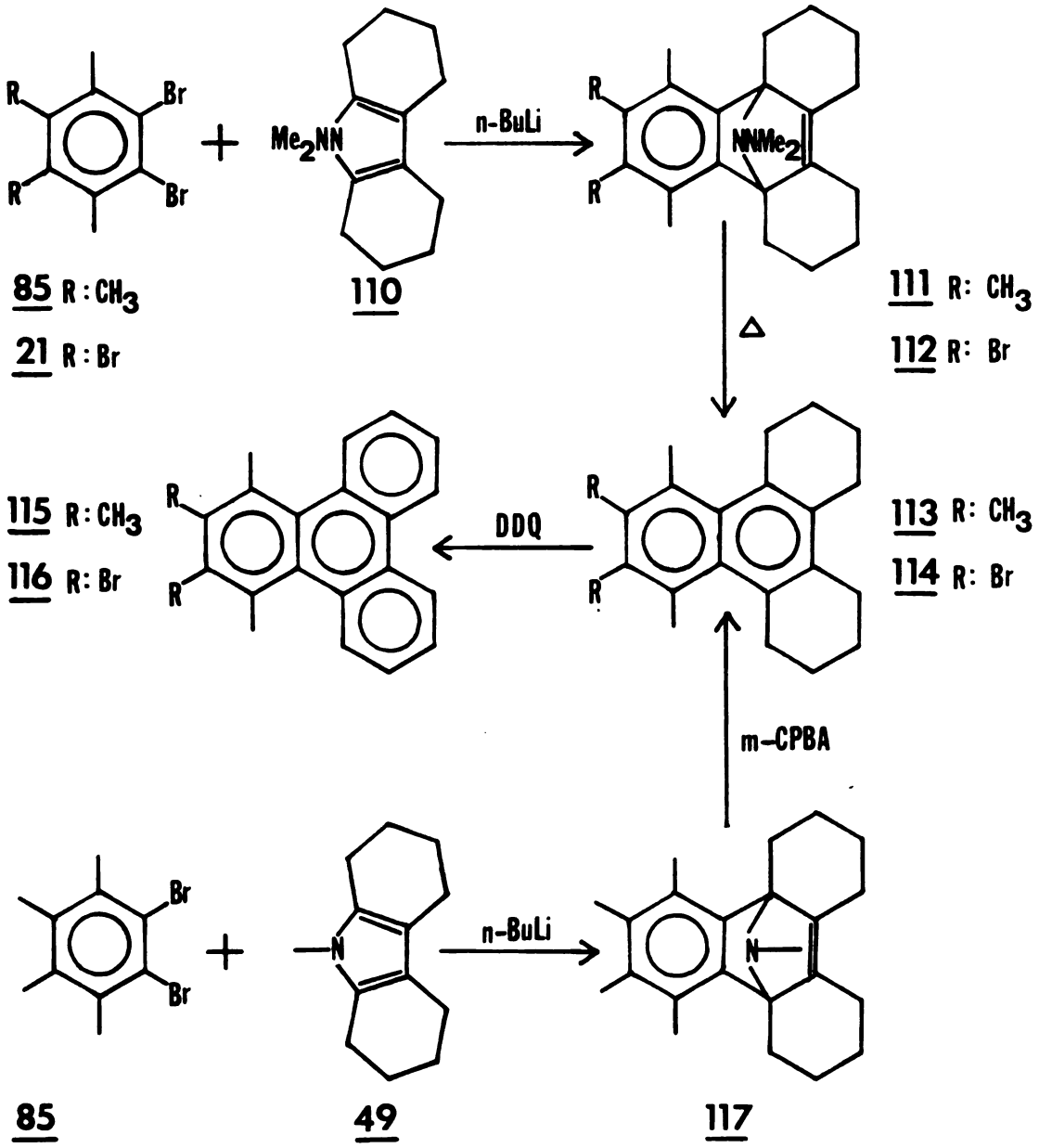
Compound 110 can be obtained from the reaction of 2,2'-biscyclohexanone 109 with 1,1-dimethylhydrazine. Reaction of 110 with a benzyne indicated that it is a susceptible diene both electronically and sterically. Thus, treatment of dibromoprehnitene 85 with n-butyllithium and 110 gave a 62% yield of adduct 111, which was converted



109 110

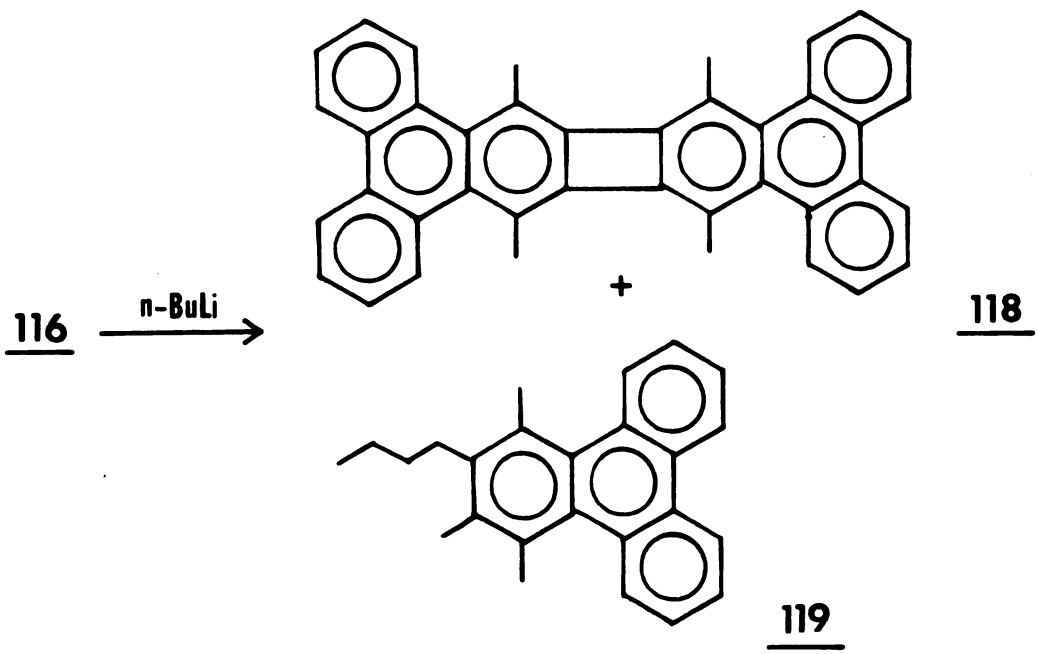
on heating to 1,2,3,4,5,6,7,8-octahydro-9,10,11,12-tetramethyltriphenylene 113. Dehydrogenation of 113 with dichloro-dicyanoquinone gave 1,2,3,4-tetramethyltriphenylene 115. Compound 113 could also be obtained by the m-CPBA

oxidation of 117. The ^{1}H NMR($CDCl_3$) spectrum of 115 shows peaks at δ2.03(s, 6 H), 2.78(s, 6 H), 7.30(m, 4 H), 8.03 (m, 2 H), 8.30(m, 2 H).



Conventional methods for preparing triphenylenes usually give symmetric derivatives, either by trimerization of a benzene moiety[33] or by building up three new benzene rings from a trifunctionalized benzene.[34] Therefore, the method described here is particularly useful, since it constitutes a new synthesis for unsymmetric triphenylenes.

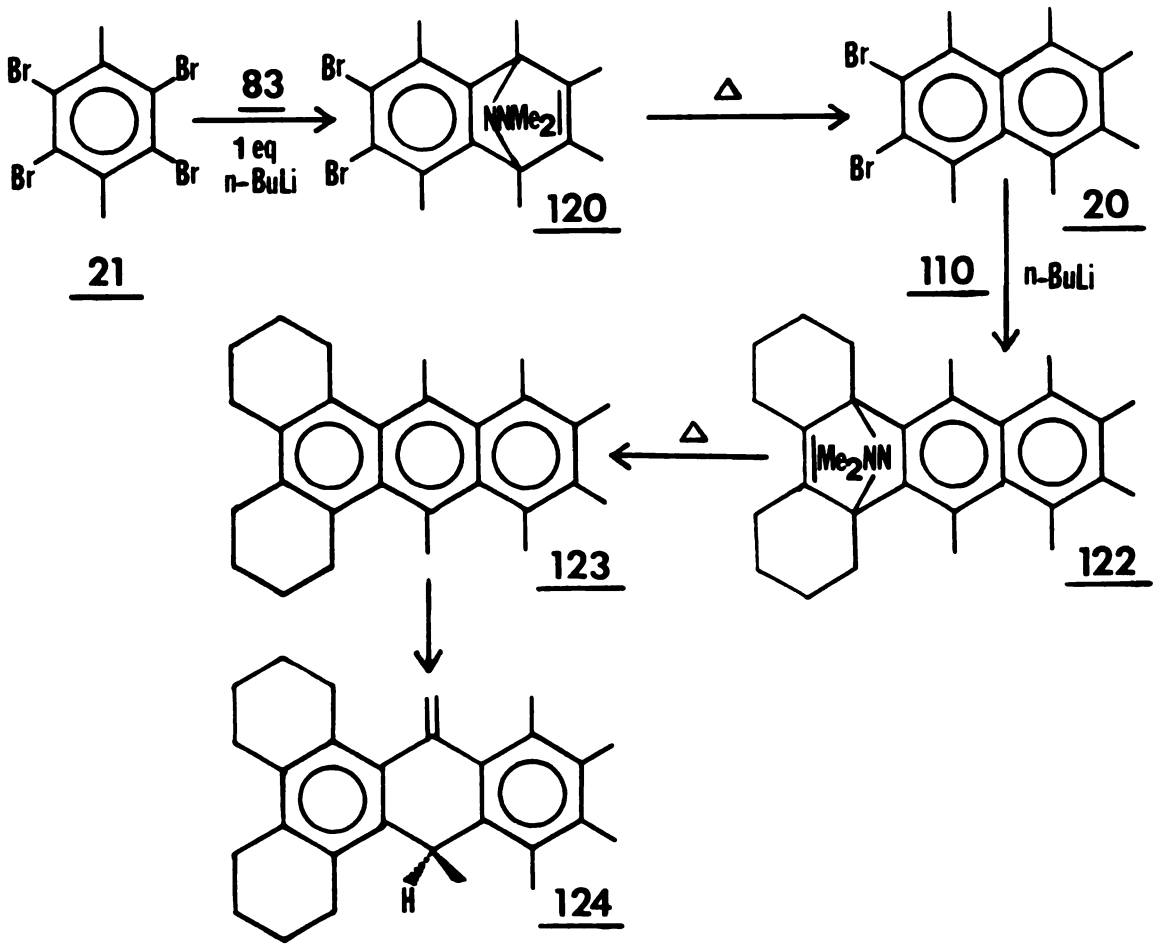
2,3-Difunctionalized triphenylenes can also be prepared by the same sequence. Thus 110 was reacted with the benzyne derived from 21 and one equivalent of n-butyllithium in toluene. The adduct 112 was obtained in 88% yield.



Similarly, 1,4-dimethyl-2,3-dibromo-5,6,7,8,9,10,11,12-octahydrotriphenylene 114 and 1,4-dimethyl-2,3-dibromotriphenylene 116 can be subsequently obtained by the same

pyrolysis and dehydrogenation process. Attempts were made to couple two triphenylenes by reacting 116 with n-butyllithium. However, only a trace of the expected bis-triphenylene 118 was detected by GC-Mass spectral analysis, along with the butylated triphenylene 119. Attempts to isolate 118 or 119 were not successful.

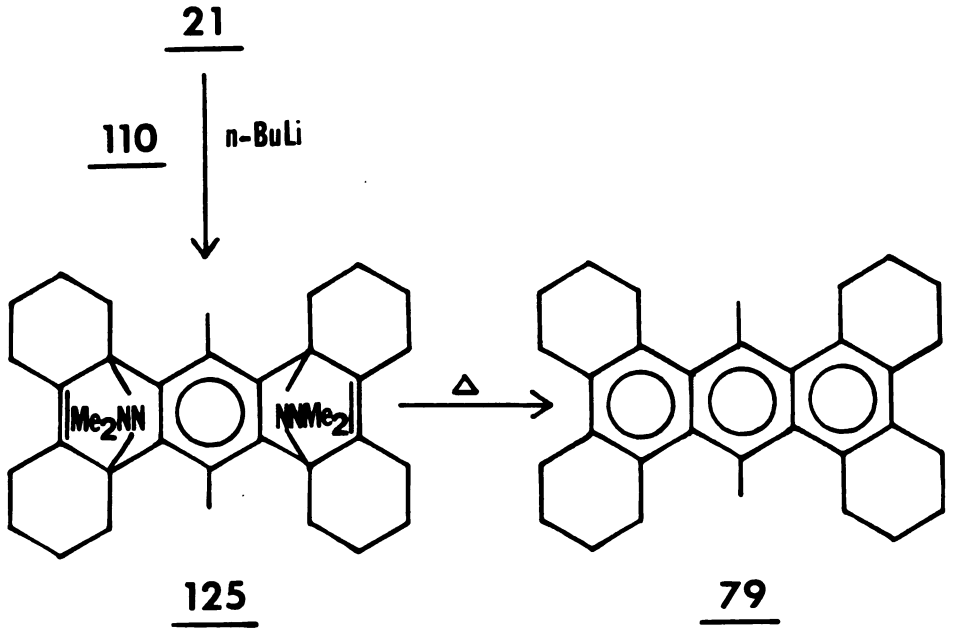
As suggested previously (Scheme 7, page 19), unsymmetric anthracenes can be prepared by using bis-aryne equivalents in a stepwise process. The following example explores this possibility. Treatment of 21 with one equivalent of n-BuLi in the presence of one equivalent of N-(dimethylamino)-tetramethylpyrrole 83, gave N-(dimethylamino)-6,7-dibromo-1,2,3,4,5,8-hexamethyl-1,4-dihydronaphthalen-1,4-imine 120 in 62% yield. This mono-adduct was then converted to 2,3-dibromohexamethylnaphthalene 20 quantitatively by pyrolysis at 200°C. Compound 20 has been prepared before from dimethylisatin in six steps with an overall yield of 39%.[8] The current synthesis, which involves only two steps with an overall yield of 62%, represents a significant improvement. Reaction of 20 with n-butyllithium and pyrrole 110 gave N-(dimethylamino)-bis-(tetrahydrobenzo[1,2;3,4])-5,6,7,8,9,10-hexamethylanthracen-1,4-imine 122, which was aromatized by heating at 150°C. This gave anthracene 123 quantitatively, as yellow crystals. Anthracene 123 was not stable in solution, and isomerized to 124 rapidly at room temperature. This rearrangement can be catalyzed by a trace of CF_3COOH, with



which the transformation of 123 to 124 was complete within 5 min. Presumably the facile isomerization of 123 is caused by the rigidity of the anthracene skeleton as a consequence of the fused ring substitution. Distortion of the molecular geometry required for accommodating the peri-interaction, is no longer as easily achieved as in decamethylanthracene.

Using this argument, an anthracene derivative such as 126 should be even more rigid and thus more labile toward

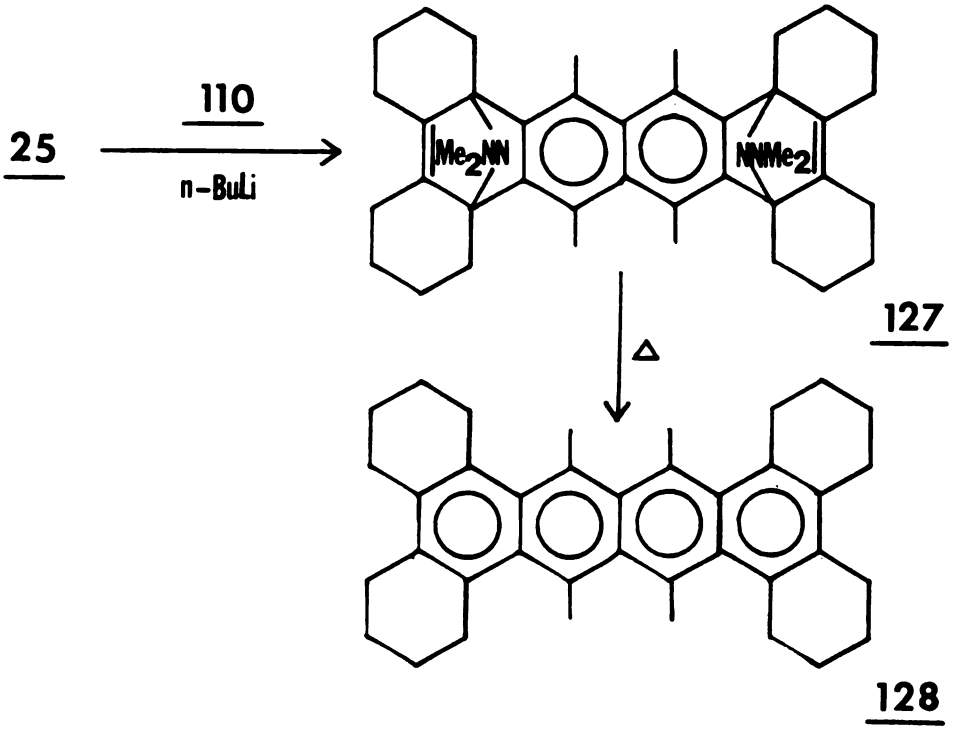
isomerization. Indeed, pyrolysis of bis-adduct 125, which



was obtained from the reaction of bis-aryne equivalent 21 with 110, gave what is presumably 79 as a yellow powder. Purification of this powder could only be accomplished by rapid recrystallization from $CHCl_3$/MeOH solution, and always gave a substantial loss of 79 by decomposition. The loss of 79 is not a clean isomerization reaction as in the case of 123. Several intractable products were found in the mixture, and they were not separable.

An even more difficult situation was encountered in the preparation of naphthacene derivative 128, obtained as a red powder from the pyrolysis of 127. A correct molecular

ion peak was found at m/e 500 in the mass spectrum of this powder. However, no satisfactory ^{1}H NMR spectrum could be obtained, probably for two reasons, the insolubility of the red powder in organic solvents and the rapid decolorization of the red solution during the period of running the spectrum. It is believed that naphthacene derivative 128 was generated by this reaction, but conclusive evidence could not be obtained.

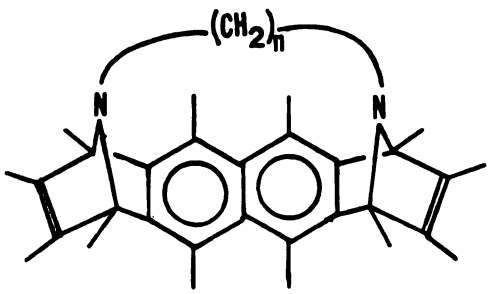


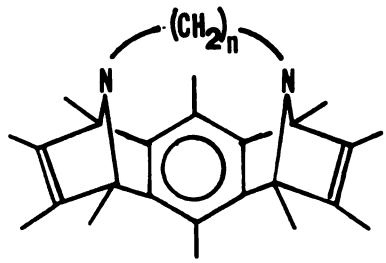
7. Attempts to Prepare Bis-adduct with a N-N Bridge.

Compounds with distorted arene rings, such as the cyclophanes, in which more than two atoms of an arene ring are

incorporated into a large ring system, have been of interest for the study of molecular strain.[35] Most investigations have dealt mainly with the geometry of the molecule itself. For instance, how much distortion from planarity can an arene ring accommodate? How will an arene ring behave when the ring and bridge are compressed face to face? The questions concern how the physical properties and reactivities will deviate from those of the normal molecule.

It seemed of interest to prepare the bridged compounds 129 - 134 to study the possibility that the planarity of the benzene or naphthalene rings could be altered by changing the number of methylene groups in the bridge. It seemed feasible to prepare these compounds either by the reaction on a bis-aryne equivalent with a bridged bis-pyrrole such as 135 - 140 in a one to one fashion, or by



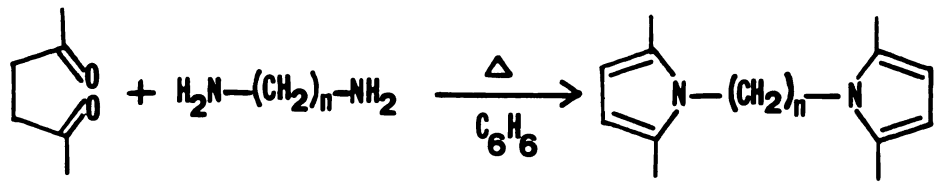


129 n=6
130 n=7
131 n=8

132 n=3
133 n=4
134 n=5

the reaction of a bis-aryne equivalent with functionalized pyrroles 145 (Scheme 10, page 57) which can subsequently undergo intramolecular cyclization to form a ring.

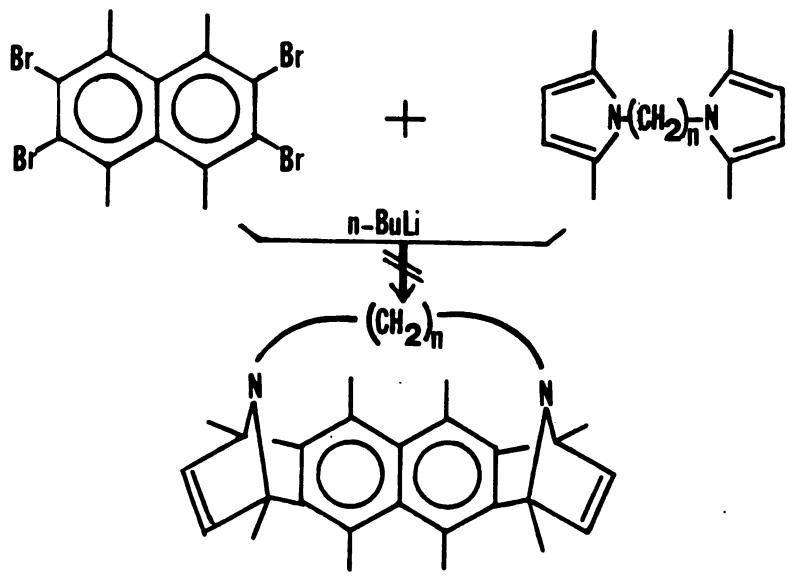
The bridged bis-pyrroles 135 - 140 were prepared in excellent yield from the corresponding diamines and 2,5-hexanedione, using the same method used for the preparation of pyrrole 45.



n: 3,4,5,6,7,8.

135—140

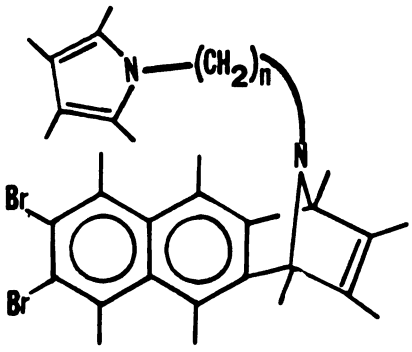
The reaction of bis-pyrrole 135 - 140 with one equivalent of bis-aryne equivalent 25 was tried in the following ways: high dilution technique, simultaneous addition, inverse



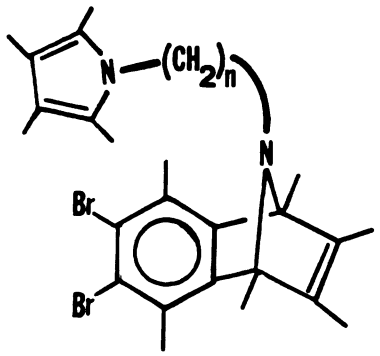
141

addition. However, no adduct of type 141 could be obtained; only polymeric residues were formed.

It was found by Hart and co-workers[11] that a mono-adduct of the type 143 can be obtained in fair yield by reacting one equivalent of n-butyllithium and tetrabromo-p-xylene with one equivalent of a bis-pyrrole in toluene at -78°C. Nevertheless the subsequent intramolecular benzyne addition did not lead to the expected bridge compound despite all efforts. Presumably, the geometry of the mono-adduct 142 is such that it can only undergo an intermolecular Diels-Alder reaction rather than the intramolecular process. Consequently, attempts to prepare and cyclize these mono-adducts were abandoned.

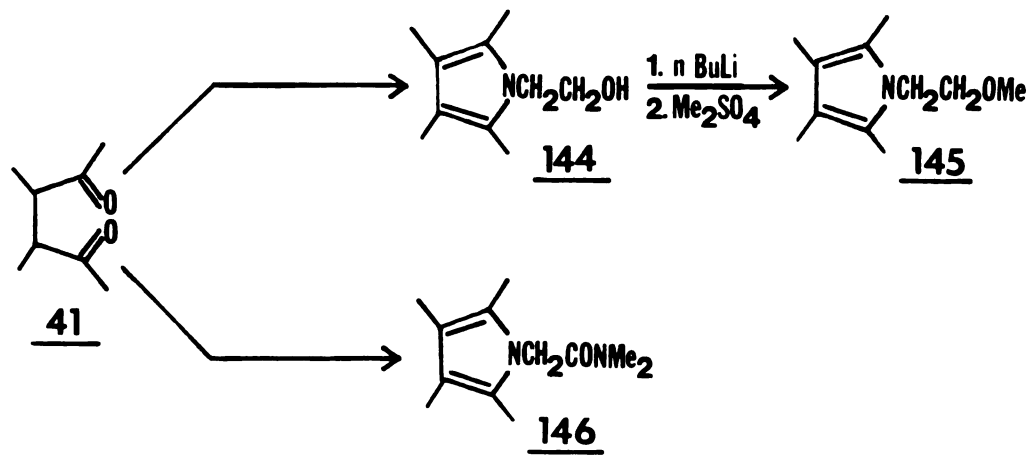


142

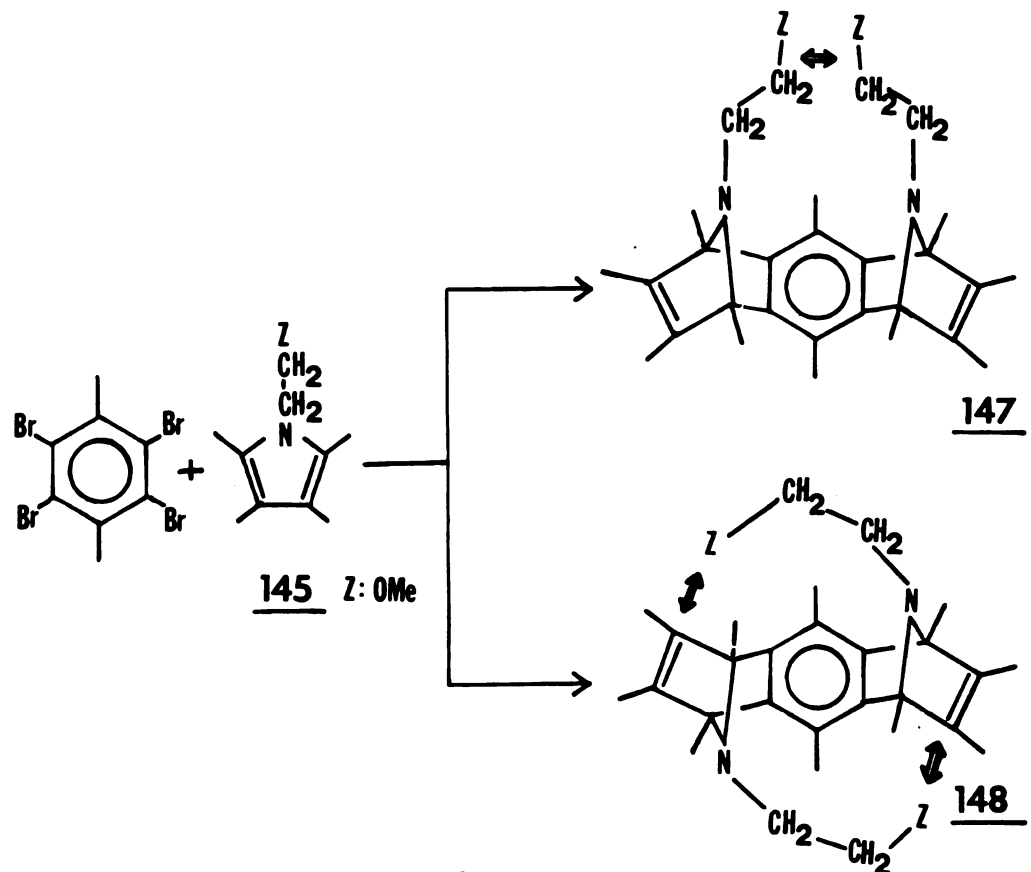


143

Instead, the second approach (Scheme 10) was tried. Pyrrole 144 was prepared by the reaction of diketone 41 with 2-aminoethanol. The O-anion of 144 was then methylated



with dimethyl sulfate to give N-(2-methoxyethyl)-pyrrole 145. One bis-adduct isomer predominated (147:148 = 1:10)



Scheme 10

from the reaction of 21 with 145 was isolated in 77% yield. Its ^{1}H NMR($CDCl_3$) spectrum was consistent with the structure, having peaks at δ1.58(s, 12 H), 1.65(s, 12 H), 2.20 (s, 6 H), 2.28(t, 4 H, J=8 Hz), 3.23(s, 6 H) and 3.33(t, 4 H, J=8 Hz). An X-ray crystallographic analysis showed that the bis-adduct had the anti configuration (Figure 4). Therefore subsequent ring cyclization to the bridged compound 133 was clearly impossible. However, it might be possible to prepare a doubly bridged compound as indicated on structure 148.

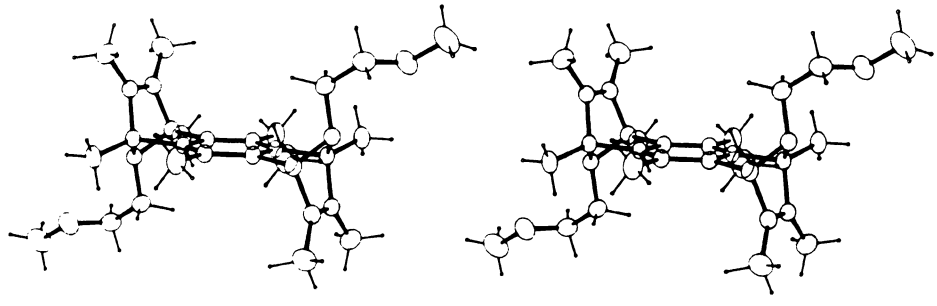
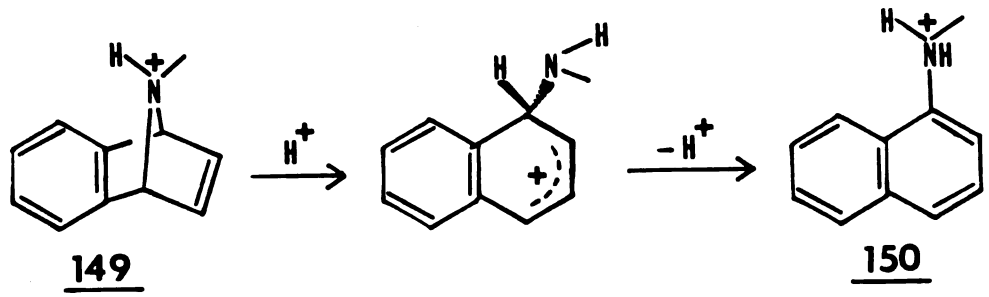


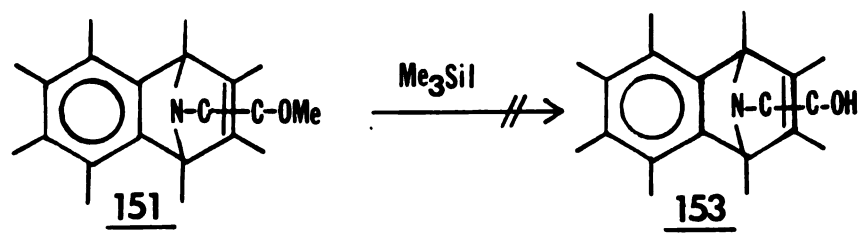
Figure 4. Stereo drawing of bis-adduct 148 (Z = OCH_3).

Attention was then focussed on manipulation of the methoxy group to a useful function for later conversions. Acidic deprotection of the methyl ether with concentrated hydrogen iodide was not plausible because it is well known that exposure of a naphthalen-1,4-imine such as 149 to acid will lead to an aromatized α-naphthylammonium salt 150.[36] Therefore, this method was not pursued. Accordingly, we applied the procedure developed by Jung.[37]

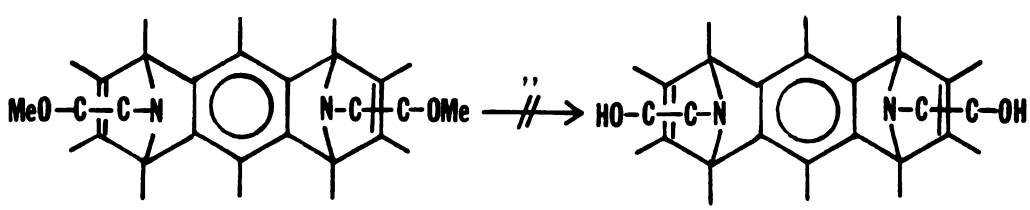


149 150

However, difficulties in removing the methyl group were encountered with this method also. More than 95% of mono-adduct 151 or dimethoxy bis-adduct 148 was recovered when the adducts were refluxed with trimethylsilyl iodide, even after 96 hours at reflux.



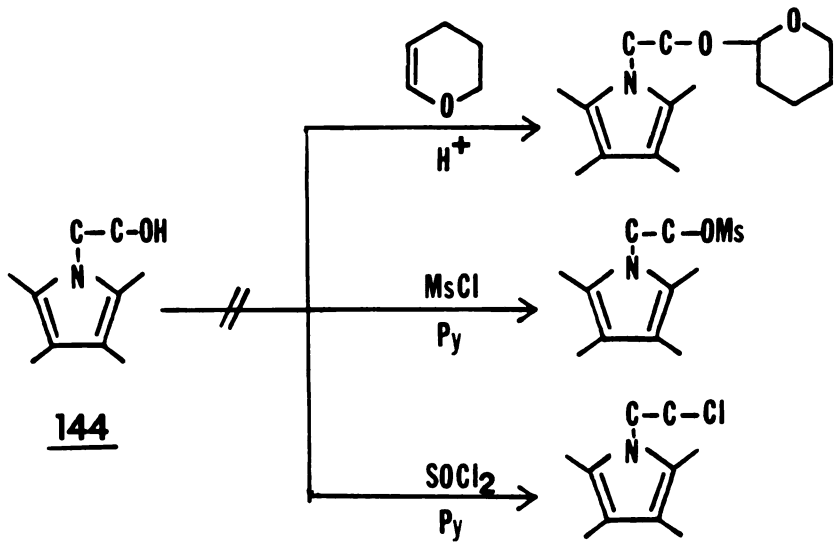
151 153



148 154

Since pyrrole 144, with the unprotected hydroxy group, did not provide any bis-adduct 154 in a bis-aryne

cycloaddition, various protecting procedures for the OH group were tried. These are listed in Scheme 11. Unfortunately none of them were successful due to the instability of pyrrole 144 in acid.

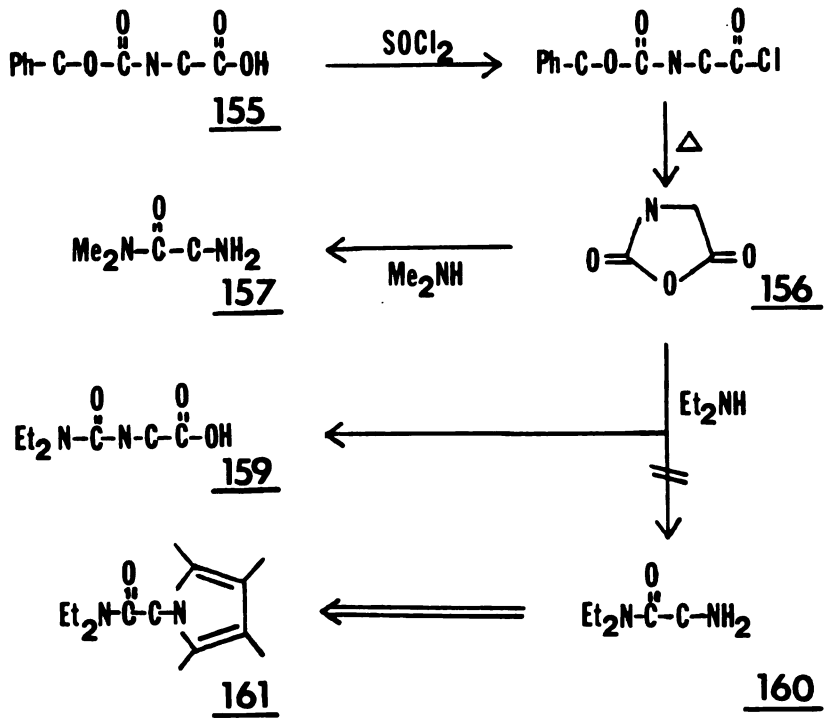


Scheme 11

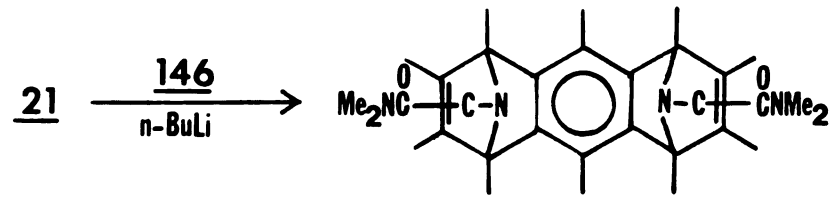
The unsatisfactory attempts at protecting the hydroxyl group or deprotecting the methoxyl group prompted us to search for another functionality. The use of N-butyllithium for generating the bis-aryne equivalent does not leave many choices. A recent study[38] on the lithiation of functionalized benzenes implies the compatibility of the N,N-dialkylamide group with n-butyllithium at low temperature. This suggested that an amide group on the pyrrole might solve this problem. The desired pyrrole could be derived from

the reaction of a diketone with the dimethylamide of glycine.

Glycine N,N-dimethylamide 157 was prepared from the reaction of glycine anhydride 156 with dimethylamine,[39] and provide pyrrole 146 (page 57) quantitatively by the previously mentioned procedure.



However, treatment of 146 with bis-aryne equivalent 21 only gave a 6% yield of bis-adduct (stereochemistry not known). Possibly the reaction was complicated by competition between the lithium-halogen exchange of 21 by n-butyllithium and nucleophilic addition to the amide group



158

by n-butyllithium. It was thought that the N,N-diethylamide pyrrole 161 would have a better chance for cycloaddition, due to a decreased tendency for 1,2-addition of n-butyllithium to the carbonyl group. Unfortunately, the reaction of diethylamine with 156 did not give the expected glycine N,N-diethylamide 160 but the acid derivative 159.

All of these difficulties discouraged us from further investigating this aspect of the project. Two possibilities for further efforts might be to search for a proper functional group which is compatible with n-butyllithium, or to adopt methods that do not require n-butyllithium to generate the bis-benzyne equivalents.

EXPERIMENTAL

1. General Procedures

^{1}H NMR spectra were measured in $CDCl_3$ or CCl_4 solution on a Varian T-60 or on a Bruker WM-250 spectrometer with chemical shifts reported in δ-units from tetramethylsilane as the internal standard. ^{13}C NMR spectra were determined on a Varian CFT-20 spectrometer. UV spectra were determined on a Unicam SP-800 or Cary-1756 spectrometer. Mass spectra were obtained with Hitachi Perkin-Elmer RMU-6 and a Finnigan 4000 spectrometer. High resolution mass spectra were obtained with a Varian CH5 spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan. The melting points were determined on a Thomas Hoover Unimelt apparatus and are uncorrected.

2. Tetrabromo-p-xylene (21)

To a solution of p-xylene (21 g, 0.23 mol) in 100 mL of CCl_4 were added dropwise six equivalents of Br_2 at room temperature with stirring. The mixture was refluxed overnight and cooled. A saturated aqueous $NaHSO_4$ solution (about 700 mL) was then introduced until the bromine color disappeared. The precipitate was collected by filtration,

and recrystallized from chloroform/methanol to give needle-like crystals of 21 (79.5 g, 94%); mp 249-251°C (lit.[40] 251-252°C); ^{1}H NMR($CDCl_3$) δ2.78(s, 6 H); mass spectrum, m/e (relative intensity) 422(100), 341(54), 262(25), 182 (21), 102(67).

3. Bis(N-methyl)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (24)

A solution of tetrabromo-p-xylene (21, 4.22 g, 10 mmol) and pentamethylpyrrole (2.74 g, 20 mmol) in anhydrous toluene (200 mL) was cooled to -78°C under argon (most of the 21 precipitates out). To this suspension n-butyllithium (22 mmol in 30 mL of hexane) was added dropwise with constant magnetic stirring. After addition (2 h), the mixture was kept at -78°C for three hours, then warmed slowly to room temperature and left for one more hour. Water (20 mL) was added, the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over magnesium sulfate and evaporated under vacuum, and the residue was recrystallized from $CHCl_3$/hexane to give 2.97 g (79%) of a mixture of the syn and anti isomers of 24. One isomer was separated from the mixture by washing with ether (1.72 g, 45%); mp 256-258°C; ^{1}H NMR($CDCl_3$) δ1.63(s, 12 H), 1.66 (s, 12 H), 1.93(s, 6 H), 2.23(s, 6 H); mass spectrum, m/e (relative intensity) 376(8), 361(1), 322(6), 266(27),

134(7); high resolution mass spectrum, calculated for $C_{26}H_{36}N_2$, 376.28786; found, 376.29012. Attempts to purify the minor isomer were not successful; it remained a mixture of the two isomers.

4. N-Methyl-bis-(tetrahydrobenzo[1,2;3,4])-6,7-dibromo-5,8-dimethylnaphthalen-1,4-imine (37)

A suspension of tetrabromide 21 (4.2 g, 10 mmol) and octahydrocarbazole[17] 49 (1.89 g, 10 mmol) in 200 mL of anhydrous toluene was cooled to -78°C, and n-BuLi (11 mmol, diluted 5-fold with hexane from the commercially available 2.4 M reagent) was added using a constant rate addition funnel over 2 h, under argon atmosphere. The mixture was stirred for 3 h, warmed to room temperature for 1 h, water (20 mL) was added, the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give crude product, which was recrystallized from methanol/chloroform to provide 3.24 g (72%) of pure adduct 37; mp 168-169°C; ^1H NMR($CDCl_3$) δ1.52 (m, 12 H), 1.85(s, 3 H), 2.20-2.65 (m, 4 H), 2.50(s, 6 H); mass spectrum, m/e (relative intensity) 453(45), 451(76), 449(40), 436(13), 423(25), 408(32), 394(13), 370(5), 290(5), 188(100).

5. Bis(N-methyl)-bis(tetrahydrobenzo[1,2;3,4])-5,6,7,8,-9,10-hexamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (38)

A solution of mono-adduct 37 (2.25 g, 5 mmol) and N-methyl-tetramethylpyrrole 45 (1.5 g, 11 mmol) in anhydrous THF (200 mL) was cooled to -78°C (most of the 37 precipitated out). To this suspension kept under argon n-BuLi (8 mmol in 30 mL of hexane) was added dropwise with constant magnetic stirring. After addition (2 h), the mixture was kept at -78°C for three additional hours, then warmed slowly to room temperature and left for one hour. Water (20 mL) and methylene chloride (50 mL) were added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried with magnesium sulfate and concentrated under vacuum. The residue was triturated with acetone (20 mL) and filtered to give 1.71 g (80%) of pure bis-adduct 38 (a mixture of two stereoisomers). The mixture was chromatographed on alumina with hexane/ether as eluent. The first fraction (0.12 g) was a mixture of two isomers, the second fraction gave a pure isomer (1.59 g, 75%); for the major isomer; mp 265-266°C; ^{1}H NMR($CDCl_3$) δ1.60-2.01(m, 12 H), 1.63(s, 6 H), 1.66(s, 6 H), 1.86(s, 3 H), 1.96(s, 3 H), 2.20-2.56(m, 4 H), 2.30 (s, 6 H); mass spectrum, m/e (relative intensity) 428(29), 413(3), 400(2), 374(27), 359(6), 188(8), 56(100); high resolution mass spectrum calculated for $C_{30}H_{40}N_2$, 428.31916;

found, 428.322426.

6. 2,3-Dimethyl-1,4-diphenyl-1,4-butanedione (43)

To a solution of propiophenone (67 g, 0.5 mol) in 40 mL of glacial acetic acid, was added potassium permanganate (30 g 0.2 mol) in small portions with stirring over 1 h (exothermic reaction), while the temperature of the mixture was kept at 90-95°C by a cooling bath. After the solution became brown (about 2 h), the mixture was refluxed for another 3 h, then cooled to room temperature, treated with water and extracted with ether. The extract was washed with 10% aqueous Na_2CO_3 solution, then water and dried ($MgSO_4$). After removal of the ether, the resulting oil was purified by chromatography on alumina with hexane as eluent, to give 13.4 g of the white 1,4-diketone 43; mp 202°C (lit.[41] no mp reported); ^1H NMR($CDCl_3$) δ1.23(d, 6 H, J=8 Hz), 3.83(m, 2 H), 7.23(m, 6 H), 7.80(m, 4 H); mass spectrum, m/e (relative intensity) 266(24), 161(17), 147(8), 105(100), 77(20).

7. 2,5-Diphenyl-1,3,4-trimethylpyrrole (47)

A mixture of 1,4-diketone 43 (4.8 g, 18 mmol), methylamine (40 mL, 40% aqueous solution) and benzene (200 mL) was heated under reflux for 10 h, the water being removed continuously with a trap. The solution was dried with $MgSO_4$ and evaporated under reduced pressure. The residue

was washed with 95% EtOH, and gave essentially pure pyrrole 47 (4.35 g, 88%) after filtration; mp 107-109°C (lit[42] 101-102°C); ^{1}H NMR($CDCl_3$) δ 2.08(s, 6 H), 3.31(s, 3 H), 7.26(s, 10 H).

8. N-Methyl-1,2,3,4,5,6,7,8-octahydrocarbazole (49)

A mixture of 1,4-diketone 109[43] (13.5 g, 0.07 mol) and 40% aqueous methylamine solution (300 mL) in 200 mL of benzene was refluxed for 8 h. Additional (200 mL) 40% methylamine solution was added and the resulting mixture was then refluxed overnight. The aqueous layer was separated and extracted with 200 mL of diethyl ether. The combined organic layers were washed with water several times, dried over anhydrous $MgSO_4$ and concentrated to give 14.8 g of crude white crystals which were recrystallized from petroleum ether to give 13 g (100%) of pyrrole 49; mp 94-96°C (lit[17] 94°C); ^{1}H NMR(CCl_4) δ1.5-1.8(m, 8 H), 2.5-2.7(m, 8 H), 3.25(s, 3 H).

9. N-Methyl-2,3,4,5-tetraphenylpyrrole (50)

To a solution of tetraphenylpyrrole 50a[18] (3 g, 8 mmol) in 150 mL of anhydrous THF was added NaH (0.29 g, 12 mmol). The resulting suspension was refluxed for 2 h. Dimethyl sulfate (10 mL) was introduced dropwise with cooling. The solution was stirred for another 10 h, then

quenched first with MeOH and then with water (5 mL each), and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was recrystallized from hexane to give 2.07 g (67%) of 50 as white crystals; mp 209-210°C (lit[44] 209-211°C); ^1H NMR(CCl_4) δ3.36(s, 3 H), 6.76, 7.1(two broad peaks, 20 H); mass spectrum, m/e (relative intensity) 385(74), 77(100).

10. Bis(N-methyl)-1,4,5,8,9,10-hexamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (51)

Using the same procedure as for the preparation of bis-adduct 24, bis-adduct 51 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and N-methyl-2,5-dimethylpyrrole (2.8 g, 20 mmol) with n-BuLi (22 mmol). The reaction gave 2.39 g of a white powder which was recrystallized from chloroform/hexane to provide 2.33 g (73%) of 51 as a mixture of the syn and anti isomers, ratio 27/73 (determined by integrating the peaks at δ1.71 and 1.98). The mixture was chromatographed on alumina with hexane/ether as the eluent. The first fraction was a mixture of two isomers; the second fraction gave a pure isomer (1.58 g). For the major isomer; mp 242-244°C; ^1H NMR($CDCl_3$) δ1.71(s, 12 H), 1.98(s, 6 H), 2.25(s, 6 H), 6.53(bs, 4 H); mass spectrum, m/e (relative intensity) 320(40), 305(22), 279(25), 265(100), 250(45), 238(99), 222(22); high resolution mass spectrum calculated for $C_{22}H_{28}N_2$, 320.22525; found, 320.22710.

11. Bis(N-methyl)-9,10-dimethyl-tetrakis(tetrahydrobenzo-[1,2;3,4;5,6;7,8]-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (52)

Using the same procedure as for bis-adduct 24, reaction of tetrabromide 21 (4.2 g, 10 mmol) with octahydrocarbazole 49 (3.8 g, 20 mmol) and n-butyllithium (25 mmol) in THF gave bis-adduct 52 (3.7 g, 76%). One of the isomers (2.33 g, 48%) could be separated by chromatography (alumina, hexane/ether); mp 282-284°C (recrystallized from $MeOH/CH_2Cl_2$); ^1H NMR($CDCl_3$) δ1.60-2.03(m, 16 H), 2.20(s, 6 H), 2.43(s, 6 H), 2.23(m, 16 H); ^{13}C NMR($CDCl_3$) δ144.81, 142.48, 127.58, 76.32, 29.78, 26.02, 24.89, 23.80, 22.84, 15.00; mass spectrum, m/e (relative intensity) 480(33), 465(7), 291(8), 188(100); high resolution mass spectrum calculated for $C_{34}H_{44}N_2$, 480.35046; found, 480.35196.

Attempts to purify the minor bis-adduct were not successful; it was always contaminated with the major bis-adduct.

12. Bis(N-methyl)-1,4,5,8,9,10-hexamethyl-2,3,6,7-tetraphenyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (53)

Using the same procedure as for bis-adduct 24, reaction of tetrabromide 21 (3 g, 7 mmol) with 3,4-diphenyl-1,2,5-trimethylpyrrole[17] 48 (3.6 g, 14 mmol) in anhydrous THF

with n-BuLi (22 mmol) gave bis-adduct 53 (3.67 g, 59%) as a mixture of two isomers. The mixture was chromatographed on alumina with ether as eluent. The first fraction (1.22 g) was a mixture of two isomers. The second fraction gave a pure isomer (2.45 g, 39%). For the pure isomer; mp 230-232°C dec; ^{1}H NMR($CDCl_3$) δ1.70(s, 12 H), 2.21(s, 6 H), 2.25(s, 6 H), 6.91(m, 20 H); mass spectrum (CI), m/e (relative intensity) 625(M+1, 76), 447(20), 268(50), 179 (100), 149(14); high resolution mass spectrum calculated for

13. Bis(N-methyl)-2,3,6,7,9,10-hexamethyl-1,4,5,8-tetraphenyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (54)

Using the same procedure as for 24, reaction of tetrabromide 21 (2.1 g, 5 mmol) with 2,5-diphenyl-1,3,4-trimethylpyrrole 47 (2.76 g, 10.5 mmol) in anhydrous toluene with n-butyllithium (15 mmol) yielded bis-adduct 54 (1.76 g, 57%) as a mixture of the syn and anti isomers. The mixture was chromatographed on alumina with ether as eluent. The first fraction (0.71 g) was a mixture of two isomers. The second fraction gave a pure isomer (1.04 g, 37%). For the major isomer; mp 270-271°C (recrystallized from MeOH/$CHCl_3$); ^{1}H NMR($CDCl_3$) δ1.46(s, 6 H), 1.60(s, 6 H), 1.86 (s, 12 H), 7.23(m, 20 H); mass spectrum, m/e (relative

intensity) 624(0.88), 569(0.99), 516(2), 452(10), 258(6), 118(100); high resolution mass spectrum calculated for $C_{46}H_{44}N_2$, 624.35046; found, 624.35021.

14. Reaction of Tetrabromo-p-xylene with n-Butyllithium in the Presence of Pyrrole 46 (or 50)

Using the same procedure as for bis-adduct 24, tetrabromide 21 (1 g, 2.4 mmol) was allowed to react with N-methyl-2,3,4,5-tetraphenylpyrrole 50 (2.0 g, 5.2 mmol) and n-BuLi (10 mmol) in anhydrous toluene at 0°C. The reaction was worked up by the process described before to give a brown residue. This residue was chromatographed on alumina with ether as eluent to give only recovered pyrrole 50 (1.672 g, 84%). Further elution of the column with methanol gave only an oily tarry substance.

Starting with pyrrole[36] 46 and using the same procedure as described above, no adduct was found in the reaction mixture; recovered pyrrole and a polymeric powder were obtained.

15. N-iso-Propyl-2,3,4,5-tetramethylpyrrole (56)

A mixture of diketone 41 (14.2 g, 0.1 mol) and 26 mL of isopropylamine (excess) in 200 mL of benzene was refluxed until no more water could be separated in a Dean-Stark trap (about 3 h). After removal of the benzene, the residual oil was distilled under reduced pressure to give

pyrrole 56 (7.0 g, 42%); bp 92-95°C/5 torr; ^{1}H NMR($CDCl_3$) δ1.40(d, 6 H, J=7 Hz), 1.88(s, 6 H), 2.15(s, 6 H), 4.28 (q, 1 H, J=7 Hz); mass spectrum, m/e (relative intensity) 165(89), 150(41), 122(100), 108(35); high resolution mass spectrum calculated for $C_{11}H_{19}N$, 165.15175; found, 165.15072.

16. Bis(N-n-butyl)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,-5,8-tetrahydroanthracen-1,4;5,8-bis-imine (60)

Using the same procedure as for bis-adduct 24, reaction of tetrabromide 21 (4.2 g, 10 mmol) with n-butyl-2,3,4,5-tetramethylpyrrole[19] (3.6 g, 20 mmol) and n-BuLi (25 mmol) in toluene gave bis-adduct 60 (2.89 g, 64%) as a mixture of the syn and anti isomers, ratio 20/80 (determined by integrating the peak at δ1.61 and 1.55). One of the isomers (2.19 g, 48%) was isolated pure by recrystallizing the mixture from acetonitrile; mp 204-205°C; ^{1}H NMR($CDCl_3$) δ0.91 (m, 6 H), 1.33(m, 8 H), 1.61(s, 12 H), 1.65(s, 12 H), 2.06(m, 4 H), 2.25(s, 6 H); ^{13}C NMR($CDCl_3$) δ148.43, 145.58, 125.16, 77,66, 45.79, 34.59, 21.33, 17.16, 14.79, 14.10, 11.55; mass spectrum, m/e (relative intensity) 460(0.58), 406(0.63), 363(2), 352(1), 308(5), 264(0.26), 250(0.35), 326(0.44), 98(100).

Anal. Calcd for $C_{32}H_{48}N_2$: C, 83.42; H, 10.50.
Found : C, 83.47; H, 10.41.

Attempts to purify the minor isomer by chromatography (alumina, hexane/ether) were not successful. It always

was eluted as a mixture of two isomers.

17. Bis(N-iso-propyl)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (61)

Using the same procedure as for bis-adduct 24, reaction of tetrabromide 21 (4.2 g, 10 mmol) and pyrrole 56 (3.3 g, 20 mmol) with n-BuLi (25 mmol) in toluene gave bis-adduct (3.24 g) 61 as a mixture of the syn and anti isomers, ratio 25/75 (determined by integrating the peak at δ1.01 and 1.05 of the ^{1}H NMR spectrum). The major isomer was isolated by recrystallizing the mixture from methanol/water (2.12 g, 65%); mp 243-245°C; ^{1}H NMR($CDCl_3$) δ1.05(d, 12 H, J=7 Hz), 1.78(s, 12 H), 1.91(s, 12 H), 2.38(s, 6 H), 2.91(q, 2H, J=7 Hz); ^{13}C NMR($CDCl_3$) δ150.03, 147.17, 122.93, 76.03, 47.90, 23.97, 18.08, 15.78, 11.84; mass spectrum, m/e (relative intensity) 432(30), 417(7), 378(16), 349(65), 294(66), 276(15), 263(12), 149(18), 84(100).

Anal. calcd for $C_{30}H_{44}N_2$: C, 83.27; H, 10.24; N, 6.47.
Found : C, 83.40; H, 10.40; N, 6.57.

18. Bis(N-benzyl)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5-8-tetrahydroanthracen-1,4;5,8-bis-imine (62)

Using the procedure for bis-adduct 24, reaction of tetrabromide 21 (4.2 g, 10 mmol) and pyrrole 57 (4.26 g, 20 mmol) with n-BuLi (25 mmol) in anhydrous toluene at

-78°C provided bis-adduct 62 (3.21 g, 61%) as a mixture of the syn and anti isomers, ratio 25/75 (determined by integrating the peak at δ1.53 and 1.55 of ^{1}H NMR spectrum). One of the isomers could be isolated from the mixture by recrystallizing it from hexane/chloroform. However, purification of the minor isomer by chromatography (alumina, hexane/ether) was not successful; for the major isomer; mp 268-270°C; ^{1}H NMR($CDCl_3$) δ1.55(s, 12 H), 1.66(s, 12 H), 2.23(s, 6 H), 3.31(s, 4 H), 7.10(m, 10 H); mass spectrum, m/e (relative intensity) 528(0.4), 474(0.8), 420(1), 397 (2), 342(10), 329(1), 264(8), 91(100).

Anal. Calcd for $C_{38}H_{44}N_2$: C, 86.31; H, 8.38; N, 5.29.
Found : C, 86.40; H, 8.46; N, 5.25.

19. Bis(N-phenyl)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,-5,8-tetrahydroanthracen-1,4;5,8-bis-imine (63)

Using the same procedure as for bis-adduct 24, reaction of tetrabromide 21 (4.2 g, 10 mmol) with pyrrole[19] 58 (4 g, 20 mmol) and n-BuLi (25 mmol) in toluene gave bis-adduct 63 (2.56 g, 51%) as a mixture of two isomers. The major isomer could be separated from the mixture by recrystallizing it from methanol (1.56 g, 31%). Attempts to purify the minor isomer by chromatography (alumina, hexane/ether) were not satisfactory; it was contaminated by the major isomer. For the major isomer; mp 293-294°C;

^{1}H NMR($CDCl_3$) δ1.68(s, 12 H), 1.76(s, 12 H), 2.20(s, 6 H), 6.86(m, 10 H); mass spectrum, m/e (relative intensity) 500(3), 446(3), 383(8), 328(42), 291(11), 193(8), 118(100).

Anal. Calcd for $C_{36}H_{40}N_2$: C, 86.35; H, 8.05; N, 5.59.
Found : C, 86.40; H, 8.11; N, 5.61.

20. Reaction of Bis-adduct 52 with m-CPBA

To a suspension of bis-adduct 52 (500 mg, 1 mmol) and anhydrous sodium carbonate (234 mg, 2.2 mmol) in 30 mL of acetonitrile at 0°C, was added dropwise a solution of m-CPBA (421 mg, Aldrich technical grade, 85%, 2.2 mmol) in 20 mL of CH_3CN. During the addition, the solution turned yellow and then brown immediately. The resulting solution was refluxed for 5 h and cooled. Water (30 mL) and chloroform (100 mL) were added. The aqueous layer was separated and extracted with 30 mL of chloroform. The combined organic layers were dried with $MgSO_4$ and concentrated to give a brown residue which did not reveal the expected peak at 422 in the mass spectrum. Attempts to resolve the residue by TLC (alumina, hexane/benzene) were not successful.

21. N-(Dimethylamino)-tetramethylpyrrole (83)

A mixture of 3,4-dimethyl-2,5-hexanedione 41 (23.6 g, 0.16 mol) and 1,1-dimethylhydrazine (10 g, 0.16 mol) in 300 mL of benzene was refluxed with a Dean-Stark trap until no more water was formed (about 10 h). The mixture was

concentrated and distilled under reduced pressure to give pyrrole 83 (24.7 g, 90%) as a yellow oil; bp 88-92°C/4 torr; ^{1}H NMR(CCl_4) δ1.73(s, 6 H), 2.03(s, 6 H), 2.76(s, 6 H); IR(neat) 1460(s), 1380(m), 1360(s), 1250(w), 1075(m), 925(m) cm^{-1}; mass spectrum, m/e (relative intensity) 166 (100), 151(73), 136(12), 125(24), 122(90), 110(96), 106(15).

22. N-(Dimethylamino)-1,2,3,4,5,6,7,8-octamethyl-1,4-dihydronaphthalen-1,4-imine (86)

Using the same procedure as for the preparation of 37, a mixture of dibromide 85 (5.2 g, 18 mmol) and pyrrole 83 (3.4 g, 20 mmol) was treated with n-BuLi (27 mmol) in toluene. The crude product was purified by column chromatography over alumina with methylene chloride/hexane (1:1) as eluent, followed by recrystallization from chloroform/methanol to give pure 86 (4.35 g, 82%); mp 127-129°C; ^{1}H NMR($CDCl_3$) δ1.60(s, 6 H), 1.93(s, 6 H), 2.08(s, 6 H), 2.21(s, 6 H), 2.30(s, 6 H); ^{13}C NMR($CDCl_3$) δ147.16, 131.96, 126.65, 76.88, 45.31, 17.09, 16.26, 15.82, 11.13; IR(CCl_4) 1450(s), 1380(s), 1260(w), 1150(w), 1075(m) cm^{-1}; mass spectrum, m/e (relative intensity) 298(M^+, trace), 254 (trace), 240(100), 225(30), 195(5), 179(4).

Anal. Calcd for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13; N, 9.38.
Found : C, 80.62; H, 10.19; N, 9.45.

23. Octamethylnaphthalene (18)

In a 50 mL round-bottomed flask was placed the finely powdered imine 86 (300 mg. 1 mmol). The flask was fitted with a Micro-Hickman still for collecting the volatile liquid which was generated during the pyrolysis. The reaction flask was heated to 200°C in an oil bath under argon until no more bubbling was seen (about 10 min) and the residue was triturated with MeOH. An off-white crude product was obtained which upon recrystallization from methanol and hexane, gave naphthalene 18 (242 mg, 100%); mp 184-185°C (lit[3] 181-185°C); ^{1}H NMR($CDCl_3$) δ2.30(s, 12 H), 2.46(s, 12 H).

The volatile liquid trapped in the still was collected and analyzed by GC-Mass spectrometer. The GC trace showed that the liquid was a mixture of more than ten components with uninterpretable m/e numbers. The trapping experiment was repeated several times, but the composition of the liquid was not reproducible. Therefore, no further work was tried to identify the components of the mixture.

24. Bis(N-dimethylamino)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (87)

Bis-adduct 87 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and N-(dimethylamino)tetramethylpyrrole 83 (3.4 g, 20.4 mmol) with n-BuLi (25 mmol) in toluene using the same procedure as for bis-adduct 24.

The crude product was recrystallized from hexane/methylene chloride to give 87 (2.76 g, 64%) as white crystals which were a mixture of the syn and anti isomers. The mixture was resolved by column chromatography over alumina with hexane as eluent. The first fraction gave one pure isomer of 87 (1.42 g, 33%, stereo configuration not known); mp 203-206°C; ^{1}H NMR($CDCl_3$) δ1.61(s, 12 H), 1.75(s, 12 H), 2.23(s, 6 H), 2.35(s, 12 H); IR(CCl_4) 1455(m), 1440(s), 1375(m), 1245(w), 1090(w), 1050(w) cm^{-1}; mass spectrum, m/e (relative intensity) no M^+, 318(100), 303(16), 273(5), 85(16), 58(9).

The second fraction also consisted of white crystals (1.34 g, 31%); mp 190-191°C; ^{1}H NMR($CDCl_3$) δ1.61(s, 24 H), 2.20(s, 6 H), 2.28(s, 12 H); mass spectrum, m/e (relative intensity) no M^+, 318(100), 303(23), 288(6), 273(8), 85(21).

25. Pyrolysis of Bis-adduct 87

Crystalline bis-adduct 87 (500 mg, 1.15 mmol) was heated at 165°C in an oil bath under reduced pressure for 50 min. The residue was chromatographed on alumina (benzene/hexane = 1:1) to give decamethylanthracene 16 (165 mg, 45%) and its tautomer 89 (132 mg, 36%). Each compound (16, 89) had the same spectroscopic data (^{1}H NMR, Mass) as those of authentic samples.

When the pyrolysis of bis-adduct 87 was carried out for 20 min under the same conditions as in the above experiment, it was possible to isolate the mono-imine 88 from the reaction mixture by column chromatography (alumina, hexane/ether). Further pyrolysis of 88 also gave a mixture of 16 and 89 with the same ratio as in the pyrolysis of bis-adduct 87. For mono-imine 88; mp 192-194°C; ^{1}H NMR($CDCl_3$) δ1.66(s, 6 H), 1.86(s, 6 H), 2.26(s, 6 H), 2.33(s, 6 H), 2.43(s, 6 H), 2.50 (s, 6 H); mass spectrum, m/e (relative intensity) no M^+, 332(trace), 318(53), 303(22), 273(7), 43(100).

26. Oxidation of Bis-adduct 87 with m-CPBA

To a mixture of m-CPBA (517 mg, Aldrich technical grade, 85%, 2.5 mmol) and Na_2CO_3 (340 mg, 3.2 mmol) in 50 mL of acetonitrile was added dropwise a solution of bis-adduct 87 (500 mg, 1.15 mmol) in 20 mL of methylene chloride. The mixture was stirred for 5 min, then heated under reflux for 2 h. The solvent was removed by vacuum, and the residue was taken up in methylene chloride and washed with water three times. The organic layer was dried over anhydrous magnesium sulfate, concentrated and chromatographed on alumina (benzene:hexane = 1:1) to give anthracene 16 (260 mg, 72%) and its tautomer 89 (45 mg, 12%).

27. p-Dimethoxy-tetrabromobenzene (92)

A mixture of p-dimethoxybenzene (27.6 g, 0.2 mol) and 48 g of bromine in 50 mL of CCl_4 was stirred for 6 h at room temperature. A saturated $NaHSO_4$ solution was added until the bromine color disappeared. The precipitate was filtered and washed with methanol to give dibromo-dimethoxybenzene (52 g, 89%); mp 138-139°C (lit[45] 102-104°C); ^1H NMR($CDCl_3$) δ3.78(s, 6 H), 6.96(s, 2 H); mass spectrum, m/e (relative intensity) 298(51), 296(100), 294(50), 283 (34), 281(62), 279(31), 187(22), 185(21).

The crystals were used for further bromination by the following procedure. A suspension of dibromide (29.6 g, 0.1 mol) and 48 g of bromine with a catalytic amount of I_2 (0.5 g) in 50 mL of CCl_4 was refluxed overnight and then cooled. A saturated aqueous $NaHSO_4$ solution was then introduced slowly until the red color of bromine disappeared. The precipitate was collected and recrystallized from chloroform/methanol to give 92 (37.4 g, 83%); mp 193-195°C (lit[45] 194°C) ^1H NMR ($CDCl_3$) δ3.76(s, 6 H); mass spectrum, m/e (relative intensity) 456(59), 454(100), 452(61), 441(14), 439(78), 437(44).

28. Bis(N-(dimethylamino))-9,10-dimethoxy-1,2,3,4,5,6,7,8-octamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (93)

Bis-adduct 93 was prepared by the reaction of tetrabromohydroquinone dimethyl ether 92 (4.54 g, 10 mmol) and pyrrole 83 (3.4 g, 20.4 mmol) with n-BuLi (25 mmol) in anhydrous THF as in the preparation of bis-adduct 24. The bis-adduct 93 (3.22 g, 69%) was obtained as a mixture of two isomers by recrystallizing the reaction residue with methanol/ether, ratio 45/55 (determined by integrating the peak at δ3.6 and 3.63 in the ^{1}H NMR spectrum). One of the isomers could be separated from the mixture by column chromatography (alumina, hexane/ether). The first fraction was a mixture of the two isomers (1.38 g). The second fraction gave a pure isomer (1.76 g, 38%); for the pure isomer; mp 166-169°C; ^{1}H NMR($CDCl_3$) δ1.40(s, 24 H), 2.41(s, 12 H), 3.60(s, 6 H); ^{13}C NMR($CDCl_3$) δ147.30, 146.14, 144.42, 76.59, 63.56, 45.02, 14.32, 11.05; IR(CCl_4) 1460 (s), 1420(s), 1380(m), 1270(m), 1220(m), 1080(m), 1030(s) cm^{-1}; mass spectrum, m/e (relative intensity) no M^+, 350(43), 335(100), 290(7), 175(12), 117(6), 85(16).

29. 9,10-Dimethoxy-1,2,3,4,5,6,7,8-octamethylanthracene (95)

Bis-adduct 93 (466 mg, 1 mmol) was pyrolyzed at 180°C under reduced pressure (20 torr) for 30 min. The residue

was recrystallized from methanol/ether (1:1) to give anthracene 95 (347 mg, 99%) as yellow crystals; mp 118-120°C; ^{1}H NMR($CDCl_3$) δ2.38(s, 12 H), 2.76(s, 12 H), 3.33 (s, 6 H); IR(CCl_4) 1675(s), 1460(s), 1380(m), 1360(s), 1325(s), 1210(m), 1080(s), 1045(s), 920(s) cm^{-1}; UV(cyclohexane) λ_{max} 418 nm (logε 4.06), 399(4.14), 378(4.07), 280(5.27); mass spectrum, m/e (relative intensity) 350 (25), 335(100), 175(45), 160(33), 138(15), 130(16), 115(12), 84(12).

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63.
Found : C, 82.11; H, 8.64.

30. N-(Dimethylamino)-9,10-dimethoxy-1,2,3,4,5,6,7,8-octamethyl-1,4-dihydroanthracen-1,4-imine (94)

When the pyrolysis of bis-adduct 93 was carried out for only 10 min under the same conditions as in the preceding experiment, it was possible to isolate mono-imine 94 from the reaction mixture by column chromatography (alumina, hexane/benzene). Further pyrolysis of 94 converted it to anthracene 95 quantitatively.

For mono-imine 94: mp 153-155°C; ^{1}H NMR($CDCl_3$) δ1.66 (s, 6 H), 1.86(s, 6 H), 2.30(s, 6 H), 2.63(s, 6 H), 2.70 (s, 6 H), 3.51(s, 6 H); ^{13}C NMR($CDCl_3$) δ147.50, 144.47, 138.83, 134.33, 128.53, 128.39, 76.19, 62.34. 45.03, 17.09, 17.00, 14.66, 10.51; IR(CCl_4) 1640(m), 1450(m), 1380(m), 1340(s), 1220(s), 1055(s) cm^{-1}; mass spectrum, m/e

(relative intensity) no M^+, 350(35), 336(24), 335(100), 277(5), 175(9).

31. Bis(N-[dimethylamino])-1,2,3,4,5,6,7,8,9,10,11,12-dodecamethyl-1,4,7,10-tetrahydronaphthacen-1,4;7,10-bis-imine (96)

Bis-adduct 96 was prepared by the reaction of 2,3,6,7-tetrabromo-1,4,5,8-tetramethylnaphthalene 25 (1.8 g, 3.6 mmol) and pyrrole 83 (1.31 g, 7.9 mmol) with n-BuLi (10 mmol) in anhydrous THF by the same procedure used for the preparation of 24. Bis-adduct 96 (1.14 g, 62%, isomeric mixture) was obtained by triturating the reaction residue with hexane and filtering, ratio 55/45 (determined by integrating the peak at δ1.73 and 1.86 in ^{1}HMR spectrum). One of the isomers (0.51 g, 27%) could be separated from the mixture by chromatography (alumina, ether); mp 180-182°C dec; ^{1}H NMR($CDCl_3$) δ1.63(s, 12 H), 1.73(s, 12 H), 2.33 (s, 12 H), 2.63(s, 12H); mass spectrum, m/e (relative intensity) no M^+, 454(1), 396(88), 381(22), 366(10), 351(10), 183(5), 160(6), 43(100).

Separation of the minor isomer was not satisfactory; it was always contaminated with the major isomer.

32. Dodecamethylnaphthacene (28)

The fine powder of bis-adduct 96 was heated at 185°C under reduced pressure (25 torr) for 30 min. The red residual powder was recrystallized from chloroform/methanol to give naphthacene 28 (387 mg, 98%) as red shiny crystals; mp 265-267°C (lit[13] 265-266°C); ^{1}H NMR($CDCl_3$) δ2.32(s, 12 H), 2.66(s, 12 H), 2.98(s, 12 H).

33. Bis(N-[dimethylamino])-1,4,5,8,9,10-hexamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (98)

The bis-imine 98 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and N-(dimethylamino)-2,5-dimethylpyrrole[16] 97 (3.0 g, 22 mmol) with n-BuLi (25 mmol) in anhydrous toluene using the same procedure as for the preparation of bis-adduct 24. The residue was triturated with acetonitrile (20 mL) to give bis-adduct 98 as a mixture of the syn and anti isomers. The mixture was chromatographed on alumina (hexane/ether) to give a pure isomer (73 mg, 2%) and a mixture of two isomers (181 mg); For the pure bis-adduct; mp 170-171°C; ^{1}H NMR($CDCl_3$) δ1.80 (s, 12 H), 2.33(s, 6 H), 2.38(s, 12 H), 6.48(bs, 4 H); mass spectrum, m/e (relative intensity) 320(1), 305(0.5), 291(0.4), 276(15), 262(100), 247(29), 232(6), 217(5).

34. 2-(Dimethylamino)-1,3,4,7-tetramethylisoindole (103)

N-(Dimethylamino)-2,5-dimethylpyrrole[16] (3.36 g, 25 mmol), 2,5-hexanedione (4 g, 35 mmol) and aqueous acetic acid (80% V/V, 125 mL) were refluxed under argon for 20 h. The cooled mixture was basified (50% aqueous NaOH) and the precipitated solid was filtered off, washed with water and dried under vacuum to give crude isoindole 103 (2.7 g, 43%). ^{1}H NMR($CDCl_3$) δ2.55(s, 6 H), 2.65(s, 6 H), 2.89 (s, 6 H), 6.28(s, 2 H).

This is a very unstable substance which turns black rapidly upon exposure to air. It was therefore used for the following reaction without further purification.

35. Attempt to Prepare 2-(Dimethylamino)-1,3,4,5,6,7-isoindole (103a)

Starting with 3,4-dimethyl-2,5-hexanedione 41 and using the same procedure as described in the preceding experiment, the reaction gave only a black polymeric residue. No condensation product 103a could be isolated from the residue.

36. Bis(N-[dimethylamino])-1,4,5,6,7,8,11,12,13,14-decamethyl-5,7,12,14-tetrahydropentacen-5,14;7,12-bisimine (104)

Bis adduct 104 was prepared by the reaction of tetrabromide 21 (2.7 g, 10 mmol) and isoindole 103 (freshly prepared from 3.36 g of 2,4-hexanedione and 4 g of N-(dimethylamino)-2,5-dimethylpyrrole with n-BuLi (25 mmol) using the same procedure as for the preparation of bis-adduct 24. The reaction gave a gray residue which was chromatographed on alumina with ether as eluent to give one pure isomeric bis-adduct 104 (1.88 g, 56%); mp 285-286°C; ^{1}H NMR($CDCl_3$) δ2.14(s, 12 H), 2.34(s, 12 H), 2.56 (s, 6 H), 6.53(s, 4 H); ^{13}C NMR($CDCl_3$) δ150.75, 148.98, 128.47, 127.73, 122.06, 76.17, 19.48, 19.00, 15.25; mass spectrum, m/e (relative intensity) 534(1), 490(3), 476(7), 432(7), 418(15), 391(6), 85(100).

Anal. Calcd for $C_{36}H_{46}N_4$: C, 80.86; H, 8.66; N, 10.47.
Found : C, 80.49; H, 8.56; N, 10.31.

Further elution of the column with ethyl acetate only provided a purplish residue.

37. Pyrolysis of Bis-adduct 104

The crystalline bis-adduct 104 (534 mg, 1 mmol) was heated in an oil bath at 185°C under reduced pressure (20 torr, 30 min). The white crystals turned black slowly.

After 30 min at 185°C, the residue was cooled and chromatographed on alumina with benzene as eluent. Only a trace of bis-adduct 104 could be recovered from the black tar.

38. Bis(N-methyl)-1,4,5,6,7,8,11,12,13,14-decamethyl-5,7,-12,14-tetrahydropentacen-5,14;7,12-bis-imine (106)

The imine 106 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and pentamethylisoindole 107 (freshly prepared from the reaction of 3.3 g of 2,5-hexanedione and 3.6 g of 1,2,5-trimethylpyrrole with the procedure developed by Bonnett[32]) with n-BuLi (25 mmol) in anhydrous toluene, following the procedure for the preparation of bis-adduct 24. The reaction gave only one bis-adduct (stereochemistry not known, 2.01 g, 42%) which was obtained by chromatographing the residue on alumina with chloroform/ether as eluent; mp above 300°C; ^{1}H NMR ($CDCl_3$) δ2.04 (s, 6 H), 2.06(s, 12 H), 2.35(s, 12 H), 2.52(s, 6 H), 6.55(s, 4 H); mass spectrum, m/e (relative intensity) 476(9), 461(7), 421(13), 406(1), 238(3), 186(6), 56(100); high resolution mass spectrum calculated for

39. Reaction of m-CPBA with Bis-adduct 104 (or 106)

To a suspension of m-CPBA (250 mg, Aldrich technical grade, 85%, 1.2 mmol) and Na_2CO_3 (1 g, 7 mmol) in 50 mL of chloroform at 0°C, was added dropwise a solution of

bis-imine 104 (534 mg, 1 mmol) in 20 mL of chloroform. The solution was stirred for 20 min at 0°C then heated under reflux for 30 min. The solution turned deep brown at this point. Water (50 mL) was added and the organic layer was separated and dried ($MgSO_4$). A black residue was obtained from which no pure substance could be isolated.

The same oxidation procedure was also applied to the bis-imine 106 with a similar result.

40. N-(Dimethylamino)-octahydrocarbazole (110)

A mixture of 2,2'-biscyclohexanone[43] (20 g, 0.1 mol) and 1,1-dimethylhydrazine (15 mL) in benzene (300 mL) was heated under reflux overnight. The solution was concentrated and distilled under reduced pressure to give octahydrocarbazole 110 (18.4 g, 82%); bp 126-130°C/0.4 torr; ^{1}H NMR($CDCl_3$) δ1.66(m, 8 H), 2.16(m, 4 H), 2.53(m, 4 H), 2.76(s, 6 H); IR(neat) 1460(m), 1375(m); mass spectrum, m/e (relative intensity) 218(100), 203(58), 189(24), 174 (48), 161(10), 148(65); high resolution mass spectrum calculated for $C_{14}H_{22}N_2$, 218.17830, found, 218.17859.

41. N-(Dimethylamino)-bis(tetrahydrobenzo[1,2;3,4])-5,6,-7,8-tetramethyl-1,4-dihydronaphthalen-1,4-imine (111)

Imine 111 was prepared by the reaction of dibromoprehnitene 85 (2.92 g, 10 mmol) and N-(dimethylamino)-octahydrocarbazole 110 (2.18 g, 10 mmol) with n-BuLi (15 mmol)

in anhydrous THF using the procedure for the preparation of mono-adduct 37. The reaction residue was triturated with hexane/acetone to give 111 (2.17 g, 62%); mp 166-167°C; ^{1}H NMR($CDCl_3$) δ1.75-1.78(m, 8 H), 2.01-2.55(m, 4 H), 2.06(s, 6 H), 2.23(s, 6 H), 2.26 (s, 6 H), 2.46(m, 4 H); ^{13}C NMR($CDCl_3$) δ146.71, 144.07, 132.41, 127.01, 75.22, 46.10, 29.46, 24.50, 23.89, 23.54, 16.41, 16.03; mass spectrum, m/e (relative intensity) no M^+, 304(2), 292(100), 277(19), 262(5), 249(12), 235(5), 219(8).

42. N-(Dimethylamino)-bis(tetrahydrobenzo[1,2;3,4])-6,7-dibromo-5,8-dimethyl-1,4-dihydronaphthalen-1,4-imine (112)

Dibromo-imine 112 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and octahydrocarbazole 110 (2.18 g, 10 mmol) with n-BuLi (15 mmol) in anhydrous toluene, using the same procedure as for the preparation of mono-imine 37. The reaction residue was triturated with ethanol to give pure 112 (4.24 g, 88%); mp 189-191°C; ^{1}H NMR($CDCl_3$) δ1.44-2.20(m, 12 H), 2.33(s, 6 H), 2.56(s, 6 H) 2.20-2.61(m, 4 H); mass spectrum, m/e (relative intensity) no M^+, 434(trace), 424(61, 422(100), 420(46), 344(9), 342 (12), 262(18), 247(16), 234(20), 209(28), 203(32), 191(23).

43. 1,2,3,4,5,6,7,8-Octahydro-9,10,11,12-tetramethyltriphenylene (113)

A suspension of imine 117 (1.59 g, 5 mmol; see page 93) and 1 g of Na_2CO_3 in 50 mL of CH_3CN was cooled to 0°C. To this suspension m-CPBA (1.11 g, Aldrich grade, 85%) in 20 mL of CH_3CN was added dropwise with constant magnetic stirring. After addition, the mixture was refluxed for 3 h. Water (20 mL) and ether (100 mL) were added, the layers were separated, the aqueous layer was extracted with ether (50 mL), and the combined organic layers were dried and concentrated under vacuum. The residue was washed with 10 mL of MeOH to give pure 113 (992 mg, 69%). The same hydrocarbon 113 was also prepared quantitatively by the pyrolysis of 111 at 250°C for 1 h; mp 172-174°C; ^{1}H NMR($CDCl_3$) δ1.5-2.05(m, 8 H), 2.13(s, 6 H), 2.33(s, 6 H), 2.50(m, 4 H), 2.83(m, 4 H); ^{13}C NMR($CDCl_3$) δ134.58, 132.66, 131.96, 131.04, 128.75, 32.66, 26.90, 23.57, 21.72, 16.98 (two sp^3 carbons accidentally showed absorptions at 23.57); mass spectrum, m/e (relative intensity) 292(100), 277(19), 264(8), 249 (12), 234(6), 219(8).

44. 1,4-Dimethyl-2,3-dibromo-5,6,7,8,9,10,11,12-octahydrotriphenylene (114)

Crystalline dibromo-imine 112 (478 mg, 1 mmol) was heated in an oil bath at 190-200°C for 25 min. The residue

was recrystallized from methanol/chloroform to give 114 (407 mg, 97%) as white crystals; mp 217-219°C; ^{1}H NMR($CDCl_3$) δ1.5-2.15(m, 8 H), 2.15-2.85(m, 8 H), 2.60(s, 6 H); mass spectrum, m/e (relative intensity) 424(26), 422(54), 420 (29), 262(10), 247(10), 232(5), 219(6), 203(24).

Anal. Calcd for $C_{20}H_{22}Br_2$: C, 56.89; H, 5.25; Br, 37.85.
Found: C, 56.73; H, 5.22; Br, 37.80.

45. 1,2,3,4-Tetramethyltriphenylene (115)

A mixture of 113 (100 mg, 0.34 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (300 mg, 1.32 mmol) in 15 mL of anhydrous benzene was refluxed for 5 h. The resulting solution was then passed through a basic alumina column (0.5" x 3") with benzene as eluent, and concentrated to give pure 115 (67 mg, 68%); mp 175-177°C; ^{1}H NMR($CDCl_3$) δ2.43(s, 6 H), 2.78(s, 6 H), 7.3(m, 4 H), 8.03(m, 2 H), 8.30(m, 2 H); UV(heptane) λ_{max} 302 nm (sh, logε 3.86), 273(4.72), 264(4.60); mass spectrum, m/e (relative intensity) 284(100), 269(34), 254(29), 239(6), 142(22), 127(43).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09.
Found : C, 92.89; H, 7.14.

46. 1,4-Dimethyl-2,3-dibromotriphenylene (116)

A mixture of octahydrotriphenylene 114 (500 mg, 1.2 mmol) and DDQ (1.7 g, 7.5 mmol) in 50 mL of benzene was

refluxed under argon for 4 h. The solution was then passed through a basic alumina column (2" x 10") with benzene as the eluent, and concentrated to give pure 116 (316 mg, 65%); mp 212-214°C; ^{1}H NMR($CDCl_3$) δ2.93(s, 6 H), 7.05(m, 4 H), 7.93(m, 2 H), 8.23(m, 2 H); UV(heptane) λ_{max} 299 nm (log ε 4.13), 277(4.79), 267(4.63); mass spectrum, m/e (relative intensity) 416(20), 414(31), 412(14), 399(1), 254(31), 252(52), 239(76), 126(100).

Anal. Calcd for $C_{20}H_{14}Br_2$: C, 58.00; H, 3.40.
Found : C, 57.85; H, 3.39.

47. N-Methyl-bis(tetrahydrobenzo[1,2;3,4])-5,6,7,8-tetramethyl-1,4-dihydronaphthalen-1,4-imine (117)

Imine 117 was prepared by the reaction of dibromoprehnitene 85 (5.80 g, 20 mmol) and N-methyl-octahydrocarbazole 49 (3.8 g, 20 mmol) with n-BuLi (25 mmol) in 200 mL of anhydrous THF using the general procedure for cycloaddition. The residual oil was triturated with hexane to give mono-imine 117 (3.55 g, 91%); mp 255-257°C; ^{1}H NMR ($CDCl_3$) δ1.75-1.78(m, 8 H), 1.81(s, 3 H), 2.01-2.55(m, 8 H), 2.13(s, 6 H), 2.30(s, 6 H); ^{13}C NMR($CDCl_3$) δ145.45, 144.38, 131.98, 129.09, 74.34, 30.45, 28.44, 24.75, 24.46, 24.11, 16.40, 16.15; mass spectrum, m/e (relative intensity) 321(100), 306(35), 293(36), 278(86), 264(28), 188(81).

48. Reaction of n-BuLi and Dibromotriphenylene 116

To a cool (-78°C) solution of dibromotriphenylene 116 (350 mg, 0.85 mmol) in 30 mL of anhydrous THF under argon, was added dropwise a solution of n-BuLi (5 mmol in 10 mL of hexane). The solution was stirred for 3 h at -78°C and then at 0°C for an additional 2 h. Water (10 mL) and methylene chloride (30 mL) were added. The aqueous layer was separated and extracted with methylene chloride (20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to give 47 mg of a yellow residue. Separation of the residue components by preparative TLC (alumina) was not possible. However, GC-Mass analysis showed that the residue probably contained dimer 118 and the butylated compound 119.

For dimer 118; mass spectrum, m/e (relative intensity) 508(100), 493(84), 477(15), 254(15), 239(18).

For 119; mass spectrum, m/e (relative intensity) 312 (100), 269(29), 256(77), 150(70), 239(92).

49. N-(Dimethylamino)-1,2,3,4,5,8-hexamethyl-6,7-dibromo-1,4-dihydronaphthalen-1,4-imine (120)

Dibromo-imine 120 was prepared by the reaction of tetrabromide 21 (13.9 g, 33 mmol) and N-(dimethylamino)-tetramethylpyrrole 83 (5.5 g, 33 mmol) with n-BuLi (36 mmol) in anhydrous toluene using the same procedure as for mono-adduct 37. The reaction residue was triturated with 95%

ethanol to give 120 (8.68 g, 62%) which could be recrystallized from chloroform/methanol; mp 140-142°C; ^{1}H NMR($CDCl_3$) δ1.61(s, 6 H), 1.73(s, 6 H), 2.33(s, 6 H), 2.46(s, 6 H); mass spectrum, m/e (relative intensity) no M^+, 372(5), 370(10), 368(6), 210(5), 195(9), 179(9), 165(9).

50. 2,3-Dibromo-1,4,5,6,7,8-hexamethylnaphthalene (20)

Crystalline imine 120 (1 g, 2.3 mmol) was heated in an oil bath at 155°C for 5 h. The residue was then recrystallized from methanol/chloroform to give 20 (858 mg, 99%); mp 176-178°C (lit.[8] 177-178°C); ^{1}H NMR($CDCl_3$) δ2.28 (s, 6 H), 2.45(s, 6 H), 2.65(s, 6 H).

51. N-(Dimethylamino)-bis(tetrahydrobenzo[1,2;3,4])-5,6,-7,8,9,10-hexamethyl-1,4-dihydroanthracen-1,4-imine (122)

Imine 122 was prepared by the reaction of 20 (1.41 g, 3.8 mmol) and octahydrocarbazole 110 (1 g, 4.5 mmol) with n-BuLi (5 mmol) in anhydrous THF using the same procedure as for the preparation of 38. The residue was recrystallized from chloroform/methanol to give adduct 122 (1.49 mg, 91%) as white crystals; mp 192-194°C; ^{1}H NMR($CDCl_3$) δ1.40-2.05(m, 8 H), 2.26(s, 6 H), 2.31(s, 6 H), 2.43(s, 6 H), 2.56(s, 6 H), 2.05-2.80(m, 8 H); mass spectrum, m/e (relative intensity) 428(trace), 383(2), 370(76), 355(31), 340 (10), 310(3), 185(11).

52. Pyrolysis of Mono-imine 122

Crystalline mono-imine 122 (500 mg, 1.1 mmol) was heated at 190°C under reduced pressure (25 torr) for 30 min. The yellow powder (434 mg), presumably the anthracene derivative 123, rearranged gradually to 124 (419 mg, 97%) during the recrystallization process. Therefore, no satisfactory spectra for 123 were obtained.

For tautomer 124; mp 268-270°C; ^{1}H NMR($CDCl_3$) δ1.30 (d, 3 H, J=7 Hz), 1.76(m, 8 H), 2.16(s, 6 H), 2.30(s, 3 H), 2.61(s, 3 H), 2.30-3.05(m, 8 H), 4.38(q, 1 H, J=7 Hz), 5.41 (q, 2 H, $J_{1,1'}$=7 Hz, $J_{1,5}$=1 Hz); mass spectrum, m/e (relative intensity) 370(23), 355(100), 340(19), 325(5), 170(21), 149(26); high resolution mass spectrum calculated for $C_{28}H_{34}$: 370.26606; Found: 370.26370.

53. Bis(N-[dimethylamino])-9,10-dimethyl-tetrakis(tetrahydrobenzo[1,2;3,4;5,6;7,8])-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (125)

Bis-imine 125 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and octahydrocarbazole 110 (4.4 g, 20 mmol) with n-BuLi (25 mmol) in anhydrous diethyl ether using the same procedure as for 24. The residue was triturated with 30 mL of hexane to give 125 as a white powder. The product turns yellow gradually when exposed to air, as it also does in solution. Therefore,

one of the isomers was isolated by rapid recrystallization from ether for spectroscopic purposes; mp 155-163°C (turns yellow) 367-369°C dec; ^{1}H NMR($CDCl_3$) δ1.26(m, 24 H), 2.33(s, 12 H), 2.45(s, 6 H), 2.13-2.76(m, 8 H); mass spectrum, m/e (relative intensity) no M^+, 422(3), 407(2), 320 (2), 264(9), 218(28), 203(17), 116(100).

Anal. Calcd for $C_{36}H_{50}N_4$: C, 80.25; H, 9.35; N, 10.40.
Found : C, 80.13; H, 9.38; N, 10.39

54. 9,10-Dimethyl-tetrakis(tetrahydrobenzo[1,2;3,4;5,6;-7,8])-anthracene (79)

The mixture of two isomeric bis-imines 125 (500 mg, 0.92 mmol) was heated at 125°C under reduced pressure (20 torr) for 15 min to give 399 mg of a yellow powder. The powder was recrystallized from chloroform/methanol to provide shiny yellow crystals; mp 367-369°C; ^{1}H NMR(C_6D_6) δ1.25(m, 8 H), 1.46(m, 8 H), 2.26(m, 8 H), 2.40(s, 6 H), 2.85(m, 8 H); UV(cyclohexane) λ_{max} 427 nm (logε 3.19), 403(3.25), 287(4.75); mass spectrum, m/e (relative intensity) 422(76), 407(100), 392(15), 228(14), 211(23), 183(32), 161(48); high resolution mass spectrum calculated for $C_{32}H_{38}$, 422.29736; found, 422.30134.

55. Bis(N-[dimethylamino])-5,6,11,12-tetramethyl-tetrakis-(tetrahydrobenzo[1,2;3,4;7,8;9,10])-1,4,7,10-tetrahydronaphthacen-1,4;7,10-bis-imine (127)

Bis-imine 127 was prepared by the reaction of 1,4,5,8-tetramethyl-2,3,6,7-tetrabromonaphthalene 25 (2.0 g, 4 mmol) and octahydrocarbazole 110 (1.74 g, 8 mmol) with n-BuLi (10 mmol) in anhydrous THF using the procedure for the preparation of bis-adduct 24. The residue was triturated with 30 mL of hexane to give bis-imine 127 (0.942 g, 39%) as an off-white powder which turned pink when exposed to air at room temperature. One of the isomers could be separated pure from the mixture by washing the powder with ether (0.413 g, 17%), but the purification of the second isomer was not successful. It remained contaminated with the other isomer in all efforts. For the pure isomer; mp 165-169°C (turns red 293-297°C dec; ^{1}H NMR($CDCl_3$) δ1.30-2.08(m, 24 H), 2.23(s, 12 H), 2.43(s, 12 H), 2.08-2.73 (m, 8 H); mass spectrum, m/e (relative intensity) no M^+, 516(12), 500(51), 485(100), 341(16), 250(45), 178(49), 134(64).

Compound 127 turns red upon heating at 140°C. However the red powder, presumably naphthacene 128, was not soluble in any organic solvent tried for spectroscopic determinations; mp 295-297°C; mass spectrum, m/e (relative intensity) 500(77), 485(100), 250(34), 235(29), 214(18), 199(17), 185(23), 171(28).

56. Reaction of Tetrabromonaphthalene 25 with n-BuLi in the Presence of Bis-pyrroles 135-139

To a cool (-78°C) solution of tetrabromide 25 (1 g, 2 mmol) and bis-pyrrole[16] 139 (0.572 g, 2 mmol) in 175 mL of anhydrous THF under argon, was added dropwise a solution of n-BuLi (5.5 mmol) in 30 mL of hexane. The solution was stirred for 3 h and then allowed to warm up to room temperature by removing the cooling bath. The solution was stirred for an additional 3 h at room temperature and quenched with 10 mL of MeOH. Water (30 mL) and methylene chloride (200 mL) were added and the aqueous layer was extracted with methylene chloride (50 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Some yellow powder (640 mg) was obtained, mp above 370°C, it did not dissolve in any organic solvent and did not sublime. Consequently spectra were not obtained.

57. N(2-Methoxyethyl)-2,3,4,5-tetramethylpyrrole (145)

A mixture of 3,4-dimethyl-2,5-hexanedione 41 (41 g, 0.3 mol) and 2-aminoethanol (17.6 mL, 0.3 mol) in 200 mL of benzene was refluxed until no more water was separated in a Dean-Stark trap (5 h). Removal of the benzene under vacuum gave almost pure 144 (40.3 g, 83%); ^{1}H NMR(CCl_4) δ1.76(s, 6 H), 2.00(s, 6 H), 2.05(bs, 1 H), 3.53(m, 4 H).

To a cooled (0°C) solution of crude 144 (30 g, 0.18 mol) in 150 mL of anhydrous diethyl ether was added

dropwise 180 mL of n-BuLi solution (0.25 mol). The resulting solution was stirred for 2 h at 0°C, and then a solution of dimethyl sulfate (25 mL) in 25 mL of ether was introduced slowly at 0°C. After addition, the mixture was stirred overnight. Water (20 mL) was added, the layers were separated, and the aqueous layer was extracted with ether. The combined ether layers were dried ($MgSO_4$) and evaporated under vacuum. The product 145 (17.8 g, 55%) was obtained by distillation; bp 90-92°C/0.6 torr; ^1H NMR(CCl_4) δ1.80(s, 6 H), 2.01(s, 6 H), 3.16(s, 3 H), 3.23(t, 2 H, J=6 Hz), 3.70(t, 2 H, J=6 Hz); mass spectrum, m/e (relative intensity) 181(66), 166(17), 150(16), 136 (100), 122(18); high resolution mass spectrum calculated for $C_{11}H_{19}NO$, 181.14667; found 181.14448.

58. N(2-Methoxyethyl)-1,2,3,4,5,6,7,8-octamethyl-1,4-dihydronaphthalen-1,4-imine (151)

Imine 151 was prepared by the reaction of dibromoprehnitene 85 (2.92 g, 10 mmol) and pyrrole 145 (1.81 g, 10 mmol) with n-BuLi (15 mmol) in anhydrous THF using the procedure for the preparation of 37. On chromatography (alumina, hexane/ether), mono-imine 151 (2.855 g, 90%) was thus obtained as white crystals; mp 122-124°C; ^1H NMR($CDCl_3$) δ1.53(s, 6 H), 1.61(s, 6 H), 1.96(s, 6 H), 2.10(s, 6 H), 2.10(5, 2 H, J=7 Hz), 3.13(s, 3 H), 3.30 (t, 2 H, J=7 Hz); ^{13}C NMR($CDCl_3$) δ146.96, 145.17, 131.38,

128.71, 77.34, 73.97, 58.69, 45.50, 17.07, 16.25, 15.86, 11.51; mass spectrum, m/e (relative intensity) 313(5), 268(5), 259(6), 240(6), 212(5), 100(57), 59(100).

Anal. Calcd for $C_{21}H_{31}NO$: C, 80.46; H, 9.97.
Found : C, 80.56; H, 9.94.

59. Bis(N[2-methoxyethyl])-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5,8-tetrahydroanthracen-1,4;5,8-bis-imine (152)

Bis-imine 152 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and pyrrole 145 (3.5 g, 20 mmol) with n-BuLi (25 mmol) in anhydrous THF using the same procedure as for the preparation of bis-adduct 24. The residue was triturated with 30 mL of hexane to give 152 (3.47 g, 77%) as a mixture of the syn and anti isomers, ratio 10/1 (determined by integrating the peak at δ3.23 and 3.20 in the ^1H NMR spectrum). The major isomer could be isolated from the mixture by recrystallizing the residue from hexane/acetone. For the major isomer; mp 248-250°C; ^1H NMR($CDCl_3$) δ1.58(s, 12 H), 1.65(s, 12 H), 2.20(s, 6 H), 2.28(t, 4 H, J=8 Hz), 3.23(s, 6 H), 3.33(t, 4 H, J=8 Hz); ^{13}C NMR($CDCl_3$) δ148.29, 145.42, 125.39, 77.61, 74.03, 58.84, 45.41, 17.05, 14.56, 11.53; mass spectrum, m/e (relative intensity) 464(3), 419(3), 365(10), 356(4), 187(3), 100(100), 59(87); high resolution mass spectrum calculated for $C_{30}H_{44}N_2O_2$, 464.34029; found, 464.34350.

A single crystal of the major isomer 152 was grown

from acetone/hexane solution by slow evaporation. The X-ray structure was determined by Dr. D. L. Ward whose efforts are gratefully acknowledged.

Crystal data: Crystals of 152 are monoclinic; Space group $p2_1/c$; a=8.421(3), b=21.022(12), c=7.593(3)Å, β=101.50(3)°; Z=2, M=464.69; ρ_c=1.172 g cm^{-3}. Lattice dimensions were determined using a Picker FACS-I diffractometer and $MoK_{\alpha 1}$ (λ = 0.70916Å) radiation.

Intensity data were measured using MoK_α radiation (2θ = 65°) yielding 4571 total unique data and, based on $I > 2\sigma(I)$, 2793 observed data. The data were reduced [Wei K.-T. and Ward, D. L. (1976). Acta Crystallographica, B32, 2768-2773] and the structures were solved by direct methods [Main, P. (1978). "MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data." Univ. York, England.]; and the refinement was by full-matrix least squares techniques; Zalkin A. (1974), private communication.]. The final R value was 0.055. The final difference Fourier map showed densities ranging from +.38 to -.31 with no indication of missing or incorrectly placed atoms.

60. Reaction of Trimethylsilyl Iodide with Bis-imine 152 (or Mono-imine 151)

A mixture of hexamethyldisilane (0.6 g, 4 mmol) and iodine (1 g, 4 mmol) was heated at 65°C in a 20 mL flask

fitted with a reflux condenser. An exothermic reaction took place and a homogeneous solution was formed. The solution was refluxed for 2 h. Bis-imine 152 (0.47 g, 1 mmol) in CCl_4 was then added slowly at room temperature. The solution was refluxed for 72 h. Water (20 mL) and chloroform (50 mL) were added, the aqueous layer was separated and extracted with chloroform (30 mL). The combined organic solutions were dried (Na_2SO_4) and concentrated. Bis-imine 152 (427 mg, 91%) was recovered.

Starting with mono-imine 151 and using the same procedure described above, no demethylation could be observed. Only the starting imine could be isolated from the reaction mixture.

61. Reaction of Tetrabromo-p-xylene 21 with n-BuLi in the Presence of Pyrrole 144

Tetrabromo-p-xylene 21 (4.2 g, 10 mmol) was reacted with n-BuLi (25 mmol) in the presence of hydroxypyrrole 144 (417 mg, 25 mmol) using the same procedure as for the preparation of bis-adduct 24. After worked up, only a polymeric powder was obtained and most of the starting pyrrole (403 mg) was recovered.

62. Reaction of Pyrrole 144 with Methanesulfonyl Chloride

To a mixture of MsCl and pyridine (10 mL each) at 0°C, was added slowly a solution of pyrrole 144 (5 g, 30 mmol) in 50 mL of pyridine. The solution turned purple immediately with precipitation. The suspension was stirred for 3 h. Ether (100 mL) was added. The ether solution was then washed with water three times and dried (Na_2SO_4). The solvent was removed under vacuum to give a gummy black residue. No pure compounds could be isolated from this black tar.

The same result was found when pyrrole 144 was treated with thionyl chloride using the procedure described above.

63. Reaction of Dimethylamine (or Diethylamine) with N-Carboxyglycine Anhydride 156

A mixture of carbobenzoxyglycine 155 (35 g, 0.16 mol, Aldrich Chemical Co.) and 100 mL of freshly distilled thionyl chloride was warmed on the water bath at 40°C for 50 min. The precipitate which formed was collected by filtration and air dried to give N-carboxyglycine anhydride 156 (15.4 g, 86%); mp 160-162°C (lit.[39] 100°C). The crude 156 was then stirred overnight with excess anhydrous dimethylamine (40 mL) at 0°C. After evaporation of the excess amine, the residual oil was distilled under reduced pressure to give glycine N,N-dimethylamide 157 (10.1 g, 62%);

bp 110-116°C/5 torr (lit.[39] 60°C/0.8 torr). ^{1}H NMR(CCl_4) δ1.63(s, 2 H), 2.83(s, 3 H), 2.86(s, 3 H), 3.23(s, 2 H).

Starting with diethylamine and using the same method as described above, acid derivative 159 was obtained (16.5 g, 63%); rather than the expected glycine N,N-diethylamide 160. For 159: mp 95-97°C; ^{1}H NMR($CDCl_3$) δ1.11(t, 3 H, J=7 Hz), 1.28(t, 3 H, J=7 Hz), 2.90(q, 2 H, J=7 Hz), 3.20(q, 2 H, J=7 Hz), 3.66(d, 2 H, J=4 Hz), 5.26(bs, 1 H, N-H), 9.63(bs, 1 H, CO_2H); mass spectrum, m/e (relative intensity) 174(10), 159(5), 130(18), 115(7), 100(17), 72(28), 58(100); high resolution mass spectrum calculated for $C_7H_{14}N_2O_3$, 174.10044, found, 174.10140.

64. N-(2-[N,N-dimethylacetamido])-2,3,4,5-tetramethylpyrrole (146)

A mixture of 3,4-dimethyl-2,5-hexanedione 41 (6.9 g, 49 mmol) and amide 157 (5 g, 49 mmol) in 100 mL of benzene was refluxed for 6 h. Removal of the benzene under reduced pressure gave yellowish crystals which were washed with hexane to give amide pyrrole 146 (8.5 g, 84%). Amide pyrrole 146 oxidizes rapidly and turns brown when exposed to air; mp 144-146°C; ^{1}H NMR($CDCl_3$) δ1.86(s, 6 H), 2.03(s, 6 H), 2.90(s, 3 H), 2.96(s, 3 H), 4.38(s, 2 H); IR(CCl_4) 1675(s), 1660(s), 1445(w), 1400(s), 1370(m) cm^{-1}; mass spectrum, m/e (relative intensity) 208(91), 193(6), 136(100), 122(27); high resolution mass spectrum calculated for $C_{12}H_{20}N_2O$, 208.15757, found, 208.15631.

65. Bis(N-[2-(N,N-dimethylacetamido)])-1,2,3,4,5,6,7,-8,9,10-decamethyl-1,4,5,8-tetrahydroanthracen-1,4;-5,8-bis-imine (158)

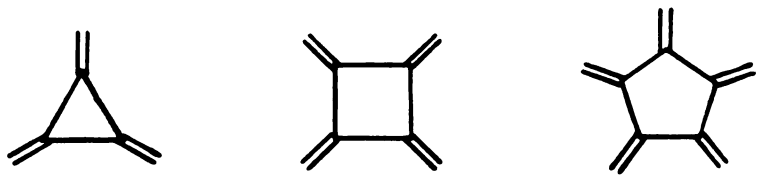
Bis-imine 158 was prepared by the reaction of tetrabromide 21 (4.2 g, 10 mmol) and amide-pyrrole 146 (4.2 g, 20 mmol) with n-BuLi (25 mmol) in anhydrous THF following the preparation of bis-adduct 24. The residue was chromatographed on alumina with ethyl acetate as eluent to give only one isomeric bis-adduct 158 (624 mg, 12%); mp 257-259°C; ^{1}H NMR($CDCl_3$) δ1.63(bs, 24 H), 2.23(s, 6 H), 2.86 (s, 4 H), 3.06(m, 12 H); ^{13}C NMR($CDCl_3$) δ172.19(CO), 147.68, 145.37, 126.18, 77.57, 49.37, 37.72, 35.99, 16.54, 14.70, 11.42; IR(KBr) 1645(s), 1470(m), 1400(m), 1275(w) cm^{-1}; UV(MeOH) λ_{max} 260 nm (logε 3.52), 253(3.53), 247(3.68), 234(4.42); mass spectrum, m/e (relative intensity) 518(13), 503(2), 464(8), 446(22), 392(14), 337(14), 127(100), 86(35); high resolution mass spectrum calculated for $C_{32}H_{46}N_4O_2$, 518.36209; found, 518.36100.

PART II

ATTEMPTED SYNTHESIS OF THIOPHENE OR FURAN FUSED RADIALENE ANALOGUES

INTRODUCTION

Radialenes, a class of "exocyclic" polyenes in which the number of exocyclic double bonds is the same as the number of ring carbons, have attracted considerable interest both with regard to synthesis[46] and theory.[47] Aside from (5)-radialene 172, each of the lower members of this series 170 - 174 has been prepared either as a very



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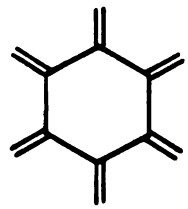

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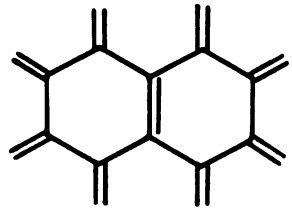

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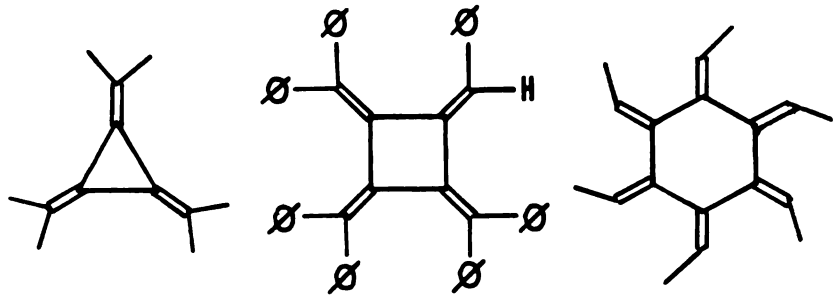
reactive hydrocarbon[48] or as a reactive intermediate.[49] Consequently, studies have been limited to spectral properties at low temperature and to comparatively few

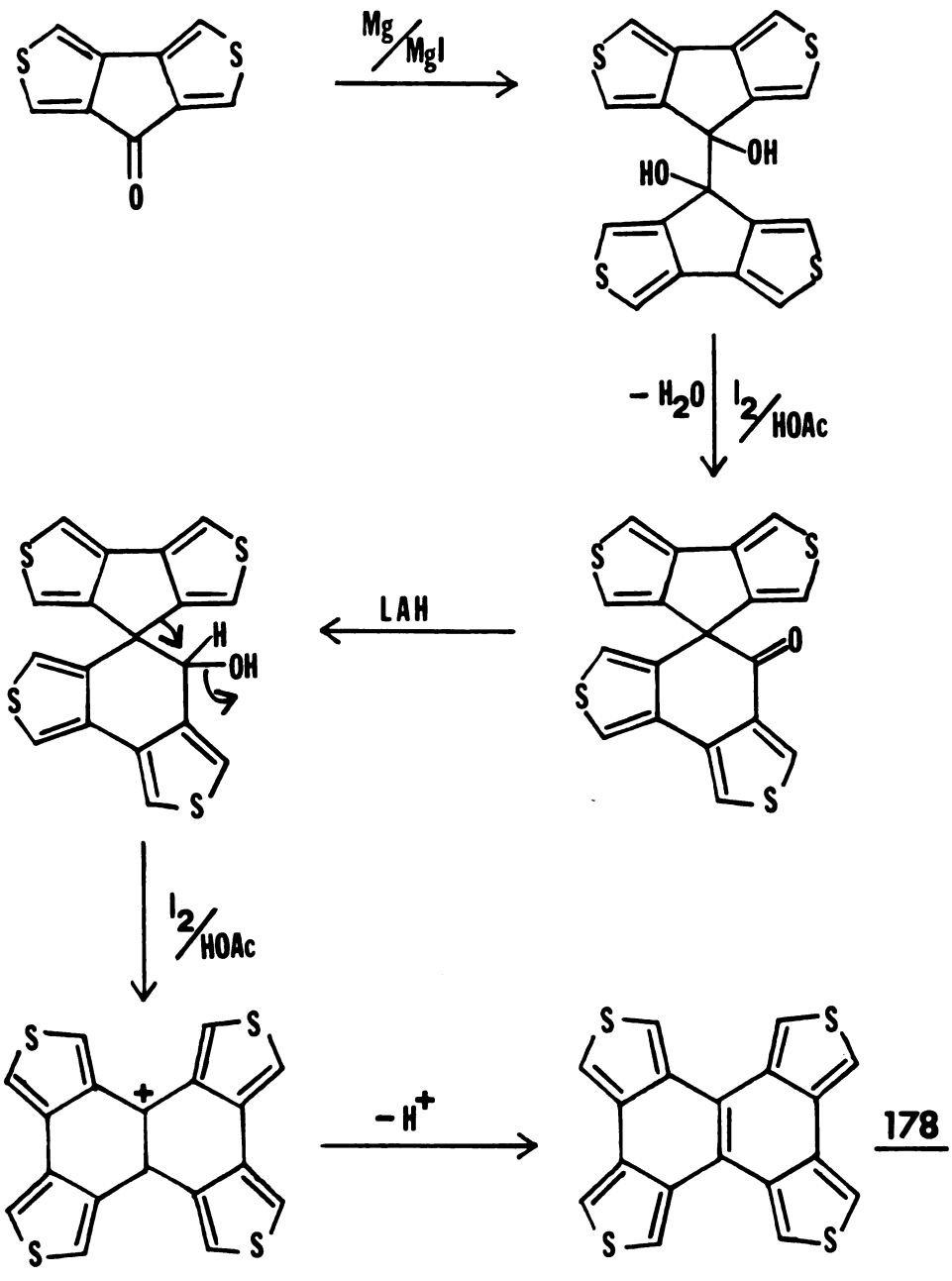
chemical reactions because of their high tendency to polymerize.



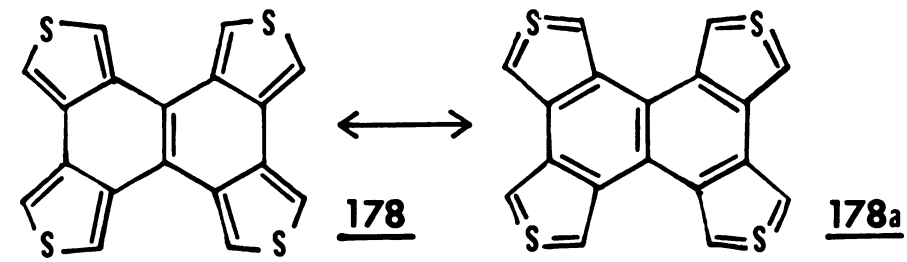
175 **176** **177**

In contrast to the instability of the parent radialenes, derivatives having substituents on the terminal carbons, such as hexamethyltrimethylenecyclopropane 175,[50a] heptaphenyltetramethylenecyclobutane 176,[50b] and hexaethylidenecyclohexane 177,[50c] are reported to be very stable hydrocarbons.

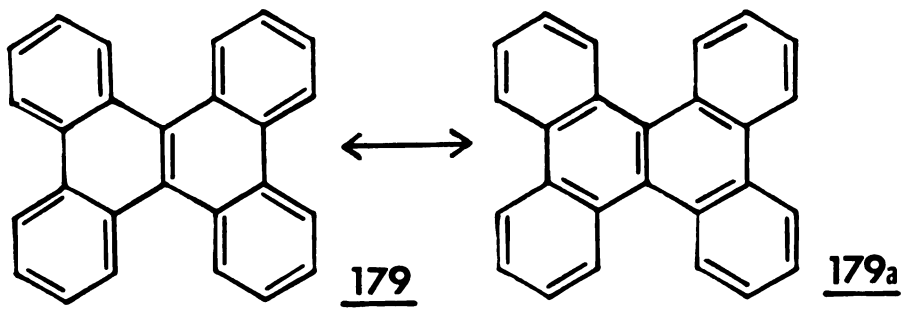
Stabilization of radialenes can also be achieved by incorporating a hetero-atom into the cross-conjugated systems. Thus, in 1972 naphthotetrathiophene 178, a naphthoradialene, was synthesized by Wynberg and Heers.[51] (As shown on page 110). Naphthotetrathiophene 178 was reported to greatly resembly dibenzo(g,p)chrysene 179 in physical properties. Therefore, it is reasonable to view a radialene such as 178 as a naphthalene which is converted in a formal sense from having ten overlapping



p orbitals associated with endocyclic "double bonds" to having those orbitals associated with exocyclic "double bonds". In other words, we might accept the concept of a



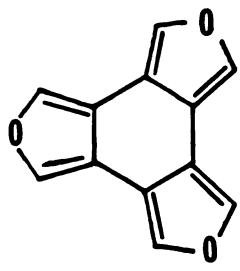
178 178a



179 179a

nonclassical condensed thiophene[52] by using the sulfur d orbitals as in structure 178a, thus restoring the endocyclic aromatic naphthalene moiety. Such a resonance hybrid may contribute to the overall stability of structure 178.

Using the same argument, it is not surprising that the fused hexaradialenes should be stable compounds because of their perfect aromatic sextet arrangement. Thus trioxo-hexaradialene 180,[53] trithia-hexaradialene 181[54] and triaza-hexaradialene 182[54] were prepared recently and described as having very similar properties to those of triphenylene 183.



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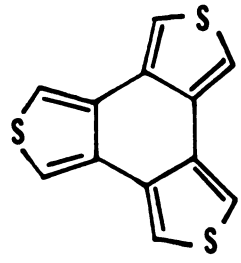

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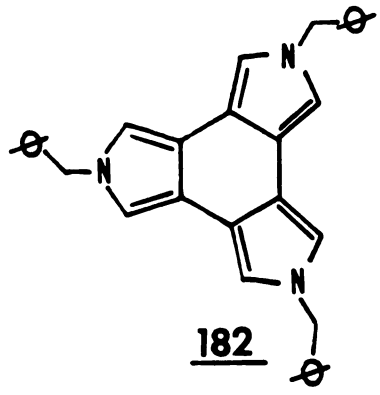

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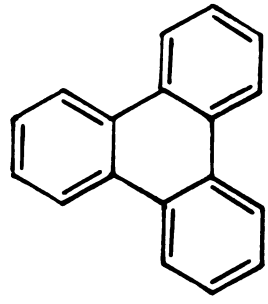

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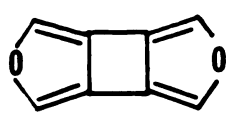
In light of the above known examples, fused tetraradialenes such as 184, 185 and 186 became very attractive targets. The main interest in synthesizing compounds 184 - 186 arose from two sources. The first is the concept of anti-aromaticity. In contrast to 178 - 183 which have $4n+2\pi$ electrons, compounds 184 - 186 have a total of $4n\pi$ electrons. Such systems are not only non-stabilized,[56] but are actually destabilized by the conjugation. The second reason for interest in those compounds is that they could provide model compounds for the study of induced



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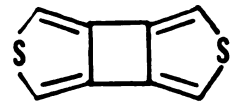

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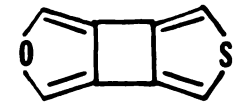

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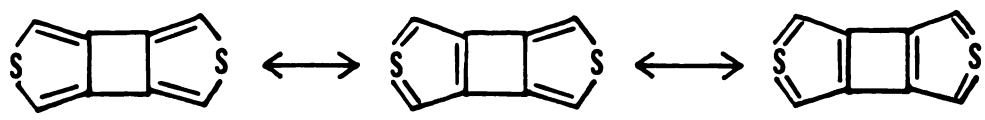
paramagnetic ring currents in a paratropic system. Each of them potentially contains a cyclobutadiene ring in the central part of the molecule.



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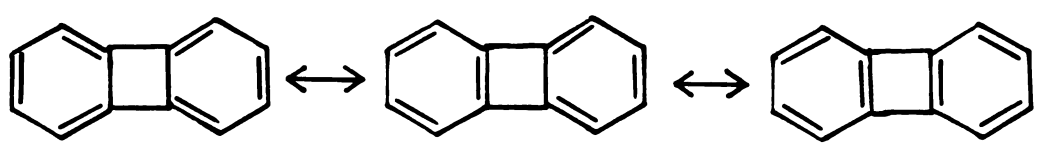
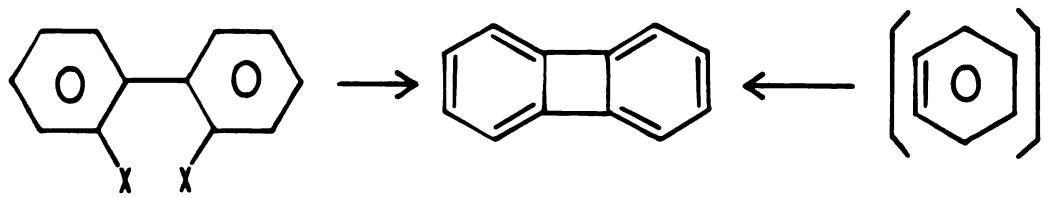


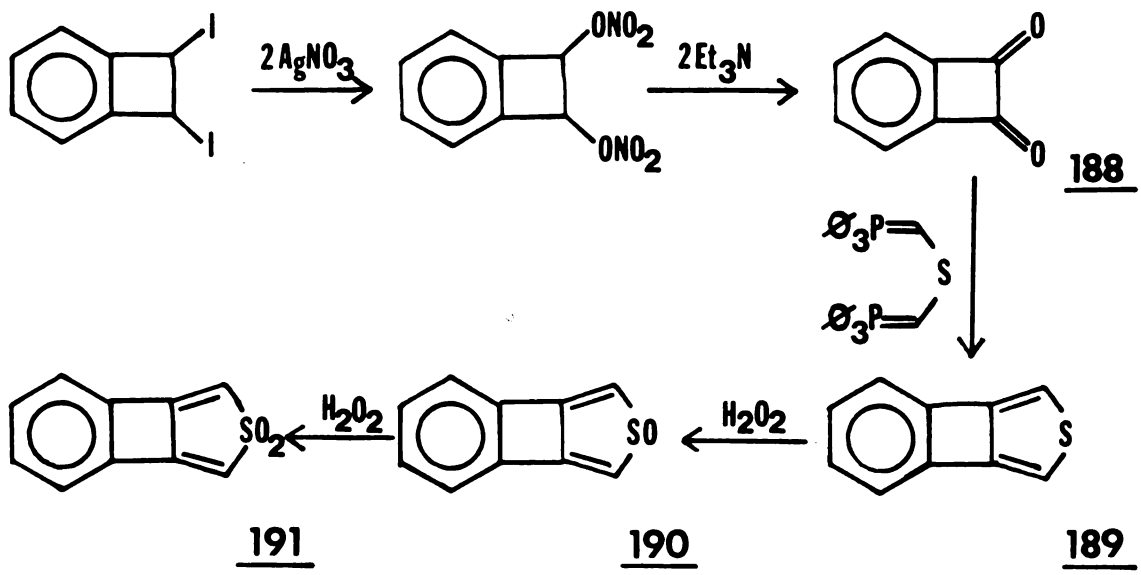
187

Biphenylene 187 was the first stable compound of this type to be prepared, and it indeed shows the predicted rather small diamagnetic current in the six-membered ring and large paramagnetic current in the four-membered ring.[57] Its preparation was easily accomplished by two classical methods as indicated in Scheme 12.[58] However, this



Scheme 12

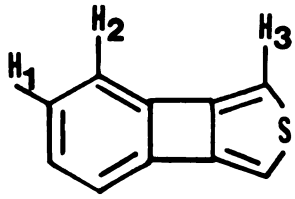
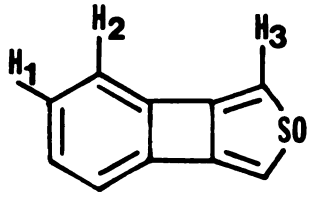
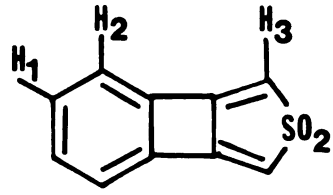
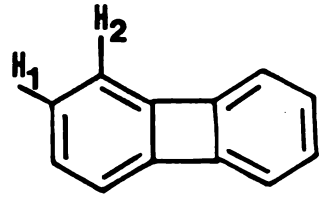
approach cannot be applied to the preparation of a compound such as 189. A bis-Wittig reaction was therefore selected as the key step in the synthesis, the $4n+2\pi$ ring being constructed in the final step. Thus, 2-thianorbiphenylene 189 was prepared from benzocyclobutadienequinone



188 in 14% yield.[59] Subsequently 189 was oxidized to sulfoxide 190 and to the sulfone 191.

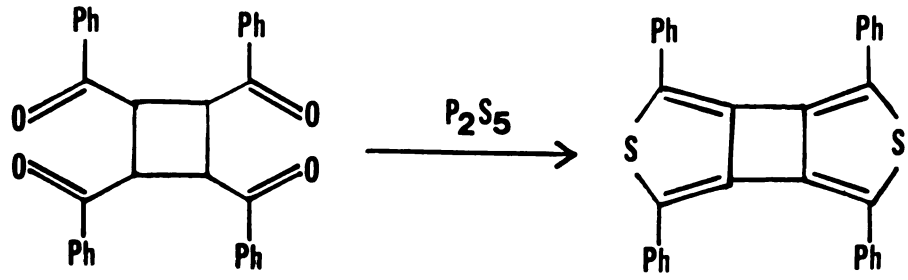
A comparison of the ^{1}H NMR absorptions of 189 - 191

Table 4. A Comparison of the ^1H NMR Chemical Shifts of Compounds 189 - 191 with Those of Biphenylene.

	$CDCl_3$	100 MHz
	H_1, H_2	H_2
 **189**	6.86 (bs)	6.49 (s)
 **190**	7.51 (m)	6.65 (s)
 **191**	7.63 (m)	6.40 (s)
 **187**	6.70 (H_1)	6.60 (H_2)

with that of biphenylene is given in Table 4. In 189 both the benzene ring protons and thiophene protons are at higher field absorption than is normal in such systems. This result was ascribed to the paratropic contribution of the four-membered ring. Oxidation of 189 to 190 lead to a downfield shift of the benzene type protons (0.65 ppm), and further oxidation to 191 resulted in a further small downfield shift. These shifts were considered to be the result of removing the paratropic component from the four-membered ring.

A different approach, construction of the five-membered heterocycles from a corresponding 1,4-diketone, was examined by Garratt.[60] The reaction of tetraketone 192 with phosphorus pentasulfide in pyridine gave a 5% yield of the thiophene fused cyclobutadiene 193. Because the yield of 193 was not reproducible, no study has been done so far on this paratropic system. Therefore, whether the stability of 193 arises from the four phenyl substituents



192 193

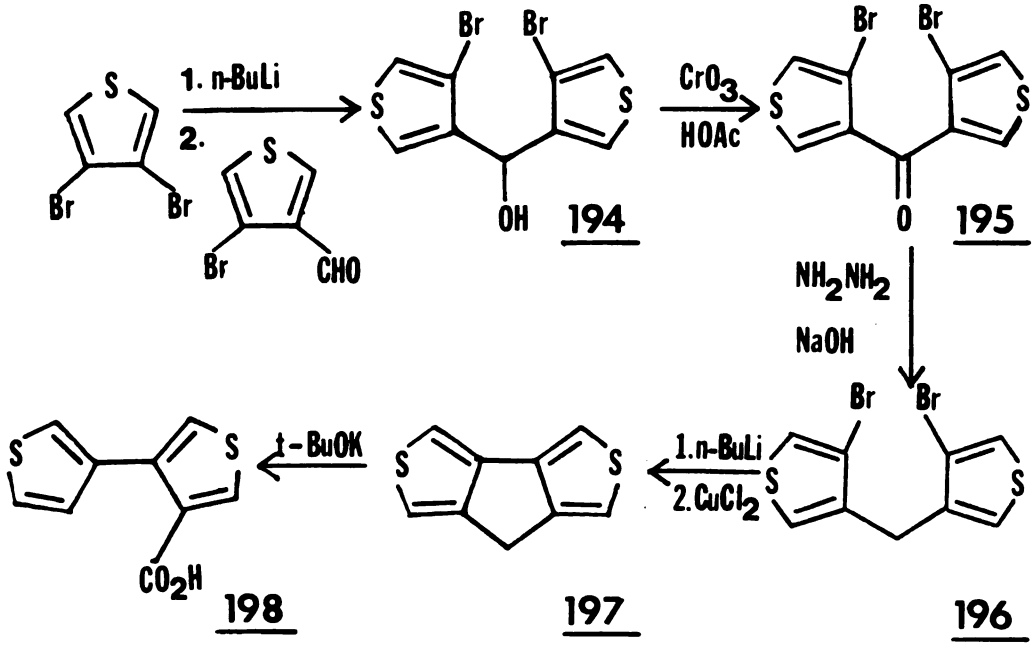
or from the stability of the parent structure itself is still not known.

Although the synthesis of the parent dithiophene 185 has been attempted previously without success,[61] we pursued this synthesis using our own approaches. The preparation of the target compounds 184 - 186 has not yet been achieved. However, we have prepared several potentially useful precursors. It is the purpose of this part of the thesis to illustrate the approaches we used and report the synthesis of the precursors we have prepared.

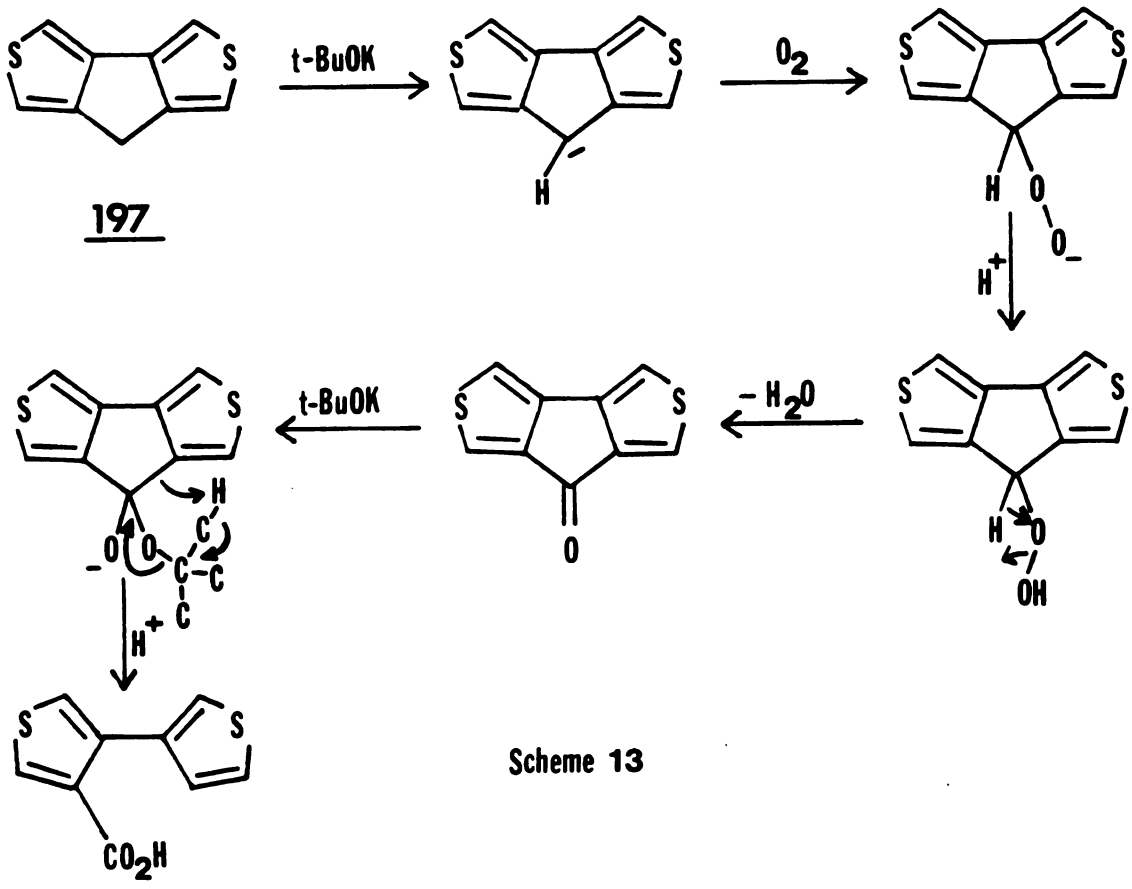
RESULTS AND DISCUSSION

1. The Coupling of Thiophene Moieties by the Ullmann Reaction

The Ullmann biaryl synthesis has been successfully applied to the coupling of five-membered heterocycles.[62] For example, an Ullmann reaction was the key step in the synthesis of cyclopentadithiophene 197, a compound having two thiophenes fused to a cyclopentane ring. Compound 197 differs from the desired 185 by only one methylene group. 3-Bromo-4-thienyllithium reacted with 3-bromo-thiophene-4-carboxaldehyde to give bis(3-bromo-4-thienyl) carbinol 194, which was oxidized to ketone 195. On



Wolff-Kishner reduction of the carbonyl group, dibromide 196 was obtained. Treatment of 196 with n-butyllithium followed by anhydrous cupric chloride provided cyclopentadithiophene 197 in a 2% total yield. Compound 197 underwent autooxidation rapidly with oxygen in the presence of

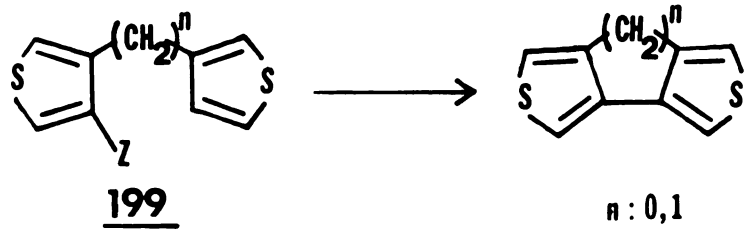


Scheme 13

potassium t-butoxide.[63] An ionic mechanism similar to that of the Haller-Bauer reaction was proposed for the ring cleavage (Scheme 13).

Although many factors are involved in the conversion

of 197 to 198, the existance of severe strain in the central five-membered ring was assumed to be the main driving force for the facile ring cleavage. This assumption implies that the closure of any bithienyls 199 (n=0 or 1) is likely to be difficult, especially if a four-membered ring is to be constructed (Scheme 14).

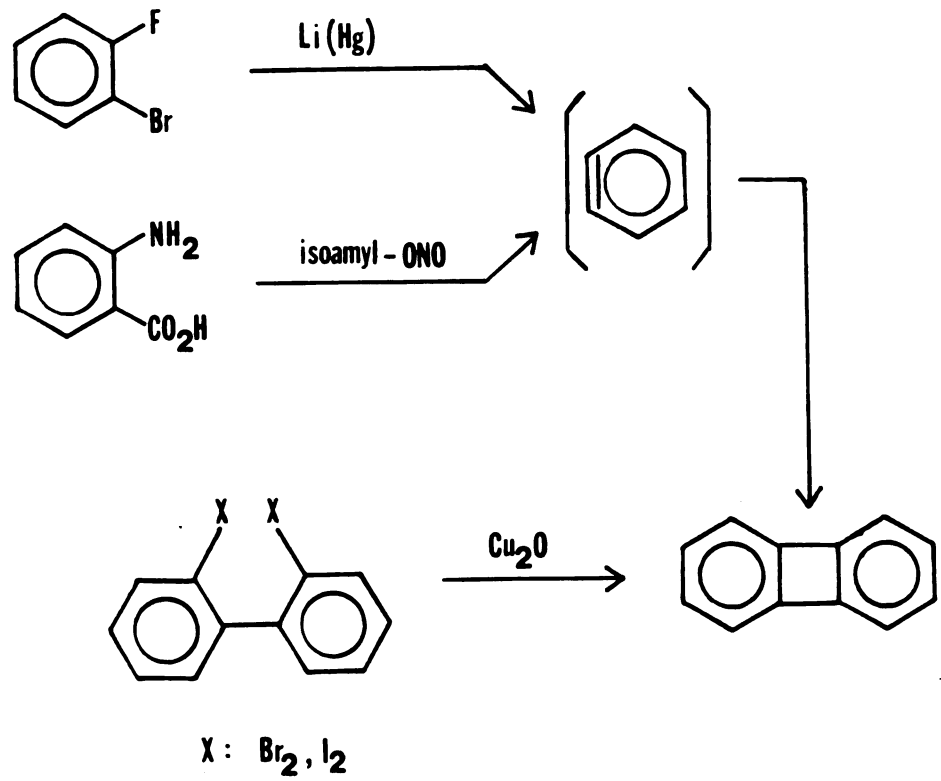


199

Scheme 14

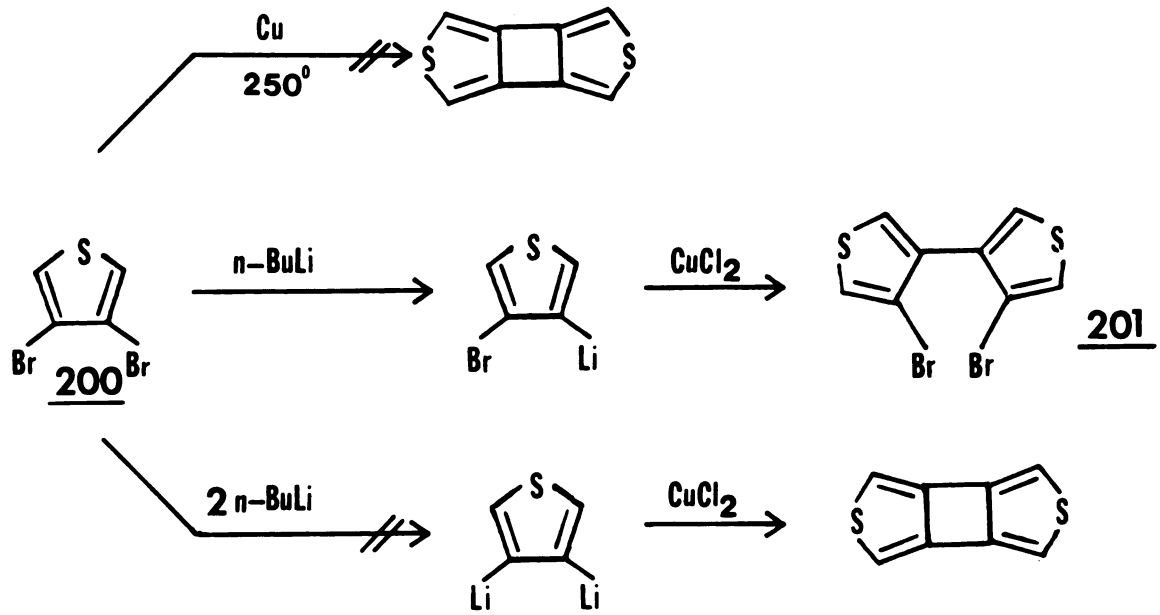
Nevertheless biphenylene, the benzenoid analog of 185, was successfully prepared by this approach, via either benzyne dimerization or intramolecular cyclization of 2,2'-dihalobiphenyls (Scheme 15).[58]

Therefore, it seemed worthwhile first to try this straightforward approach. In several instances,[58] biphenylenes cannot be obtained through the original Ullmann coupling of an o-dihalobenzene. It was therefore not surprising that when 3,4-dibromothiophene was heated at 250°C with active copper powder none of the desired compound 185 was found; only tarry products were formed. Modifications have been developed for broader application of this

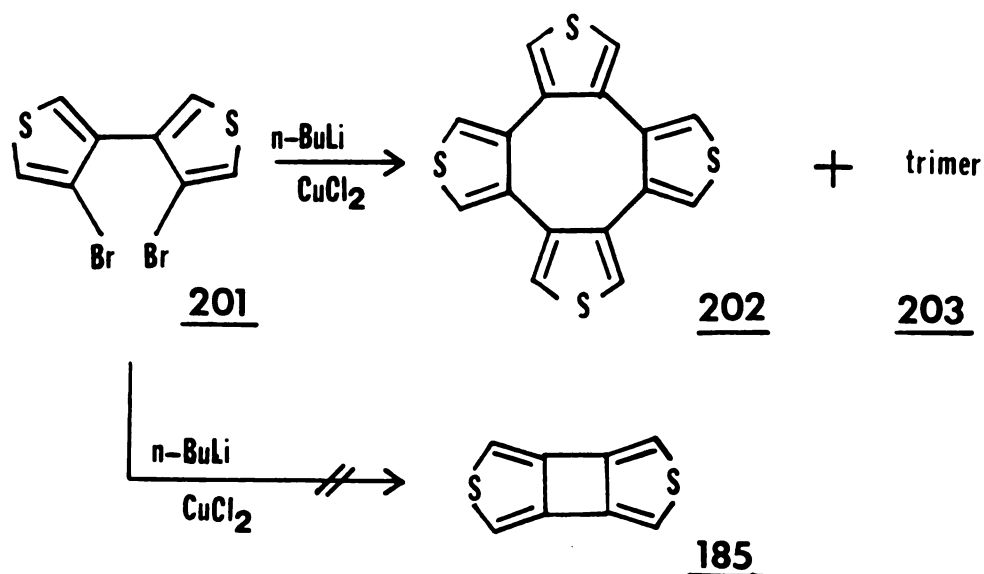


Scheme 15

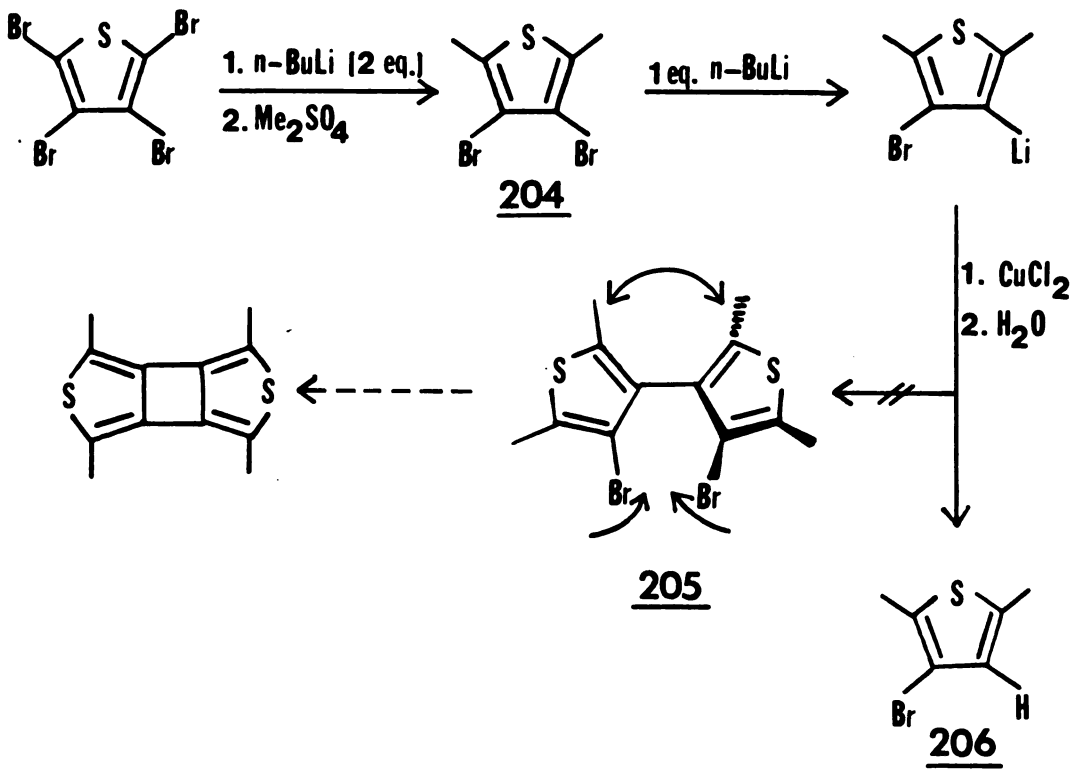
coupling reaction via lithium-copper transmetallation.[64] Thus 3,4-dibromothiophene 200 was chosen as the starting material with the hope that under high dilution conditions 200 might undergo head to head coupling. However, when 200 reacted with excess n-butyllithium followed by anhydrous $CuCl_2$, only 3,3'-dibromobithienyl 201 could be isolated from the reaction mixture. Analogously, no coupling product of 3,4-diiodothiophene was found when its solution in cyclohexane was irradiated at 253 nm with a mercury lamp.



It seemed possible that further lithiation of 201 followed by metal exchange with cupric chloride might result in an intramolecular cyclization to 185. However



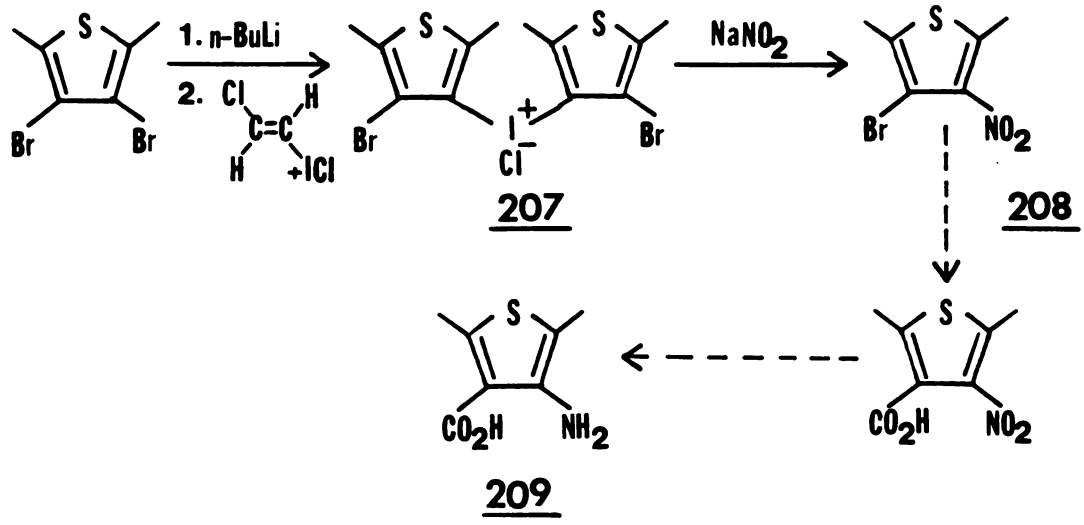
the literature[64] shows that 3,3'-dibromobithiophene only underwent dimerization to 202 and trimerization to trimer 203, with none of the expected 185 being formed. The ring strain in 185 could be the reason for lack of success in this cyclization. Therefore, 3,3'-dibromo-2,2'5,5'-tetramethylbithienyl 205 was selected as a starting material because it was reasoned that steric hindrance between two methyl groups would change the preferred conformation of 205 in favor of bond formation between 3- and 3'- positions (see structure 205). However, on treatment of 204 with n-butyllithium followed by anhydrous cupric chloride,



reduced product 206 was obtained in 75% yield instead of the required 205. Lack of coupling was presumably due to the pronounced "ortho effect" of the methyl and bromine substituents.

From these results and literature precedents,[61] we felt that this approach had to be abandoned.

Preparation of the anthranilic acid analog 209 was also tried, with the hope that a 3,4-thiophyne could be

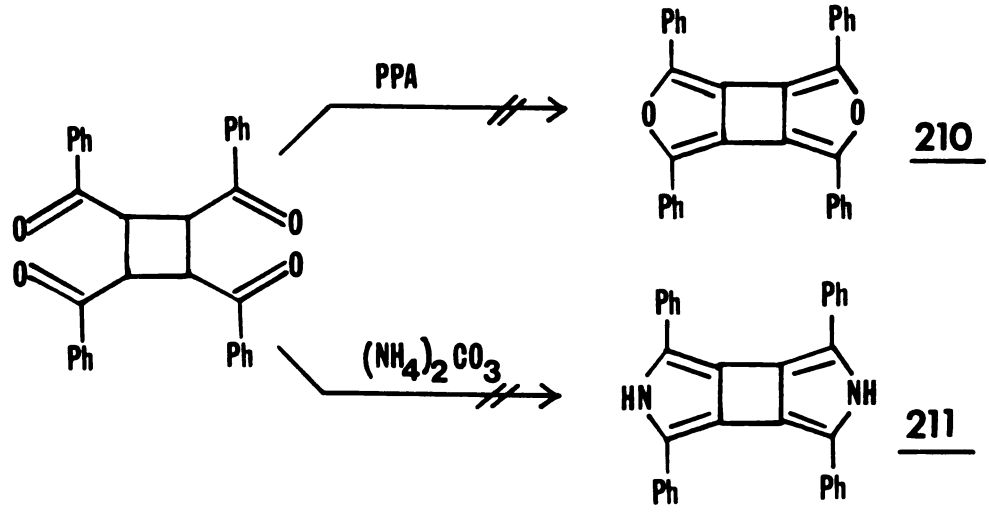


prepared and dimerized. The first two steps have been carried out (to make 208), but in disappointingly low yield. Therefore, further work using this approach was dropped.

2. Construction of the Intermediate Synthetic Target 219

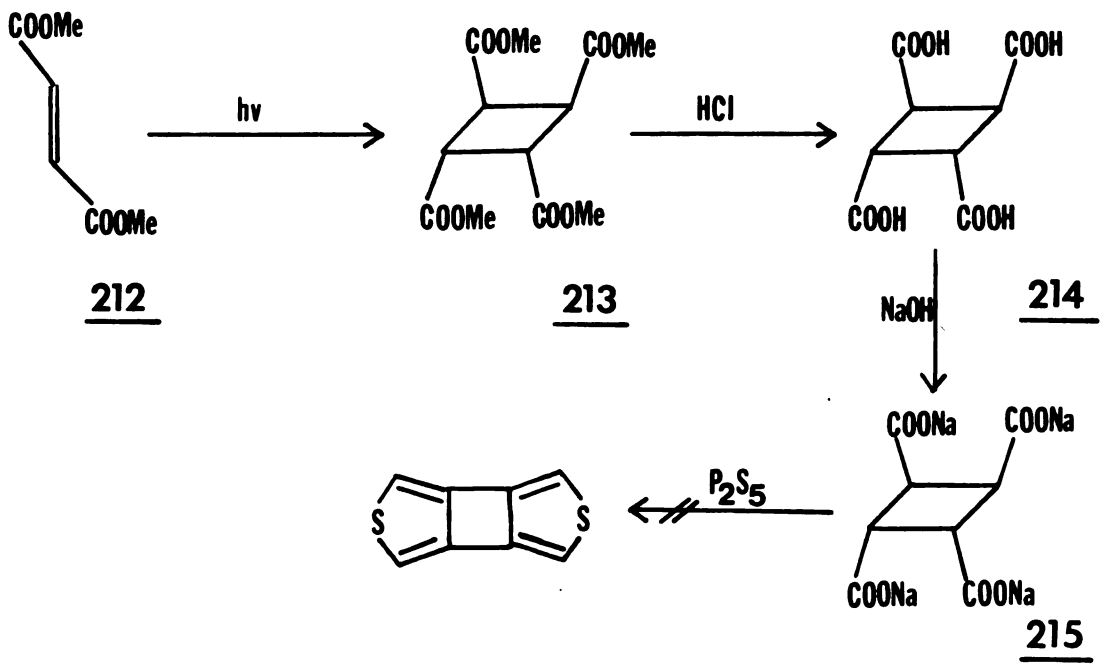
Since methods which are successful for the preparation of biphenylene proved unrewarding for synthesizing 185, attention was shifted to a different precursor which already contains the required four-membered ring.

One dithiophene derivative 193 has already been prepared using this approach,[60] although the preparation of other heterocycles (210, 211) by the analogous reaction were not successful.[65,66] The synthesis still seemed a reasonable strategy for preparing the parent dithiophene 185.

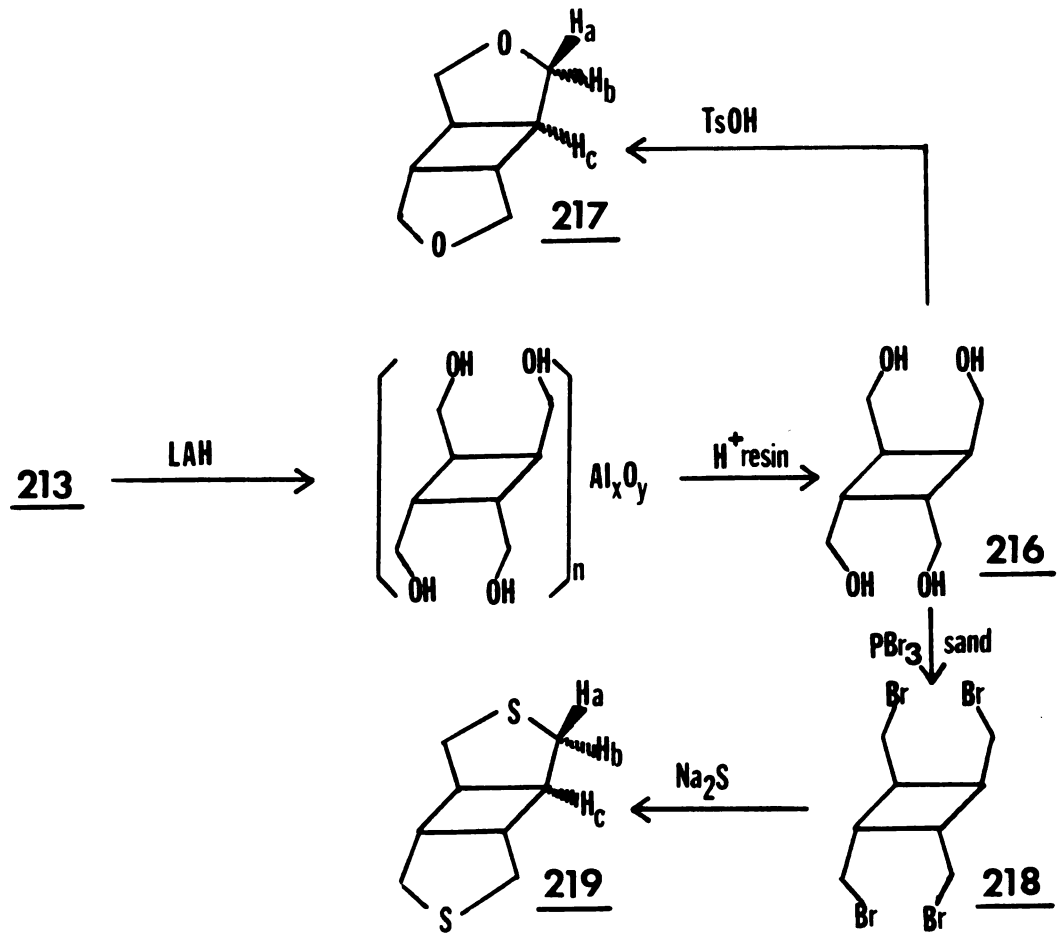


The photodimerization of dimethyl fumarate in the solid state provides only one stereoisomeric cyclobutane dimer 213, with the cis-trans-cis configuration (due to the fixed

crystal lattice structure of the monomer[67]). The technique used in the dimerization consisted of irradiating a thin layer of monomer 212 on the surface of a glass plate, using 300 nm light in a Rayonet reactor. Under these conditions monomer 212 underwent 60% conversion to cis, trans, cis-1,2,3,4-tetracarbomethoxycyclobutane 213 in 24 h. The tetra-ester 213 was hydrolyzed quantitatively to 214 with concentrated hydrochloric acid, and the acid was converted to its salt 215 with four equivalents of aqueous sodium hydroxide. However use of the Volhard-Erdman thiophene synthesis procedure,[68] i.e., pyrolysis of the salt 215 with excess of phosphorus pentasulfide, did not provide any of the desired dithiophene 185; all of the starting salt 215 was recovered.



Consequently, another synthetic plan was devised starting from 213. The tetraester was reduced with lithium aluminum hydride. Difficulties have been reported[69] in the isolation of the tetraol 216, due to complex formation between the polyol and aluminum salts from which the product



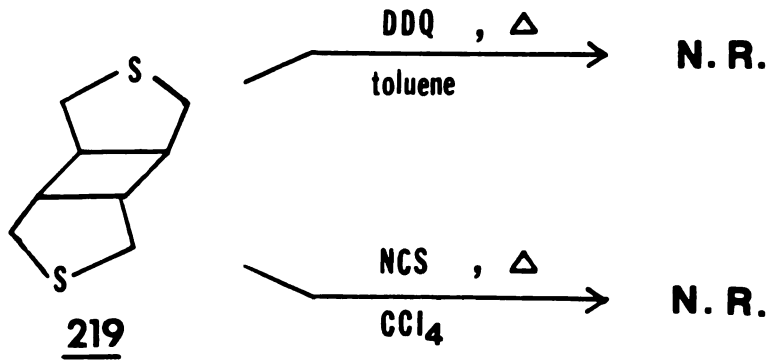
could not be separated conveniently. However, we found that if the reduction was carried out in anhydrous dioxane followed by a very careful quenching process (the amount

of water added is critical), tetraol 216 can be separated in a pure state after passing the oily product through a cationic exchange resin column. The tetraol was characterized as its benzoate by treatment of 216 with benzoyl chloride.

Tetraol 216 is very susceptible to intramolecular ether formation. For example, when 216 was reacted with phosphorus tribromide in pyridine the major product isolated from the reaction mixture was identified as 217. The mass spectrum showed a parent peak at m/e 140 and the ^{1}H NMR ($CDCl_3$) spectrum had peaks at δ2.44(d, 4 H_c, J_{bc}=4 Hz), 3.38(dd, 4 H_b, J_{ab}=9 Hz, J_{bc}=4 Hz), and 3.98(d, 4 H_a, J_{ab}=9 Hz). Decoupling results at 180 MHz were also consistent with this assignment. Upon irradiating the peak at δ2.44, the spectrum became two equal intensity doublets at δ3.38(J_{ab}=9 Hz) and 3.98(J_{ab}=9 Hz). Similarily, when irradiation was done at δ3.38, the spectrum consisted of only two singlets, at δ2.44 and 3.38. Compound 217 was also obtained in a 65% yield by the treatment of 216 with p-toluenesulfonic acid in dioxane.

Surprisingly, the conversion of 216 to its tetrabromide 218 could be accomplished by reacting PBr_3 with 216 which was coated on sea sand. The reaction gave 218 in 52% yield. Subsequently, tetrabromide 218 was treated with sodium disulfide in 95% ethanol to give bis-thioether 219 quantitatively.

Conversion of 219 to the target compound 185 was tried by reacting 219 with DDQ in refluxing solvent, or by attempting to chlorinate and dehydrochlorinate the bis-sulfide 219. However 219 could not be readily dehydrogenated nor could it be chlorinated with N-chlorosuccinimide, even under forced conditions.

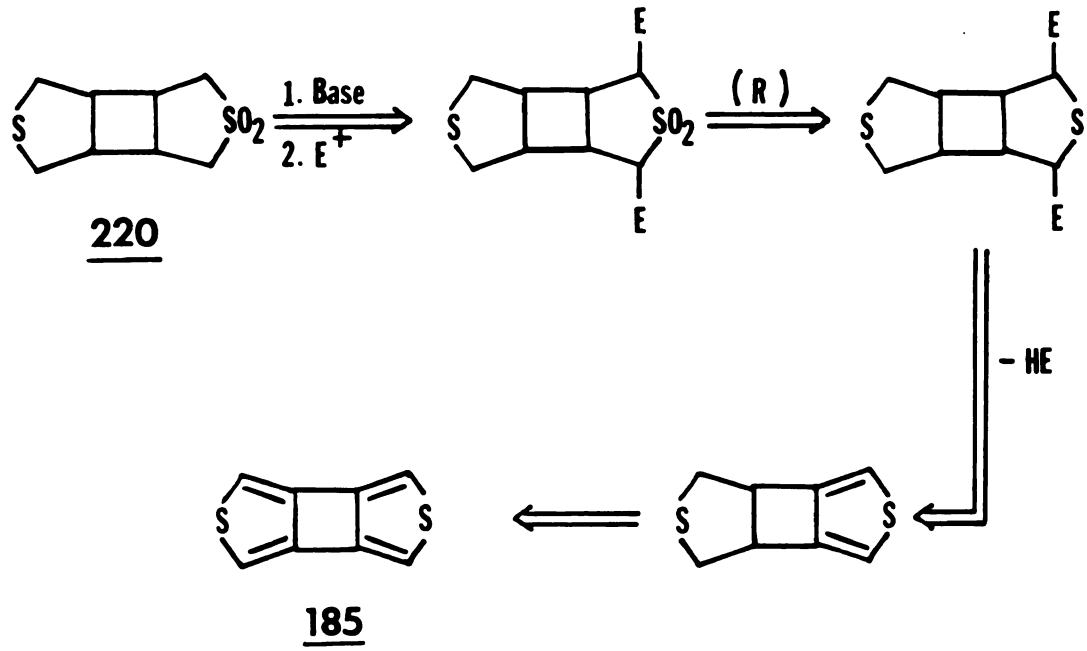


Therefore, it seemed desirable to prepare a similar synthetic target, such as 220, with a more reactive functional group which might enhance the reactivity of the compound for later manipulation.

3. Construction of the Intermediate Synthetic Target 220.

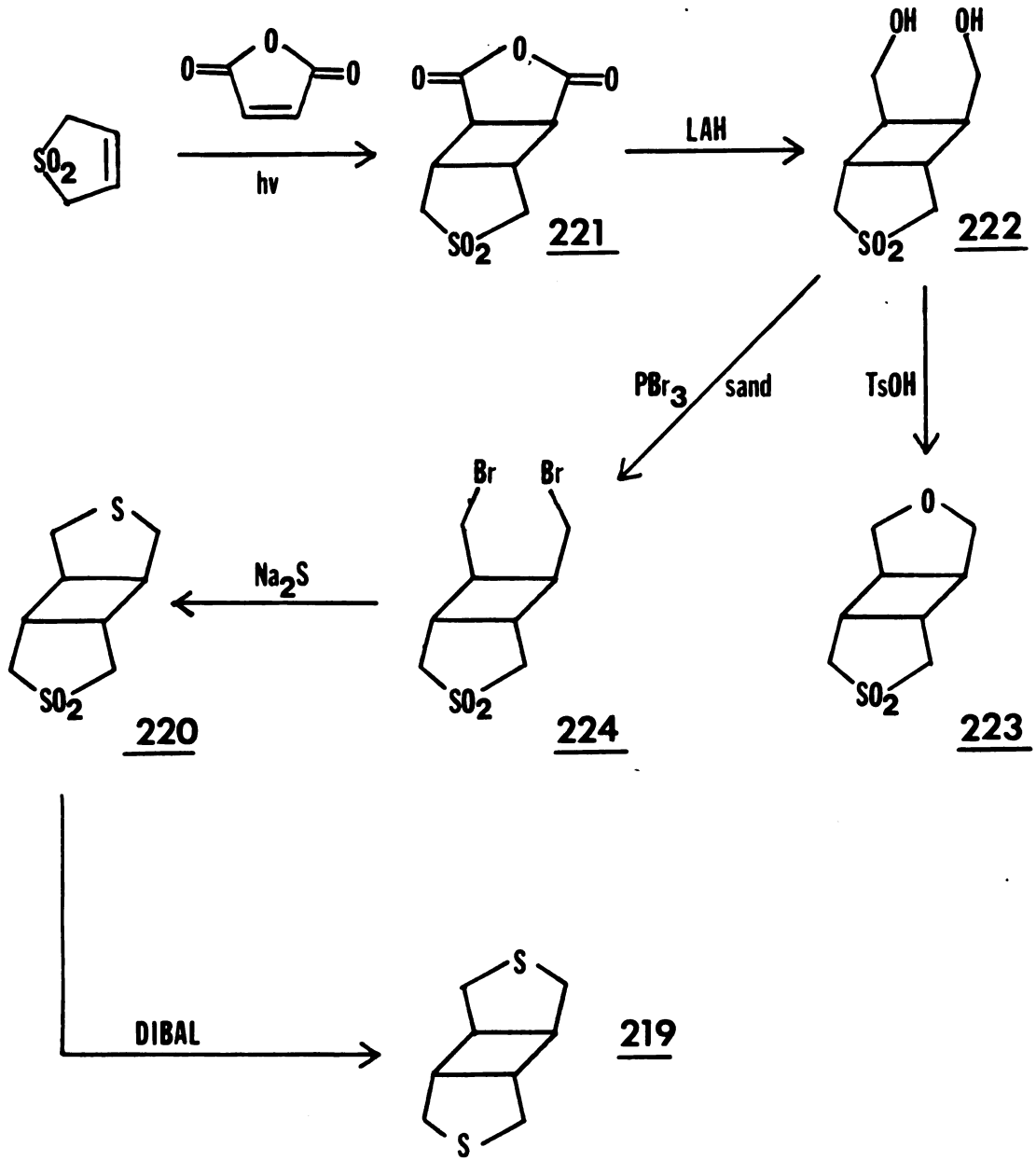
The stabilization of a carbanionic center by an adjacent sulfone group has been widely used for many valuable transformations in organic synthesis.[70] Although they are not many, some methods for the reduction of the sulfone group to a sulfide are available.[71] Consequently, another

approach to 185 was planned as outlined in Scheme 16.



Scheme 16

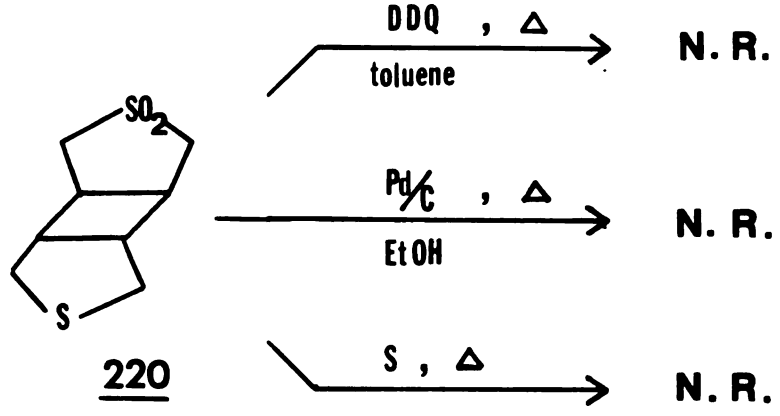
One possible way to prepare 220 would be the partial oxidation of 219 with a stoichiometric amount of oxidizing agent, but the time consuming process for the dimerization of dimethyl fumarate and the modest yield (52%) of 218 from 216 discouraged us from repeating the whole sequence. The preparation of 220 therefore was carried out as follows: photochemical cycloaddition of 2,5-dihydrothiophene-1,1-dioxide and maleic anhydride in acetone (quartz reactor, high pressure mercury-vapor lamp), gave the adduct 221 in 1 h with a yield of 60%.[72] The reduction of 221 with lithium aluminum hydride gave 222, which was treated with



PBr_3 by the same technique used for the preparation of 218, giving dibromide 224 in 82% yield. Reaction of 224 with sodium disulfide afforded the sulfone-sulfide 220 in good yield. Sulfone 220 could be reduced to sulfide 219 by

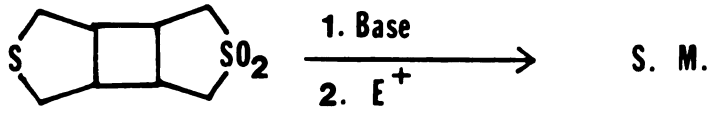
diisobutylaluminum hydride with a 97% yield (20% conversion).

Dehydrogenation of sulfone-sulfide 220 was tried by the following processes: DDQ oxidation, catalytic dehydrogenation with Pd/C and S or Se dehydrogenation. Compound 220 remained inert, although some decomposition occurred with prolonged reaction times.



More surprisingly, abstraction of the α-H adjacent to sulfone group was also not successful. All efforts to generate the carbanion by a variety of bases, or trap the carbanion (assuming it was generated) with different brominating agents, were in vain.

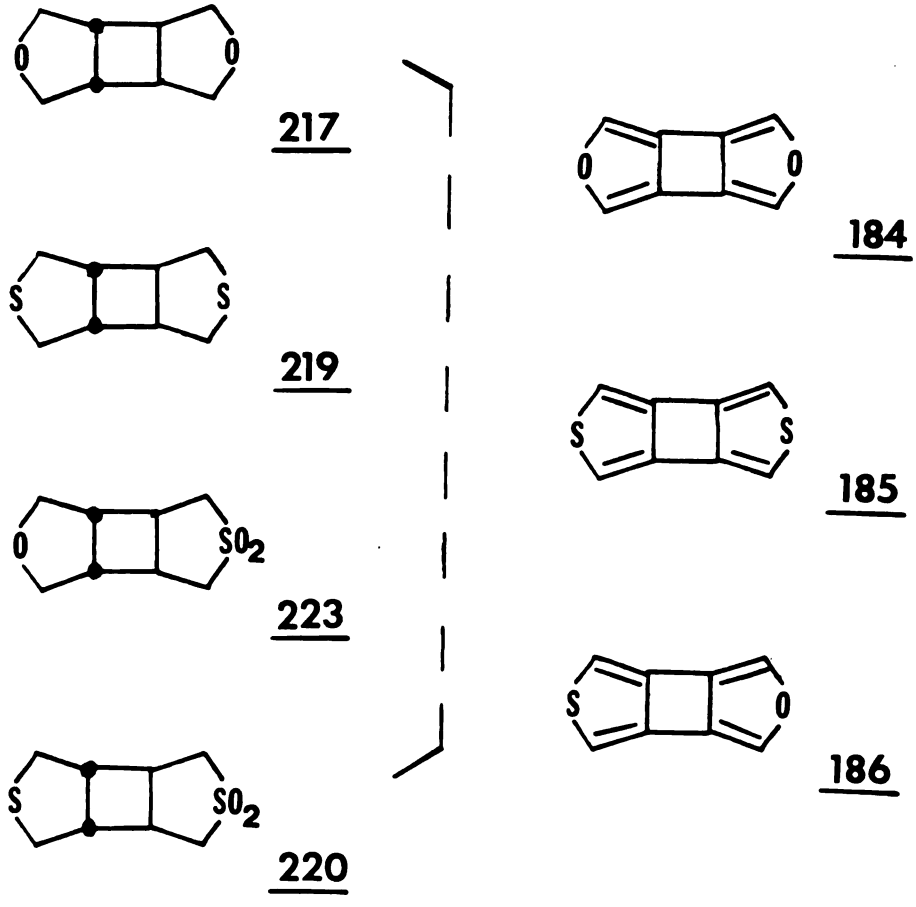
Investigations have been conducted on the acidity of cyclic sulfones.[73] The acidity heavily depends on being able to achieve the required pyramidal geometry of the carbanion. As the ring size becomes smaller, the shorter chain enforces a more rigid conformation for the pyramidal



base: n-BuLi, s-BuLi, t-BuLi, LDA.

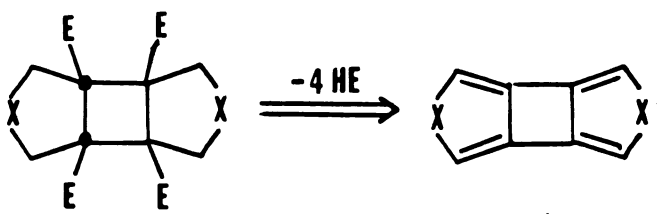
E^+ : Br_2, I_2, BrCN, bromo-Meldrum's acid.

carbanion and results in an increasing repulsion between the charge on the carbanion and the partial negative charge on the sulfone oxygen atom. Therefore, the carbanion is

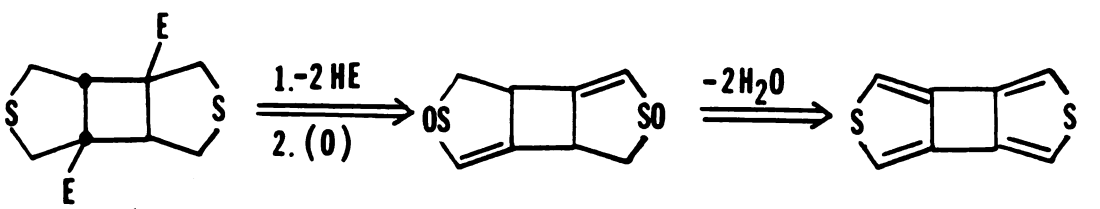


destabilized, with a resulting decrease in the acidity of the sulfone. This might be the reason for the unexpected difficulty in abstracting the α-H from sulfone-sulfide 220.

In summary, we reported the preparation of disulfide 219 and sulfone 220 along with their oxygen containing analogues 217 and 223. Although conversion to the target compounds encountered more difficulties than was anticipated, the preparation of 184 - 186 via this approach seems still plausible. Methods such as those outlined in Schemes 17 and 18 have not yet been tried. They avoid the difficulties raised during the manipulation of the α position of the sulfone, because functionalization would start at an earlier stage of the synthetic sequence.



Scheme 17



Scheme 18

EXPERIMENTAL

1. 4,4'-Dibromo-3,3'-bithienyl (201)

To a precooled (-78°C) solution of 3,4-dibromothiophene[76] (1 g, 4.2 mmol) in 150 mL of anhydrous ether under nitrogen, was added dropwise with stirring a solution of n-butyllithium (90 mmol in 50 mL of hexane). The resulting mixture was stirred for 1.5 h. Anhydrous cupric chloride (1.4 g, 10 mmol) was then introduced all at once (as crystals) while keeping the reaction temperature at -78°C. The solution turned brown slowly and was stirred for another 2 h. After removing the dry ice bath, the reaction mixture was stirred overnight and worked up by washing with 4 N HCl, and then water. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. Recrystallization of the residue from ligroin gave product 201 (0.42 g, 63%) as white crystals; mp 122-124°C (lit.[74] 127-129°C); ^{1}H NMR(DMSO-d_6) δ5.10(d, 2 H, J=3.4 Hz), 5.21 (d, 2 H, J=3.4 Hz); mass spectrum, m/e (relative intensity) 326(50), 324(82), 322(39), 245(20), 243(6), 164(100), 120(28).

2. Photolysis of 3,4-Diiodothiophene

A solution of 3,4-diiodothiophene[75] (100 mg, 0.3 mmol) in 20 mL of cyclohexane was irradiated with a high pressure mercury vapor lamp in a quartz reactor. The solution turned brown with polymeric precipitate after 20 min. The precipitate was removed by filtration. The solution was then irradiated again overnight and gave the same polymeric precipitate as found in the earlier stages of the photolysis. No compound could be isolated from the solution beside the starting thiophene.

3. Reaction of 3,4-Dibromothiophene with Electrolytic Copper

A mixture of 3,4-dibromothiophene (4.84 g, 20 mmol) and electrolytic copper powder (6.3 g, 0.1 mol) was heated in an oil bath at 200°C for 3 h. The mixture was cooled and extracted with methylene chloride (200 mL). After concentrating the organic solution, the residue was purified by chromatography (alumina, ether) to give the starting dibromothiophene (3.97 g, 82% recovered).

4. 2,5-Dimethyl-3,4-dibromothiophene (204)

To a solution of tetrabromothiophene[76] (20 g, 0.05 mol) in 300 mL of anhydrous THF at -78°C under nitrogen was added dropwise 2.4 equivalents of n-BuLi in hexane.

After stirring at -78°C for 50 min, a solution of dimethyl sulfate (18.9 g, 0.15 mol) in 10 mL of THF was introduced slowly in 15 min. The solution was stirred for 25 min at -78°C, then allowed to warm up slowly to room temperature. After 1 h at room temperature, water (20 mL) and ether (150 mL) were added, the layers were separated, and the aqueous layer was extracted with ether (50 mL). Combined organic layers were dried with $MgSO_4$ and evaporated under reduced pressure. The oily residue was recrystallized from ethanol to give 204 (10.92 g, 81%); mp 43-44°C (lit.[77] 45°C); the ^1H NMR spectrum was identical with that of an authentic sample.[77]

5. 3-Bromo-2,5-dimethylthiophene (206)

To a solution of dibromide 204 (2.7 g, 10 mmol) in 50 mL of anhydrous THF at -78°C under nitrogen was added dropwise a solution of n-BuLi (25 mmol in 10 mL of hexane) and the mixture was stirred for 35 min. The resulting solution was then transferred to a suspension of anhydrous $CuCl_2$ (4 g, 30 mmol) in 200 mL of THF at room temperature and stirred for another 4 h. Water (50 mL) was added, the aqueous layer was separated and extracted with ether (30 mL) twice. The combined organic layers were dried ($MgSO_4$) and concentrated to give a brown oil. Preparative VPC analysis (10% SE-30 on chromosorb W, 5' x 0.25', 180°C) gave thiophene 206 as the major product and some 204

(70% and 25% respectively). Both 206 and 204 have the same retention time and provide identical spectroscopic data (NMR, Mass) with that of authentic samples.[77]

6. Di[3-(2,5-dimethyl-4-bromothiophene)]iodonium Chloride (207)

To a solution of 3-thienyllithium, prepared from 1.8 g of dibromide 204 and one equivalent of n-BuLi at -78°C under nitrogen, was added a solution of trans-chlorovinyliodonium chloride[78] (freshly prepared) in 10 mL of ether and the mixture was stirred for 3 h. The dry ice bath was removed and when the temperature had risen to 0°C the mixture was poured onto water and the precipitated iodonium salt was filtered off, washed with water and acetone and dried under vacuum to give crude 207 (415 mg, 25%). The iodonium salt 207 is sensitive to air, and decomposed rapidly at room temperature. Therefore, it was used directly for the preparation of nitro derivative 208.

7. 3-Bromo-4-nitro-2,5-dimethylthiophene (208)

A mixture of iodonium salt 207 (415 mg, 0.82 mmol) and sodium nitrite (289 mg, 4 mmol) in 30 mL of anhydrous DMF was stirred at 110°C in an oil bath for 5 h. The mixture was cooled, poured onto water and extracted with ether (100 mL) twice. The combined ether layers were washed

with water, dried ($MgSO_4$) and concentrated under vacuum. The residue was purified by column chromatography (neutral alumina, ether/chloroform) to give 208 (60 mg, 15%). The further purification of 208 for elementary analysis was not successful. For 208: ^{1}H NMR($CDCl_3$) δ2.33(s, 3 H), 2.60(s, 3 H); mass spectrum, m/e (relative intensity) 237(6), 235(6), 139(31), 110(35), 109(27), 95(16), 59(60).

8. cis,trans,cis-1,2,3,4-Tetracarbomethoxycyclobutane (213)

Finely powdered dimethyl fumarate 212 (7.2 g, 0.05 mol) was spread on a glass plate and irradiated with 300 nm light in a Rayonet reactor for 2 h. The powder was collected and reirradiated in the same fashion as described for another 2 h. The residue was then recrystallized from benzene (100 mL) to give dimer 213 (3.72 g, 83% yield, 62% conversion). After evaporating the solvent, dimethyl fumarate was recovered (2.8 g, 38%). For 213: mp 143-144°C (lit.[79] 144-145°C); ^{1}H NMR($CDCl_3$) δ3.68(s, 12 H), 3.73(s, 4 H).

9. Hydrolysis of cis,trans,cis-1,2,3,4-Tetracarbomethoxycyclobutane

Dimer 213 (10 g, 34 mmol) was heated on a steam bath with concentrated hydrochloric acid until it had dissolved. The solution was evaporated to dryness under vacuum. After

recrystallizing the residue twice from hexane/acetone, the reaction gave tetracid 214 (7.94 g, 100%); mp 224-226°C, dec. (lit.[79] 220-225°C). The acid was then mixed with 5.5 g of sodium hydroxide (4 equivalents) in 50 mL of water and stirred for 2 h. Removal of the water under vacuum and air drying overnight gave 11.9 g of the tetrasodium salt, which was used for following reaction without further purification; mp above 300°C.

10. The Reaction of Salt 215 with Phosphorus Pentasulfide

A mixture of salt 215 (11.9 g, 37 mmol) and 20 g of P_2S_5 was heated to 250°C for 3 h. The slurry was cooled and extracted with 300 mL of chloroform. The resulting chloroform solution was concentrated to give 0.7 g residue. The residue did not dissolve in organic solvents but was soluble in water. However no absorption in ^1H NMR(D_2O) spectrum could be seen.

11. cis,trans,cis-1,2,3,4-Tetrahydroxymethylcyclobutane (216)

A solution of tetraester 213 (7.5 g, 26 mmol) in 50 mL of anhydrous dioxane was added into a boiling slurry of LAH (4.0 g, 0.11 mol) in 100 mL of dioxane so that a steady boiling was maintained. The mixture was cooled after 6 h refluxing. The unreacted LAH was decomposed stepwise by

adding 4 mL of H_2O, 4 mL of 15% NaOH and 100 mL of 95% EtOH. The slurry was stirred for another 3 h. The precipitate was filtered off and extracted with dioxane in a Soxhlet extractor for 48 h. After the removal of the dioxane from the combined filtrates, an oily almost pure tetraol 216 (3.624 g, 80%) was obtained. The tetraol can be purified by passing the oil through a cationic exchange resin column (Cowax 200-400 mesh, 2" x 5"). The ^1H NMR spectrum of 216 in D_2O shows absorptions at 72 and 154 cps upfield from water in the expected 2:1 ratio as reported.[80]

The tetraol was characterized as its benzoate and recrystallized from 1-butanol; mp 104-105°C (lit.[80] 104-105°C).

12. Cyclobuta[1,2-c;3,4-c']octahydrodifuran (217)

A solution of tetraol 216 (300 mg, 1.7 mmol) in 20 mL of dioxane containing a catalytic amount of p-toluenesulfonic acid (100 mg) was stirred at 50°C overnight. The solution was cooled and the dioxane evaporated under reduced pressure. Water (20 mL) and methylene chloride (100 mL) were added, and the aqueous layer was separated and extracted with methylene chloride (20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The brown residue was sublimed at 100°C (10 torr) to give octahydrodifuran 217 (154 mg, 65%). The octahydrodifuran was recrystallized from pentane; mp 73-75°C; ^1H NMR($CDCl_3$)

δ2.44(d, 4 H_c, J_{bc}=4 Hz), 3.38(dd, 4 H_b, J_{ab}=9 Hz, J_{bc}=4 Hz), 3.98(d, 4 H_a, J_{ab}=9 Hz); mass spectrum, m/e (relative intensity) 140(39), 108(5), 95(15), 81(25), 79(43), 70(65), 69(100); The decoupled ^1H NMR(180 MHz) spectrum was described in the text (page 128); high resolution mass spectrum, calculated for $C_8H_{12}O_2$: 140.08373; Found: 140.08374.

13. cis,trans,cis-1,2,3,4-Tetrabromomethylcyclobutane (218)

Tetraol 216 (3.5 g, 20 mmol) was mixed with 5 g of anhydrous sand (commercial grade, Fisher Scientific Company) in a 50-mL round-bottomed flask under nitrogen, and freshly distilled PBr_3 (2.5 mL) was then introduced dropwise. The mixture was warmed slightly (to about 70°C) until no more fumes evolved (2 h). The mixture was then heated under reflux for another 1 h. The resulting red slurry was cooled and extracted with methylene chloride (200 mL). The organic solution was washed with water twice (50 mL) and dried over $MgSO_4$. After removal of solvent under reduced pressure, tetrabromide 218 was obtained as an off-white powder which was recrystallized from chloroform/methanol to give 218 (4.2 g, 52%); mp 95-97°C (lit.[80] no mp reported); ^1H NMR($CDCl_3$) δ2.73(bs, 4 H), 3.56(bs, 8 H); mass spectrum, m/e (relative intensity) 428(1), 347(6), 267(28), 187(48), 185(45), 135(52), 133 (58), 105(94).

To a solution of tetraol 216 (557 mg, 3.1 mmol) in 20 mL of freshly distilled pyridine at room temperature was added dropwise 8.37 g (31 mmol) of freshly distilled PBr_3. The solution turned brown after 5 h of stirring. Ether (100 mL) was added, followed by 20 mL of water (exothermic reaction). The ether layer was washed with water five times to remove the pyridine completely. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by preparative TLC (alumina, hexane/ether = 1:1) to give octahydrodifuran 217 (252 mg, 57%) and a trace amount of tetrabromide 218 (less than 2%).

14. Cyclobuta[1,2-c;3,4-c']octahydrodithiophene (219)

To a boiling solution of sodium disulfide (5.25 g, 67 mmol) in 350 mL of ethanol (95%), was added dropwise a solution of tetrabromide 218 (3.5 g, 8.2 mmol) in 20 mL of dioxane. The solution was refluxed for 4 h and then cooled. After removal of the ethanol under vacuum, water (50 mL) and ether (200 mL) were added. The aqueous layer was separated and extracted with ether (50 mL). The combined organic layers were dried with $MgSO_4$ and concentrated. The residue was recrystallized from ethanol to give octahydrodithiophene 219 (1.32 g, 92%); mp 106-108°C; ^1H NMR ($CDCl_3$) δ2.59(d, 4 H_c, J_{bc}=4 Hz), 2.62(d, 4 H_a, J_{ab}=12 Hz), 2.76(dd, 4 H_b, J_{bc}=4 Hz, J_{ab}=12 Hz); ^{13}C NMR($CDCl_3$) δ45.50, 38.63; mass spectrum, m/e (relative intensity) 172(55),

139(8), 125(10), 97(9), 85(100); high resolution mass spectrum, calculated for $C_8H_{12}S_2$: 172.03805; Found: 172.03807.

15. Reaction of Octahydrodithiophene 219 with DDQ (or NCS)

(a) A mixture of octahydrodithiophene 219 (700 mg, 4 mmol) and DDQ (4.15 g, 18 mmol) in 150 mL of anhydrous benzene was refluxed for 15 h. The solution was cooled and the precipitate was filtered off. The filtrate was then passed through a column of basic alumina (1" x 10") with benzene as the eluent. The starting octahydrodithiophene 219 was recovered (493 mg, 70%). Further elution of the column with ethyl acetate did not provide any organic substance.

(b) A suspension of octahydrodithiophene 219 (870 mg, 5 mmol) and N-chlorosuccinimide (6.65 g, 50 mmol) in 300 mL of carbon tetrachloride was refluxed for 18 h. The solution was cooled and concentrated. The residue was triturated with 35 mL of CCl_4 to give 5.24 g of a solid powder (unreacted NCS and succinimide). The filtrate was concentrated to provide 746 mg (85%) of unreacted octahydrodithiophene 219.

16. 3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride-3,3-dioxide (221)

A solution of 2,5-dihydrothiophene-1,1-dioxide (12 g, 0.11 mol) and maleic anhydride (5 g, 0.05 mol) in 500 mL of acetone was irradiated with a high pressure mercury-vapor lamp in a quartz reactor for 1.5 h. The precipitate was filtered off and rinsed with acetone to give pure 221 (6.3 g, 60%); mp 289-290°C (lit.[72] 292-293°C).

17. 6,7-Dihydroxymethyl-3-thiabicyclo[3.2.0]heptane-3,3-dioxide (222)

A mixture of 221 (8 g, 37 mmol) and lithium aluminum hydride (4.5 g, 120 mmol) in 300 mL of anhydrous THF was refluxed overnight. The mixture was cooled and hydrolyzed stepwise with 4.5 mL of water, 4.4 mL of 15% aqueous NaOH and 9 mL of water. The resulting mixture was filtered and the solid material subsequently was extracted for 24 h with methanol in a Soxhlet extractor. Removal of the solvent from filtrate gave almost pure diol 222 (5.98 g, 79%), which was recrystallized from acetone; mp 94-96°C (lit.[72] 80-82°C); The ^{1}H NMR spectrum of 222 in D_2O reveals four resonances at 52, 78, 98, and 106 cps upfield from water in the expected 2:2:1:1 ratio; mass spectrum (CI), m/e (relative intensity) 207(M+1, 100), 189(19), 171(25), 107(15), 105(24).

18. 6,7-Dibromomethyl-3-thia-bicyclo(3.2.0)heptane-3,3-dioxide (224)

Diol 222 (500 mg, 2.5 mmol) was mixed with 2 g of anhydrous sea sand (Fisher Scientific Company) in a 50-mL round-bottomed flask under nitrogen. Freshly distilled PBr_3 (1.68 g, 6 mmol) was introduced dropwise into the flask. The mixture was heated under reflux for 2.5 h to give a red slurry which was cooled and extracted with methylene chloride (200 mL). The organic layer was washed with water twice (50 mL each) and dried ($MgSO_4$). After the removal of solvent under vacuum, the reaction gave dibromide 224 (661 mg, 82%) as white crystals, which were recrystallized from chloroform/methanol; mp 119-121°C; ^1H NMR($CDCl_3$) δ2.93(m, 4 H), 3.06(bs, 4 H), 3.46(m, 4 H); mass spectrum (CI), m/e (relative intensity) 333(M+1, 100).

Anal. Calcd for $C_8H_{12}SO_2Br_2$: C, 28.93, H, 3.64; Br, 48.12

Found : C, 29.05; H, 3.58; Br, 48.18.

19. Tricyclo(5.3.0.$0^{2,6}$)-3-thia-9-oxodecane-3,3-dioxide (223)

A mixture of diol 222 (200 mg, 0.97 mmol) and a catalytic amount of p-toluenesulfonic acid (20 mg) in 100 mL of ether was refluxed overnight. The solution was cooled and washed with water (3 x 30 mL) to remove the p-toluenesulfonic acid completely. The organic layer was

dried with $MgSO_4$ and concentrated. Upon recrystallizing the residue from chloroform/hexane, the reaction gave 223 (160 mg, 88%); mp 121-123°C (lit.[72b] 129-130°C); ^1H NMR($CDCl_3$) δ3.01(m, 4 H), 3.13(bs, 4 H), 3.50(m, 2 H), 4.00(d, 2 H, J=11 Hz); mass spectrum, m/e (relative intensity) 188(79), 94(54), 91(19), 79(100), 39(15); high resolution mass spectrum; calculated for $C_8H_8SO_3$: 188.05072; Found : 188.05246.

20. Tricyclo(5.3.0.$0^{2,6}$)-3,9-dithiadecane-3,3-dioxide (220)

To a boiling solution of sodium disulfide (7 g, 90 mmol) in 200 mL of ethanol (95%) and 20 mL of HMPA, was added dropwise a solution of 224 (3 g, 9.2 mmol) in 20 mL of acetone. The solution was refluxed for 3 h. After removal of the ethanol, water (50 mL) and ether (50 mL) were added. The aqueous layer was separated and extracted with ether (50 mL). The combined organic layers were dried with $MgSO_4$ and concentrated. The residue was recrystallized from ethanol to give sulfone 220 (1.80 g, 97%) as white crystals; mp 202-204°C (lit.[72b] 195-196°C); ^1H NMR ($CDCl_3$) δ2.38-2.63(m, 6 H), 2.83-3.03(m, 6 H); ^{13}C NMR ($CDCl_3$) δ54.87, 46.18, 38.52, 36.22; mass spectrum, m/e (relative intensity) 204(20), 188(20), 172(86), 139(22), 125(20), 94(42), 86(83), 85(100); high resolution mass spectrum, calculated for $C_8H_{12}S_2O_2$: 204.02788; Found: 204.02806.

21. Reaction of Sulfone 220 with Diisobutylaluminum hydride

To a solution of sulfone 220 (715 mg, 3.5 mmol) in 50 mL of toluene at room temperature was added a solution of diisobutylaluminum hydride (15 mmol) in 50 mL of toluene. The mixture was refluxed for 6 h and then cooled. Ethanol (20 mL) and water (20 mL) were added. The aqueous layer was separated and extracted with methylene chloride (20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated. The residue was chromatographed on a preparative alumina plate with ether as eluent. The first fraction gave octahydrodithiophene 219 (117 mg, 20% conversion, 97% yield). The second fraction gave starting sulfone 220 (572 mg, 80%).

22. Reaction of Sulfone 220 with DDQ (or NCS)

(a) A mixture of sulfone 220 (1.1 g, 5 mmol) and DDQ (2.78 g, 12 mmol) in 100 mL of toluene was refluxed for 4 h. The solution was cooled and the precipitate was filtered off. The filtrate was then passed through a column of basic alumina (1" x 10") with benzene as the eluent. The sulfone 220 (862 mg, 86%) was the only organic compound recovered from the column.

(b) A suspension of sulfone 220 (382 mg, 1.8 mmol) and NCS (749 mg, 5.6 mmol) in 200 mL of CCl_4 was refluxed for 4 h. The solution was cooled to -10°C. The unreacted

NCS and succinimide were filtered. The filtrate was concentrated to give a yellow residue which was recrystallized from chloroform and consisted of recovered sulfone 220 (274 mg, 72%).

23. Attempts to brominate Sulfone 220

To a solution of t-butyllithium (4 mL, 2.0 M) in 20 mL of anhydrous hexane at -78°C under argon was added a solution of sulfone 220 (1 g, 5 mmol) in 50 mL of anhydrous THF. The solution was stirred at -78°C for 30 min. Subsequently cyanogen bromide (1.2 g in 20 mL of THF) was introduced into the solution and the mixture was stirred for another 3 h, then allowed to warm up slowly to room temperature and left overnight. Water (20 mL) and ether (100 mL) were added. The organic layer was dried ($MgSO_4$) and concentrated. The residue was triturated with acetone to give sulfone 220 (613 mg). The filtrate was chromatographed on alumina (methylene chloride) to recover additional 220 (249 mg, overall 86%).

Different bases, such as s-BuLi, LDA, and bromination agents, such as NBS, bromo-Meldrum's acid, have been applied to the procedure described above. However, only sulfone 220 was recovered in all cases.

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