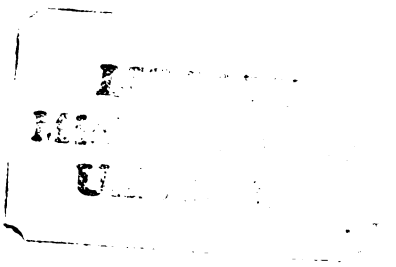

This is to certify that the

dissertation entitled

USE OF DI-ARYNE EQUIVALENTS IN THE

SYNTHESIS OF NOVEL ARENES

presented by

Mary Ann Babin Meador

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Harold Hart
Major professor

Date November 11, 1983

USE OF DI-ARYNE EQUIVALENTS IN THE SYNTHESIS OF NOVEL ARENES

By

Mary Ann Babin Meador

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1983

ABSTRACT

USE OF DI-ARYNE EQUIVALENTS IN THE
SYNTHESIS OF NOVEL ARENES

By

Mary Ann Babin Meador

Di-aryne equivalents, generated from tetrahalobenzenes and n-butyllithium, were used to synthesize a variety of peri-substituted anthracenes and phenanthrenes. The procedure involved bis-cycloaddition to substituted furans or pyrroles, followed by aromatization of the bis-adducts in various ways.

The photochemistry of the crowded arenes was studied. It was found that the series of 9,10-dialkoxyoctamethylanthracenes, as well as 9-methoxyoctamethylanthracene, formed 9,10-Dewar-isomers on irradiation, but these were much less stable than the 9,10-Dewar-anthracenes produced from irradiation of decamethylanthracene and 9-t-butylanthracene. Irradiation of 1,2,3,4,5,6,7,8-octamethylanthracene at -78°C produced an unknown radical species as evidenced by its ESR spectrum. There is no precedent in the literature for such behavior.

Mary Ann Babin Meador

The synthesis of novel iptycenes from di-aryne equivalents was described. In 1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide)(I), both double bonds are effective dienophiles. Thus, I gives a bis-adduct with anthracene which on dehydration gives 5,9,14,18-tetrahydro-5,18[1',2']:9,14[1",2"]-dibenzenoheptacene(II). That is, I is a 2,3;6,7-anthradiyne equivalent. The central anthracene moiety in II adds benzyne to give the novel horseshoe-shaped 5,7,9,14,16,18-hexahydro-5,18[1',2']:7,16[1",2"]:9,14[1"',2"']-tribenzenoheptacene.

Similarly, 6,7-dibromo-1,4-dihydronaphthalene-1,4-epoxide(III) is a 2,3;6,7-naphthadiyne equivalent. Reaction of III with anthracene produces an adduct which on dehydration gives 2,3-dibromo-6,11-dihydro-6,11[1',2']-benzenonaphthacene(IV). Reaction of IV with n-butyllithium and furan gives an adduct which can be deoxygenated with low valent titanium to give 5,14-dihydro-5,14-[1',2']-benzenopentacene.

With Love, to Mike

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to Professor Harold Hart for his encouragement and guidance throughout the course of this study, as well as his limitless patience through my bout with morning sickness.

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

I would like to thank my family and friends for their love and support over the past few years. I especially owe my parents a debt I can never repay.

Last and most, I thank my husband, Mike, for never allowing me to quit.

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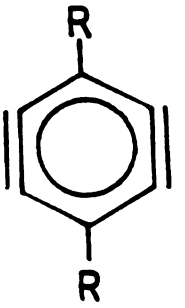
INTRODUCTION

Benzynes have been used extensively in organic synthesis for many years.[1] In comparison, investigation of the enormous potential of di-aryne equivalents for the construction of complex ring systems has only begun.

Use of the terms di-aryne and di-benzyne does not necessarily imply that the reactions which will be discussed proceed through intermediates such as 1 and 2. Dibenzynes, however, have been proposed as intermediates in certain mass



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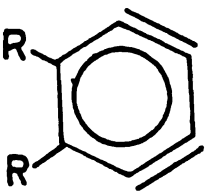
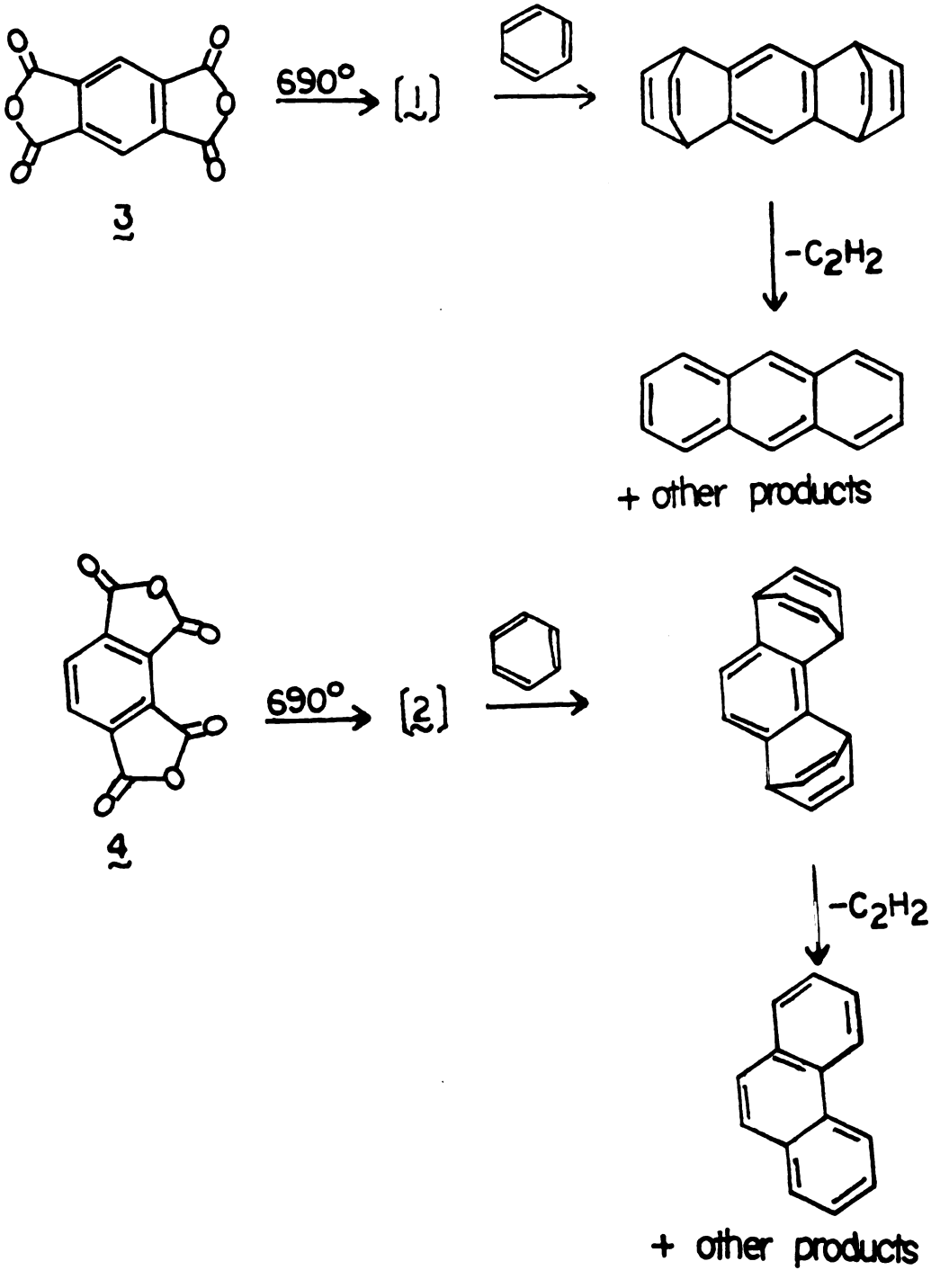


2

spectral fragmentations, and have been used to rationalize products from the co-pyrolysis of pyromellitic (3) or mellaphanic (4) dianhydrides with benzene[2] (see Scheme 1). These reactions may proceed as postulated, or they might



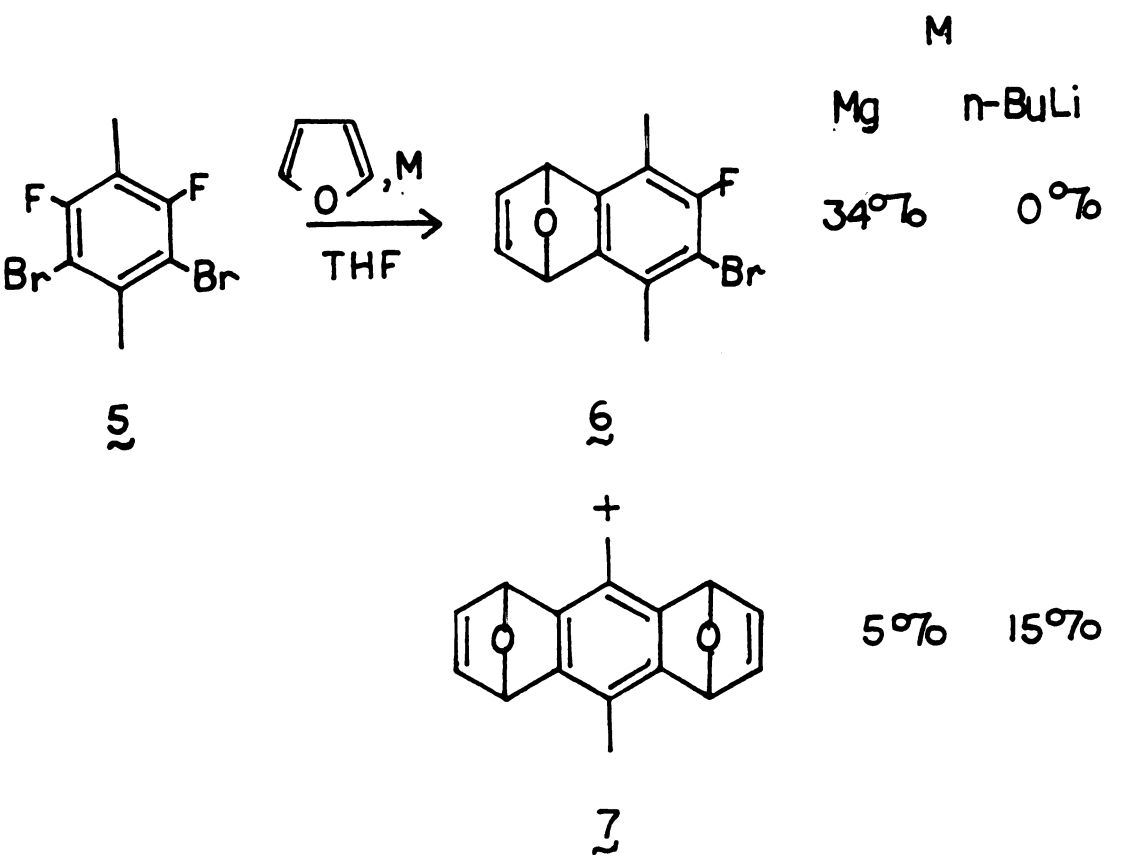
3

4

Scheme 1.

proceed in a stepwise manner. Indeed, when a less active arene, such as chlorobenzene, is used as the trapping agent, products which still contain one anhydride ring are observed.

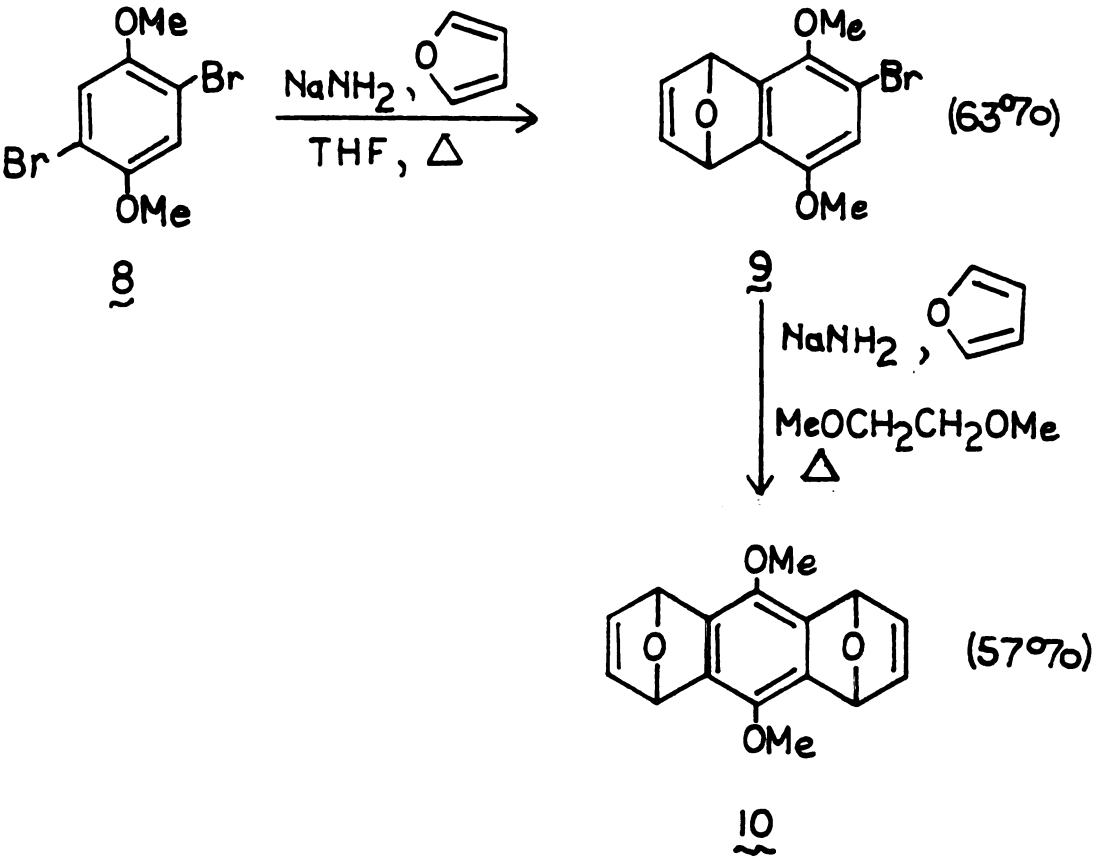
Wittig[3] introduced di-aryne equivalents in 1959 with the conversion of 5 to 7. The yield of 7 was low, however,



and 5 was a difficult starting material to prepare.

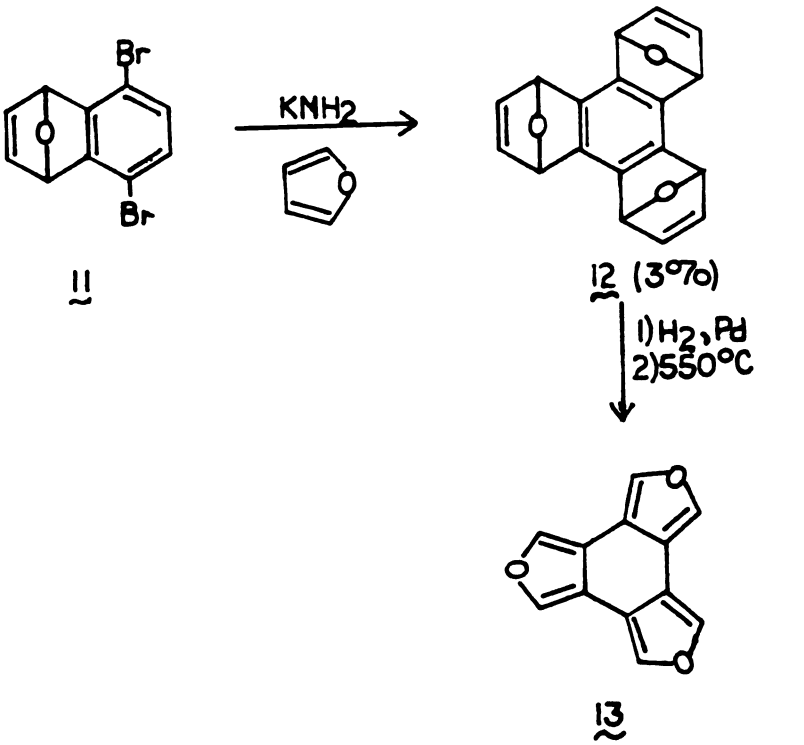
Giles[3] used a di-aryne equivalent to synthesize the bis-epoxide, 10. But the reaction was carried out in two steps since a higher reaction temperature was required for

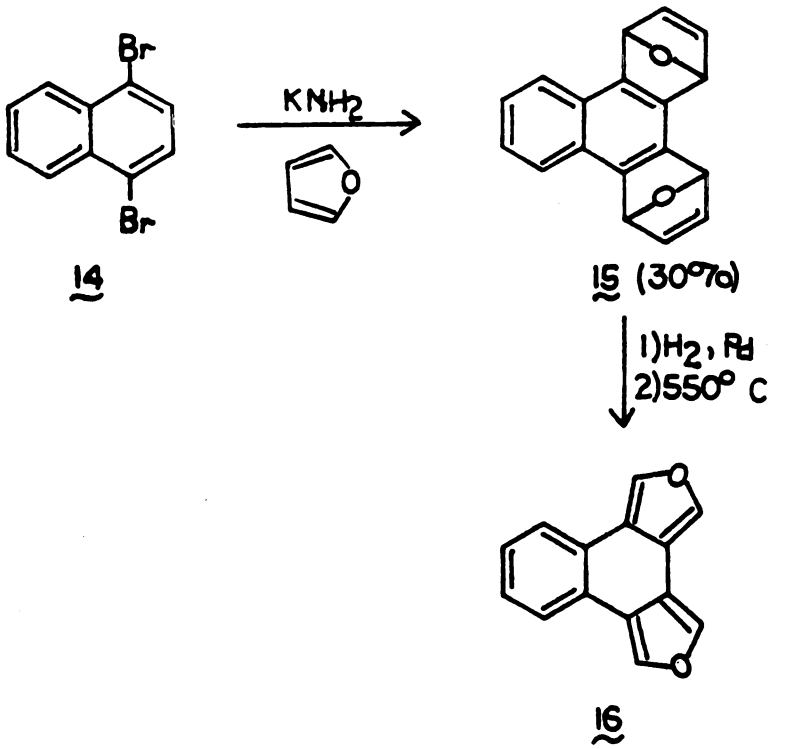
addition of the second furan moiety than for the first. The overall yield of bis-adduct 10 for the two-step process was 36%.



8 9 10

Wege and Stringer,[5] in work reported after studies on di-arynes were initiated in this laboratory, synthesized some novel furan derivatives of triphenylene (i.e., 13 and 16) via o-di-aryne equivalents (see Scheme 2). The reported yields of the bis-adducts 12 and 15 were low. However, much unreacted starting material, as well as mono-adduct, was recovered in each case, since the authors

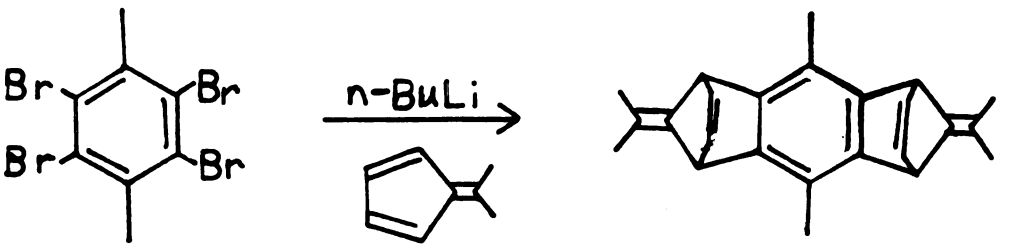

Br
Br
KNH2
11
12 (3%)
1)H2, Pd
2)550°C
13


Br
Br
KNH2
14
15 (30%)
1)H2, Pd
2)550° C
16

Scheme 2.

stated that allowing the reactions to go to completion resulted in degradation of the products. Thus, the degree of conversion was actually much higher than the reported yield.

An improved method of generating di-aryne equivalents has been developed by Hart and co-workers in recent years.[6] The method makes use of the relatively easy-to-prepare tetrabromoarenes, such as 17. Reported yields for these

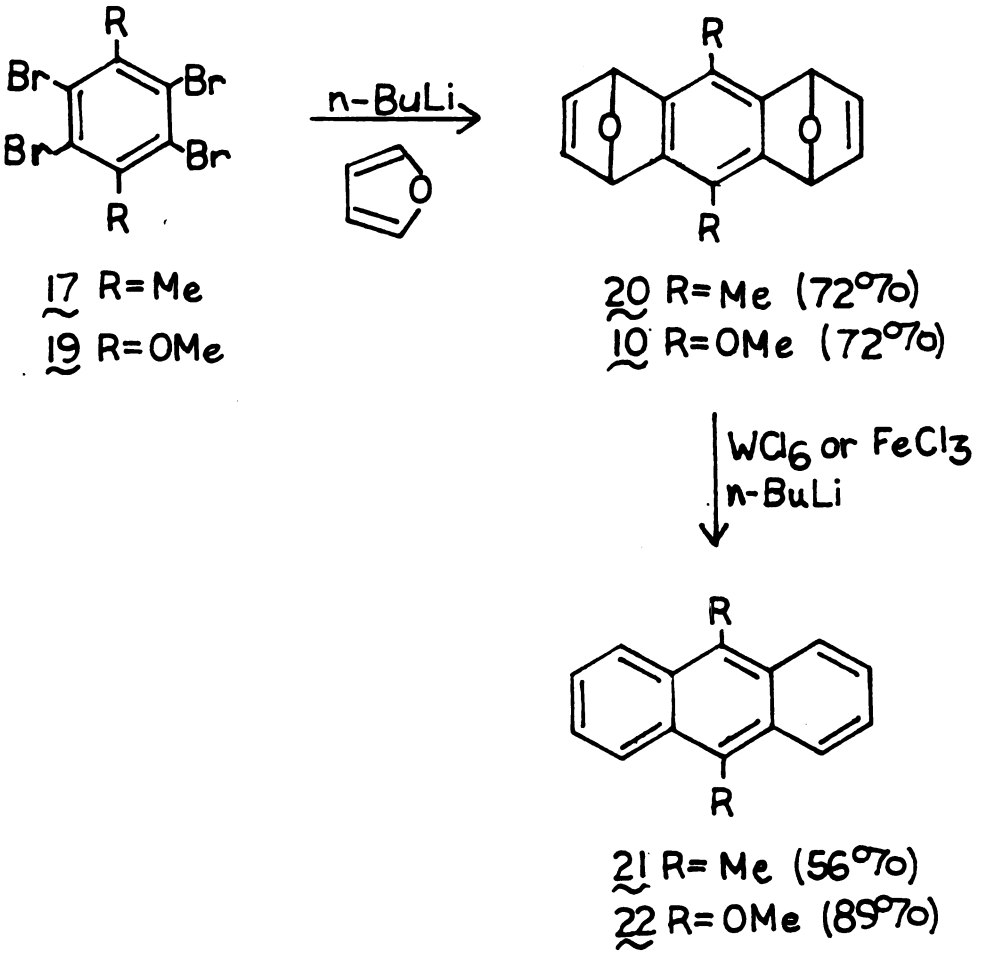


17 18 (70%)

reactions are generally good (60-80%), and the scope of the method is limited only by compatibility of the diene (and substituents on the dienophile) with n-butyllithium.

Di-aryne equivalents have been shown to be particularly useful in the synthesis of fused aromatic systems.[6-10] A wide range of substituted anthracenes have been synthesized by Hart and co-workers[6,8] in two steps from suitably substituted benzenes. The procedure involves bis-annelation of substituted furans or pyrroles, followed by aromatization in various ways. For example, the bis-epoxides,

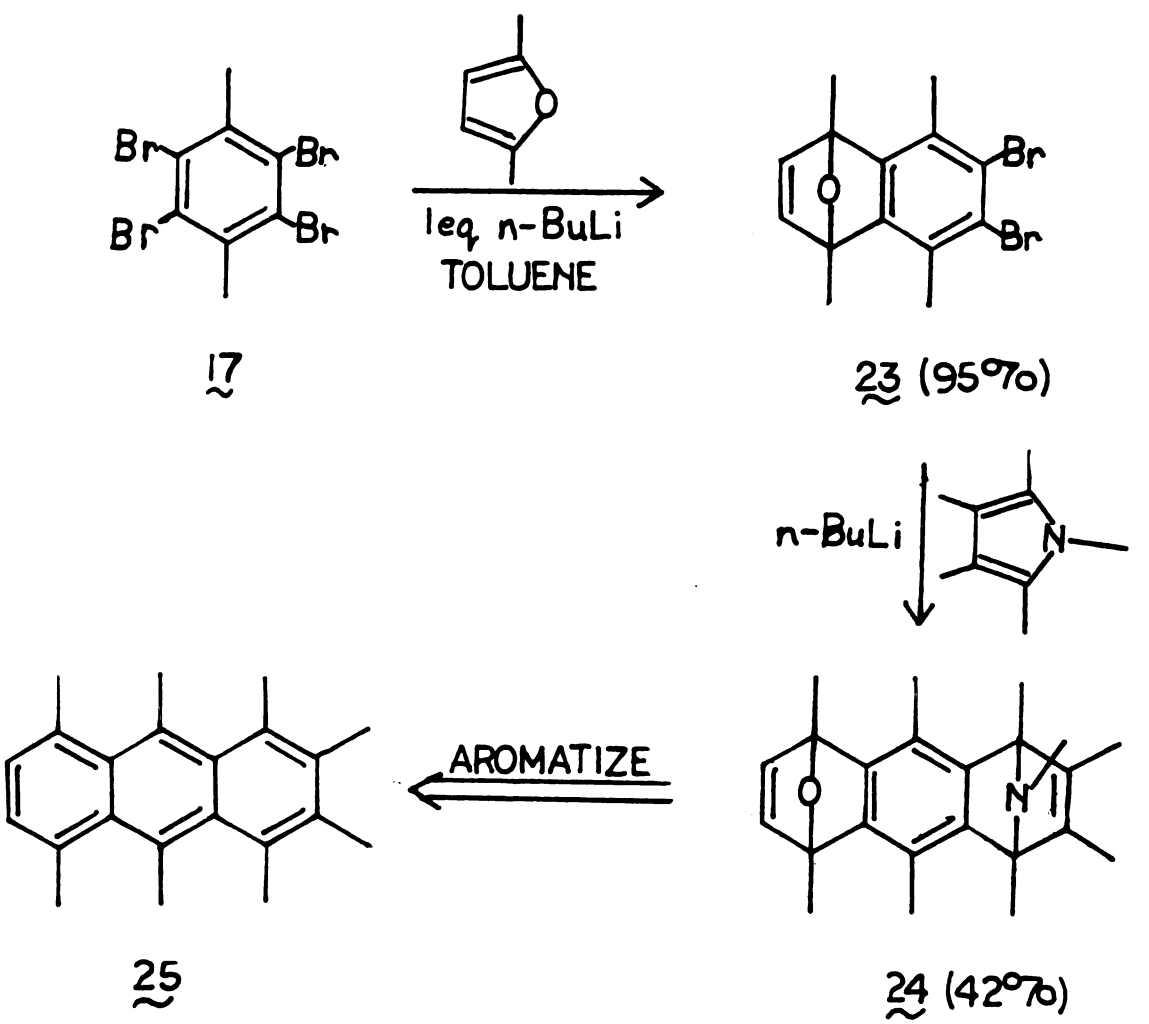
20 or 10, can be prepared in good yield from 17 or 19, and furan. Deoxygenation is carried out in a single step using



low valent metals such as tungsten or iron,[8] as opposed to indirect procedures which involve two steps, hydrogenation followed by dehydration.

Since the bis-annelation proceeds stepwise,[6] the reaction can be used to make unsymmetric anthracenes. For

example, the mono-adduct, 23, can be prepared from 17 and 2,5-dimethylfuran using one equivalent of n-butyllithium. Adding one equivalent each of N-methyltetramethylpyrrole and n-butyllithium to the reaction mixture gave the unsymmetric bis-adduct, 24. Here, the choice of solvent was important. With ether or tetrahydrofuran as solvent no mono-adduct 23 could be isolated. This is probably because

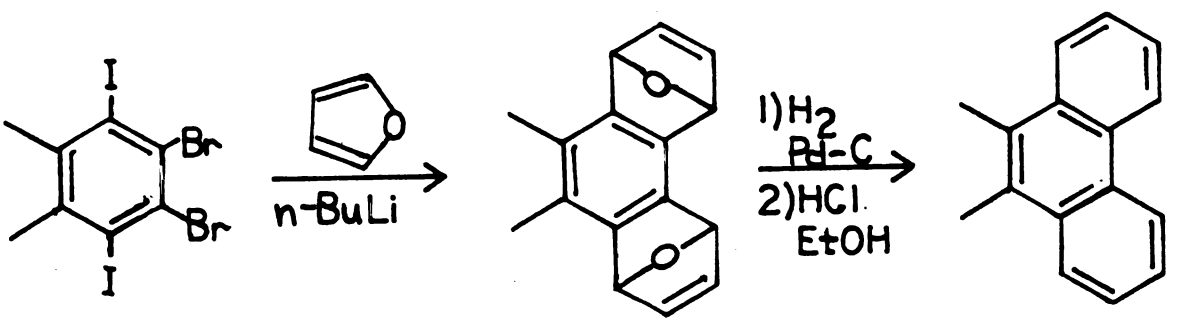


17 23 (95%)

25 24 (42%)

the greater solubility of 23 allows it to be metalated faster than tetrabromo-p-xylene, 17. If toluene is used as solvent, the solubility of 17 is increased, giving a good yield of 23.

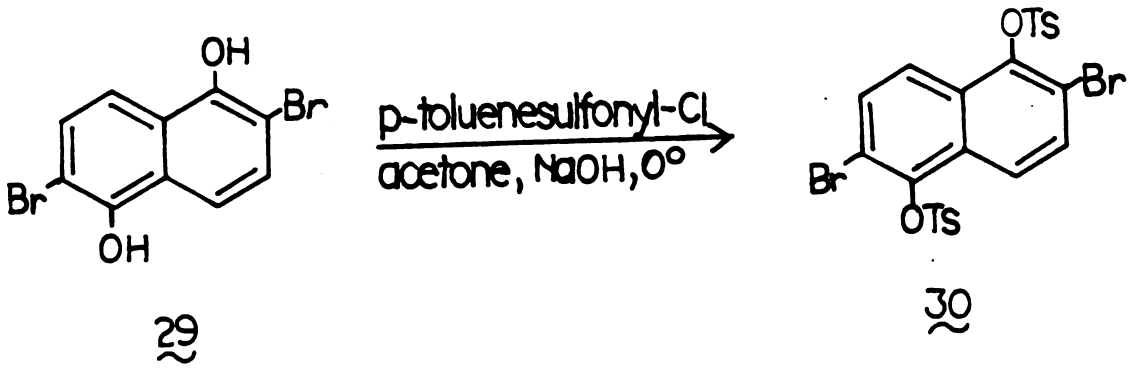
Extension of this methodology to phenanthrenes has been achieved by Hart and Shamouilian[9] by using 4,5-dibromo-3,6-diiodo-o-xylene, 26, as the o-di-benzyne precursor.



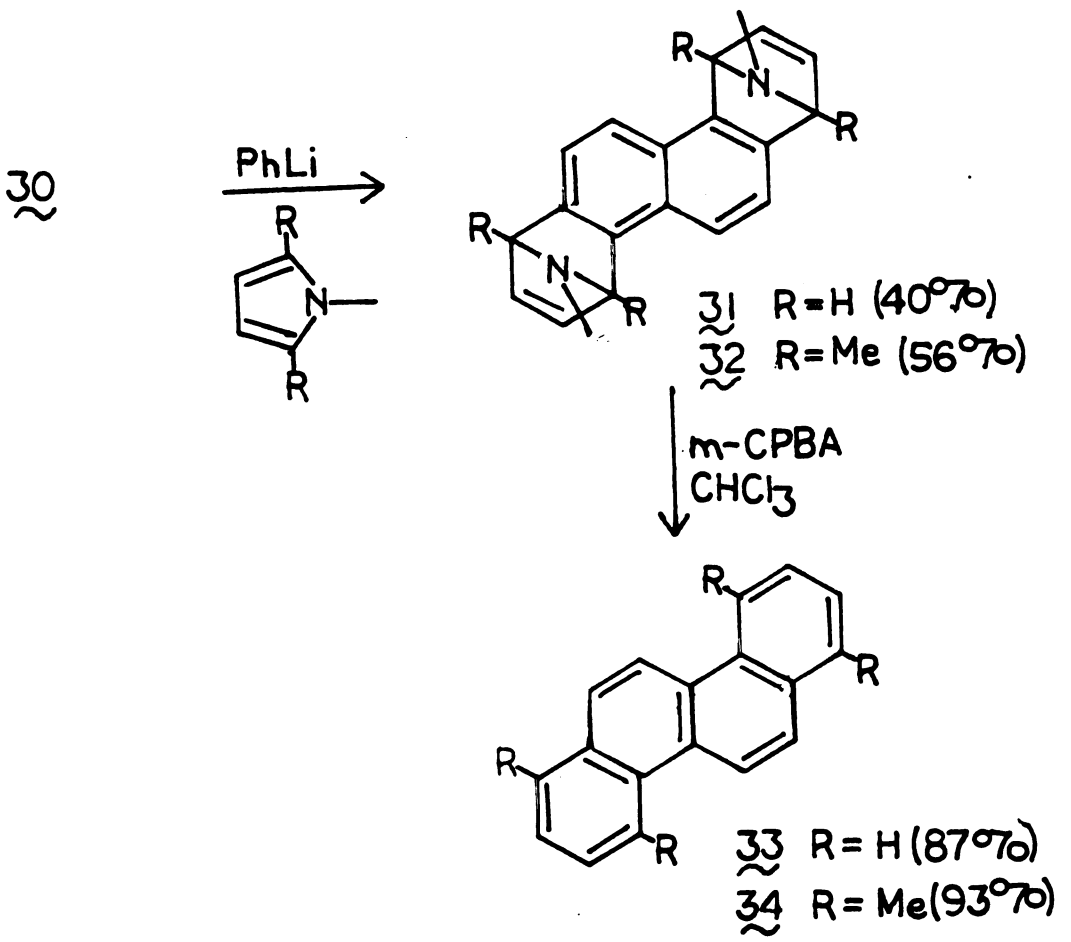
26 27 28

This reagent was selected in order to direct lithiation to give the desired product (iodine exchanges faster than bromine).

LeHoullier and Gribble[10] recently used a similar method for generating a naphthadiyne equivalent in the two-step synthesis of chrysenes, 33 and 34 (see Scheme 3). The 2,6-dibromo-1,5-bis-[(p-tolylsulfonyl)oxy] naphthalene, 30, was easily prepared in 94% yield from commercially available 29.

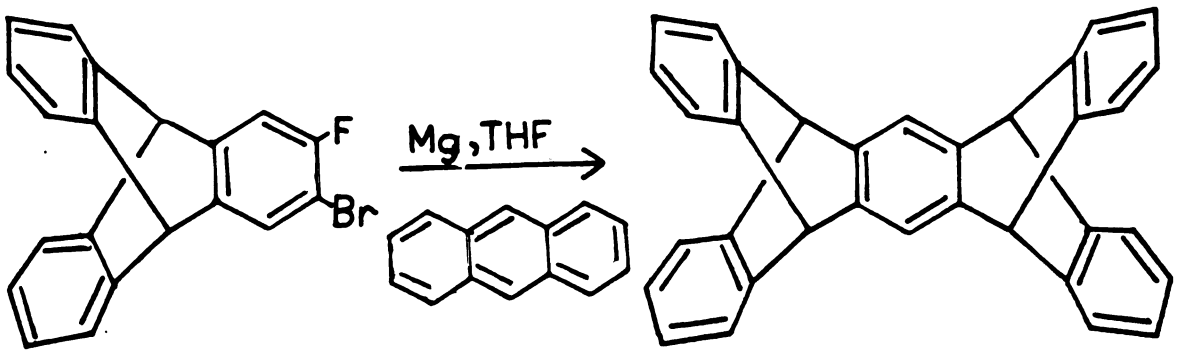


29 30



Scheme 3.

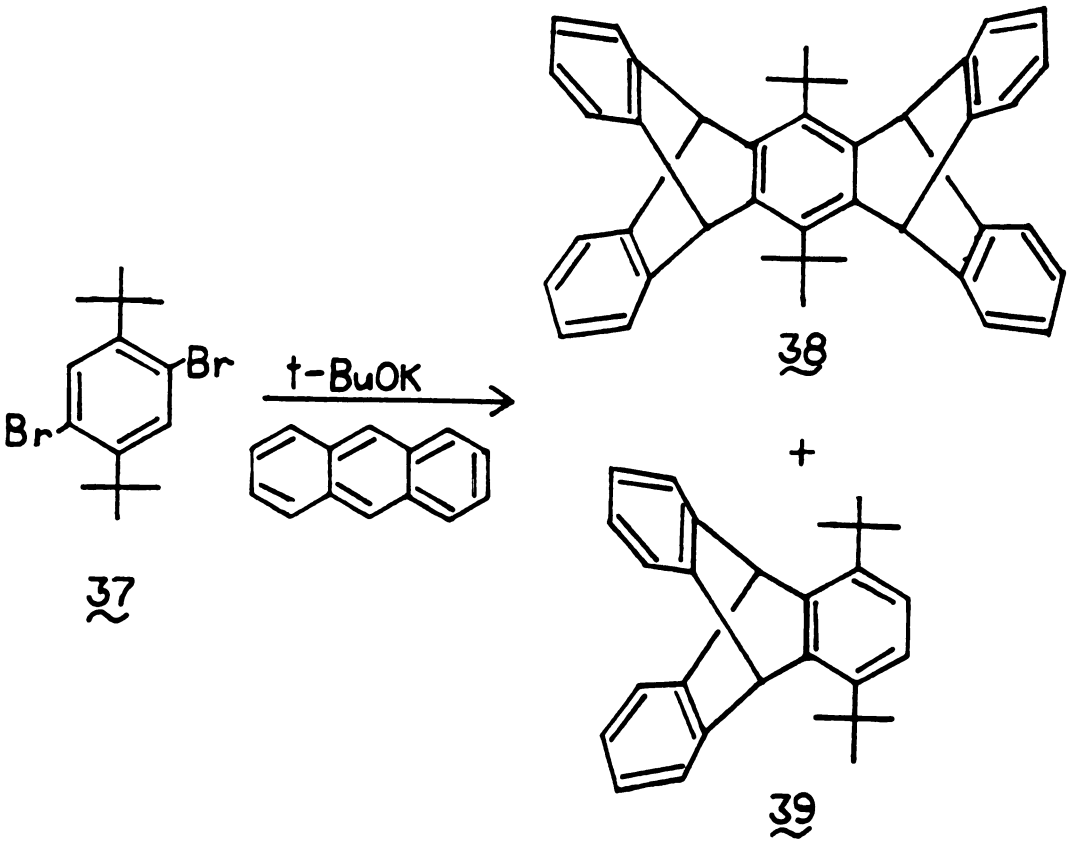
Di-arynes can be trapped by anthracene to give some novel "iptycenes."* The pentiptycene, 36, was first prepared from triptycyne equivalent, 35, (not itself trivial to make!) in a 10% yield.[12] The overall yield of 36 from available starting materials was only 1.2% (5 steps).



35 36

The di-t-butyl derivative, 38, was synthesized from di-aryne precursor 37 in a 2% yield, along with some 1,4-di-t-butyl-triptycene, 39.[13]

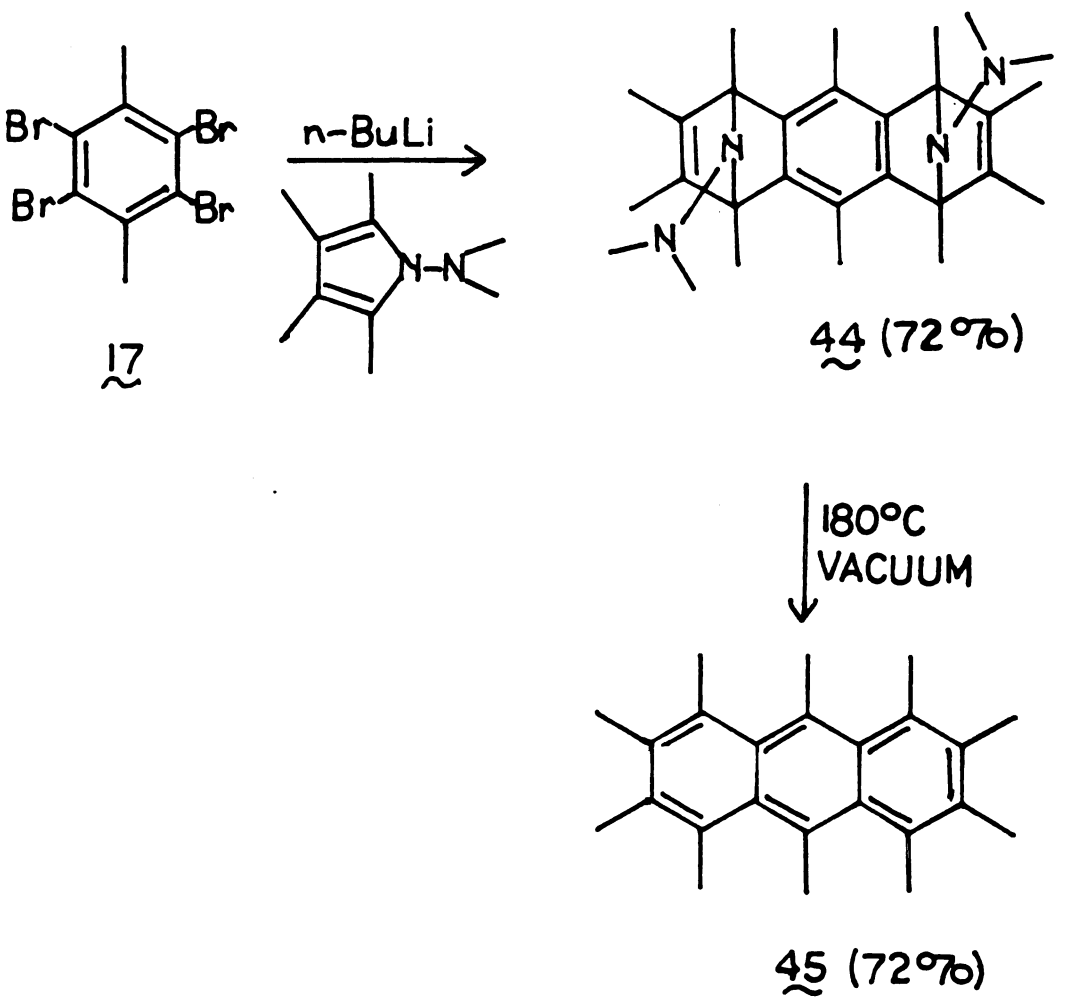
*The name "iptycene" emphasizes the relationship between these compounds and the parent structure, triptycene. A prefix indicates the number of separated arene planes; thus, 35 above is a triptycene (three planes) and 36 is a pentiptycene (five planes).[11]



Hart, Shamouilian and Takehira[11] have synthesized 36 in a much improved yield, and in only one step from available starting materials. They also prepared the new o-pentiptycene, 41, and 1.1.2(b)^b.1.1 pentiptycene, 43 (see Scheme 4).

Di-arynes have been shown to be useful synthons for fused aromatic compounds containing large peri-substituents.[6,7] Since the steric strain is introduced over two steps -- the first an exothermic benzyne reaction, and the second driven by aromatization -- the molecule is cajoled into accepting

it. For example, decamethylanthracene, 45, was synthesized[6] in 72% overall yield from 17 and N,N-dimethylaminotetramethylpyrrole, a substantial improvement over the

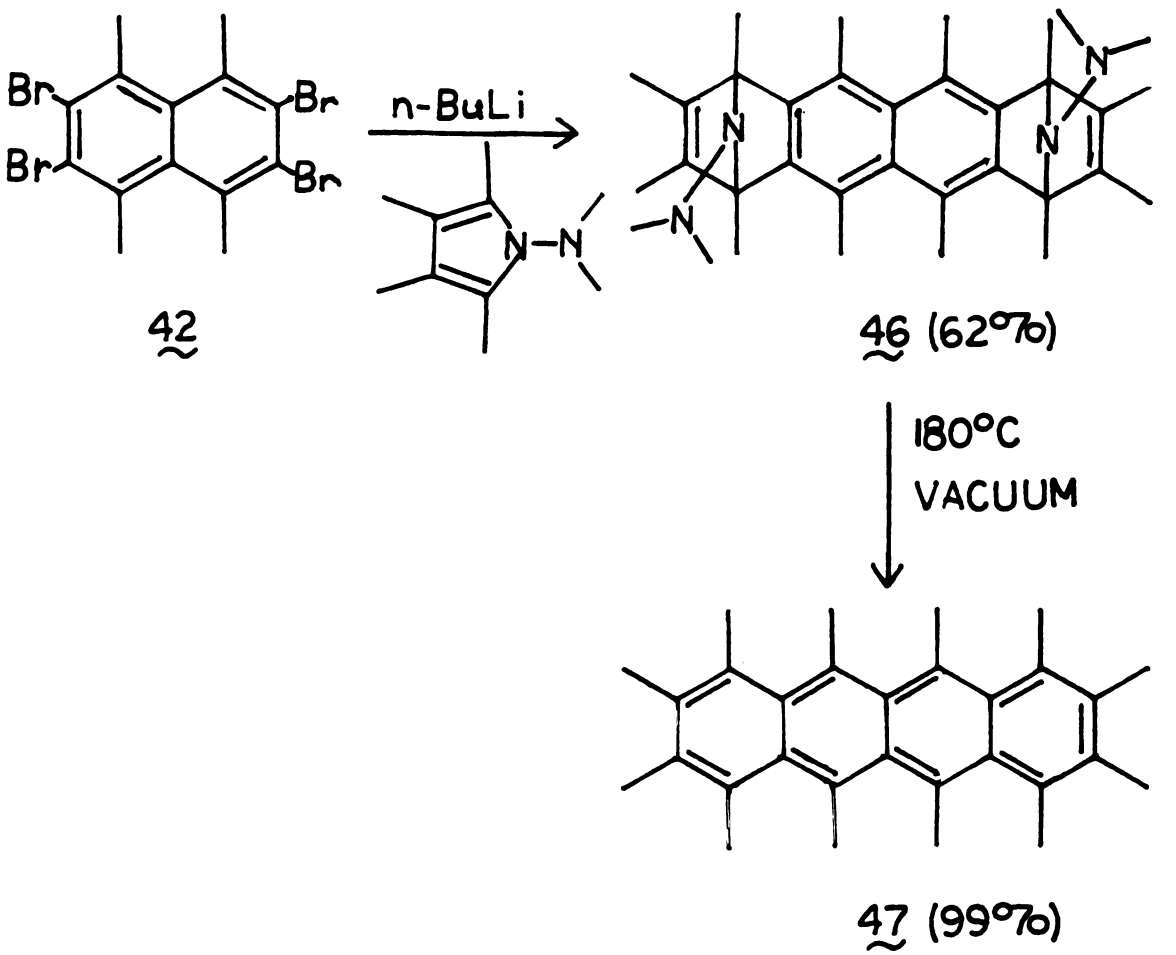


17

44 (72%)

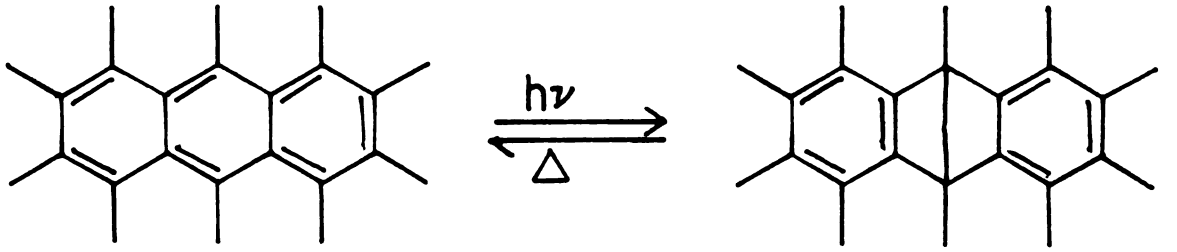
45 (72%)

earlier eight-step synthesis.[14] Similarly, dodecamethylnaphthacene, 47, was prepared from the naphthadiyne equivalent 42 in a 62% overall yield.[6]

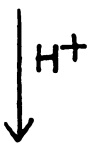


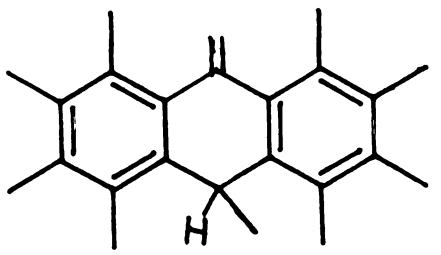
42 → 46 (62%) → 47 (99%)

Compounds such as 45 undergo some unusual reactions as a consequence of the steric strain in the system. For example, decamethylanthracene, 45, in the presence of a trace amount of acid, will isomerize to the tautomer 48.[14] Irradiation of 45 in benzene (or ether) produces the 9,10-Dewar-isomer 49, which thermally reverts to the anthracene. Both of these rearrangements serve to buckle the middle ring, relieving the four methyl-methyl peri-interactions.



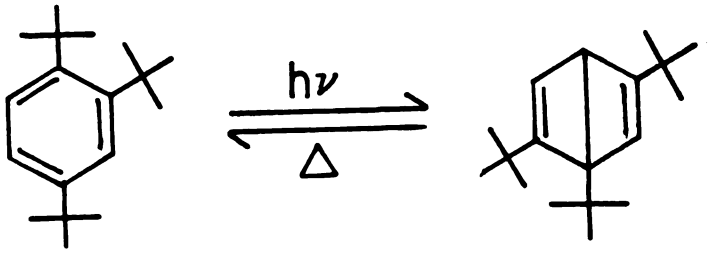
45 49





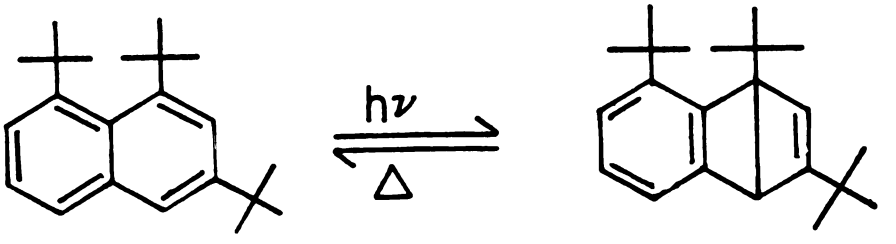
48

Other aromatic compounds containing sterically bulky substituents also undergo photochemical valence isomerization to their Dewar-isomers. The first example of such compounds was van Tamelen's 1,2,4-tri-t-butylbenzene, 50.[15] Again, the Dewar-isomer, 51, thermally rearranges to the starting material.



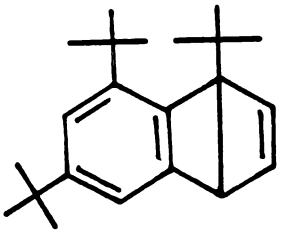
50 51

Peri-di-t-butylnaphthalenes such as 52 also have been photolyzed to afford hemi- Dewar-naphthalenes.[16a] Curiously, 52 gave the hemi-Dewar, 53a, as the sole isomer.



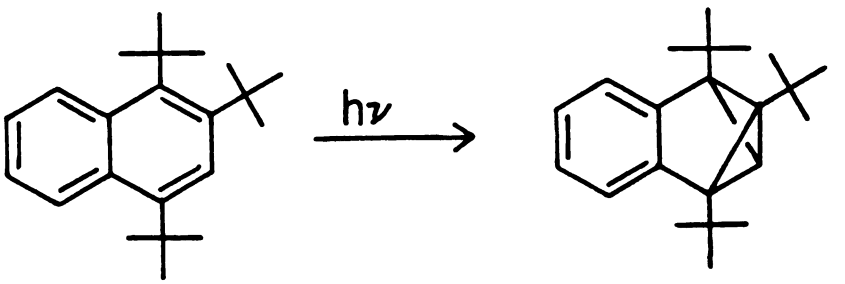
52 53a

None of the hemi-Dewar-isomer 53b could be detected.



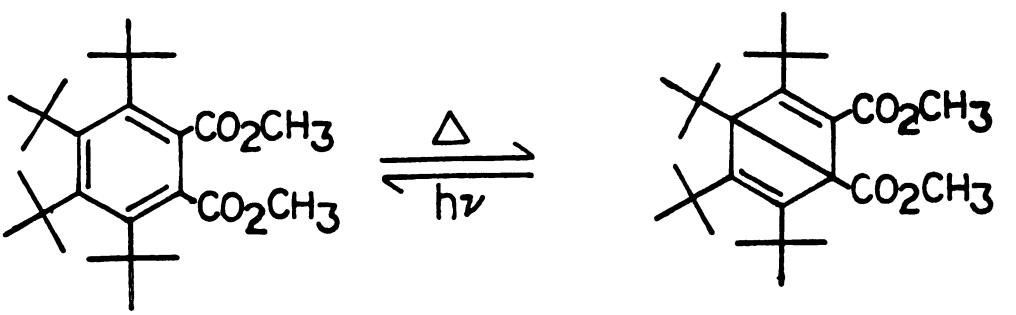
53b

Some tri-t-butylnaphthalenes also yield hemi-naphthavalenes under irradiation. For example, naphthalene 54 photolyzes to hemi-naphthavalene 55 in 95% yield.[16b]



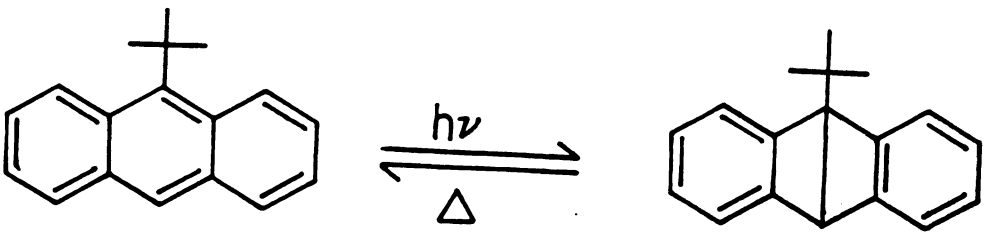
54 55

Surprisingly, the 1,2,3,4-tetra-t-butylbenzene 56 is converted <u>thermally</u> to its Dewar-isomer, 57 which reverts to 56 <u>photochemically</u>.[17] This reversal in reactivity clearly indicates that the Dewar-benzene 57 is actually lower in energy than its very crowded, aromatic valence isomer, 56.



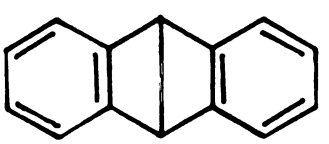
56 57

9-t-Butylanthracene 58 is the only other anthracene reported to photoisomerize to a 9,10-Dewar-anthracene, 59.[18] Other Dewar-anthracenes have been synthesized through

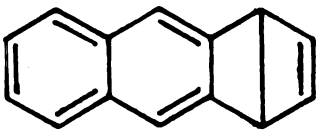


58 59

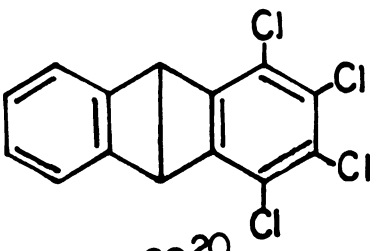
chemical means, however.[19-22] These are shown in Figure 1.



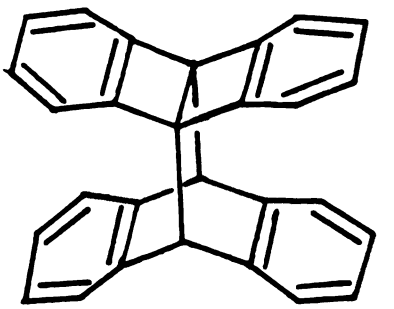
60[21]



61[22]



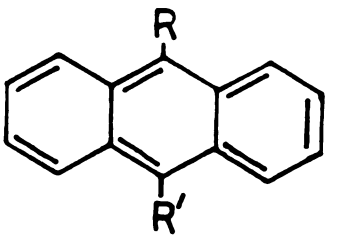
62[20]

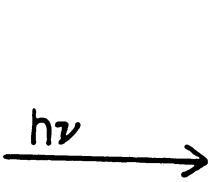


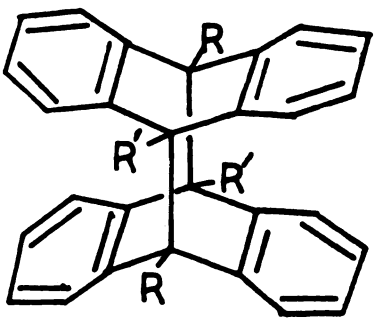
63[19]

Figure 1. Other Dewar-anthracenes.

Less crowded anthracenes, such as 64, are known to photodimerize,[23] but only if unsymmetrically substituted in the 9,10-positions. The reactions generally give the head-to-tail isomer, 65. The only exception is with



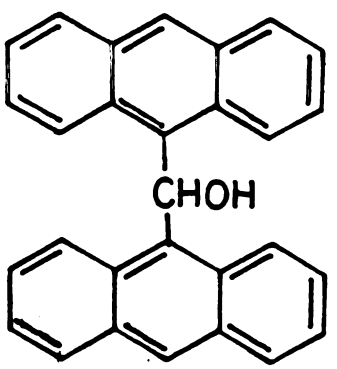




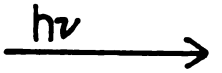
64a R = R' = H
b R = Me, R' = H
c R = MeO, R' = H
d R = Me, R' = MeO

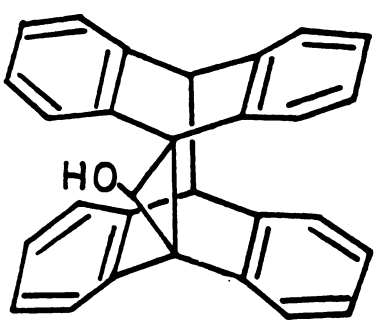
65

anthracenes linked as in 66.[26] Here, the only possible product is the head-to-head isomer 67.



66





67

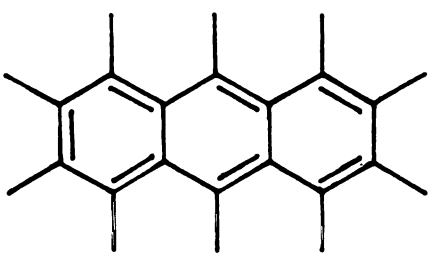
This thesis will deal, in part, with the synthesis of some other peri-strained anthracenes through di-aryne equivalents. In order to examine the conflict between steric bulk and aromatic character that is inherent in these hindered compounds, their photochemical valence isomerizations and other interesting reactions will be discussed.

In addition, extension of bis-annelations to the synthesis of some other novel compounds, such as "iptycenes," will be described.

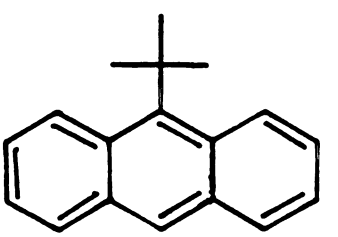
RESULTS AND DISCUSSION

Part I. Synthesis and Reactivity of Sterically Crowded Anthracenes

In both decamethylanthracene, 45, and 9-t-butylanthracene, 58, the 9,10-Dewar-isomers are photochemically accessible most likely because steric bulk destabilizes the fully aromatic structure relative to its valence isomer. The question arises, then, of how much steric bulk is necessary to drive the reaction.



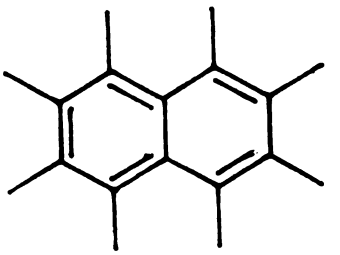
45



58

It is clear that the anthracene system is more sensitive to steric strain than either naphthalenes or benzenes. A single 9-t-butyl group is enough to give rise to the 9,10-Dewar-anthracene in the case of 58. The naphthalene system requires at least 1,8-di-t-butyl substitution, and,

permethylanthracene, 45, is photoisomerized very readily, whereas permethylnaphthalene, 68, does not photoisomerize at all.[27]



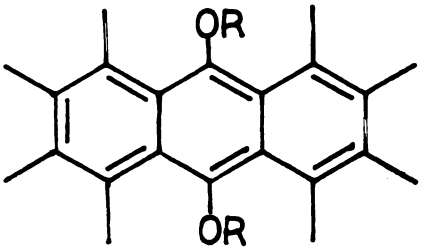
68

These observations are not surprising since it is well-established that anthracenes are highly reactive in the 9,10-positions. This is because the two, smaller, isolated aromatic rings in the product may have as much (or even more) aromatic stabilization as the reactant. Hence, less resonance energy is lost in going from an anthracene to its 9,10-Dewar isomer than in the same reaction with naphthalene or benzene (benzene losing the most).

Due to this relative ease of photoisomerization, it was of interest to further explore the photochemistry of other peri-substituted anthracenes. In this part, the synthesis of a variety of such compounds will be described and their photochemistry examined.

A. Preparation of Arenes

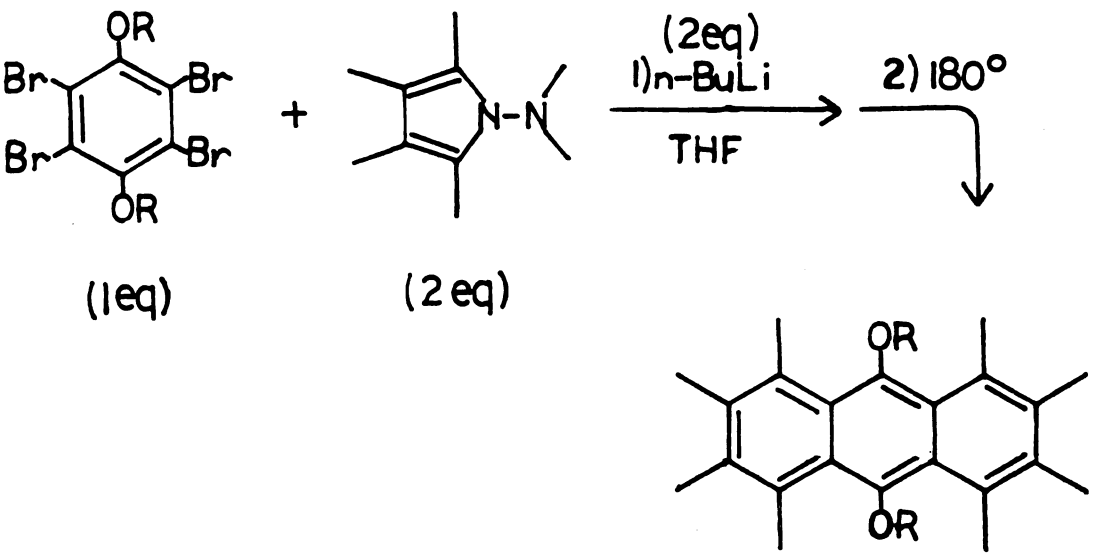
The first compounds selected for study were a series of 9,10-dialkoxyoctamethylanthracenes, 69, 71, and 73. These compounds should be nearly as crowded as decamethylanthracene, 45, but not as sensitive to acid. In addition, varying the R-group to change the degree of steric hindrance would be, synthetically, very simple. These compounds were synthesized



69 R = Me
71 R = Et
73 R = i-Pr

as shown in Table 1, from the corresponding di-aryne equivalent and N,N-dimethylaminotetramethylpyrrole. In a typical procedure, 5 mmol of the di-aryne equivalent and 10 mmol of the pyrrole in 50 mL dry tetrahydrofuran were cooled to -78°C and stirred (under argon) as 12 mmol n-butyllithium in 30 mL hexane was added dropwise over two hours. The mixture was allowed to come slowly to room temperature,

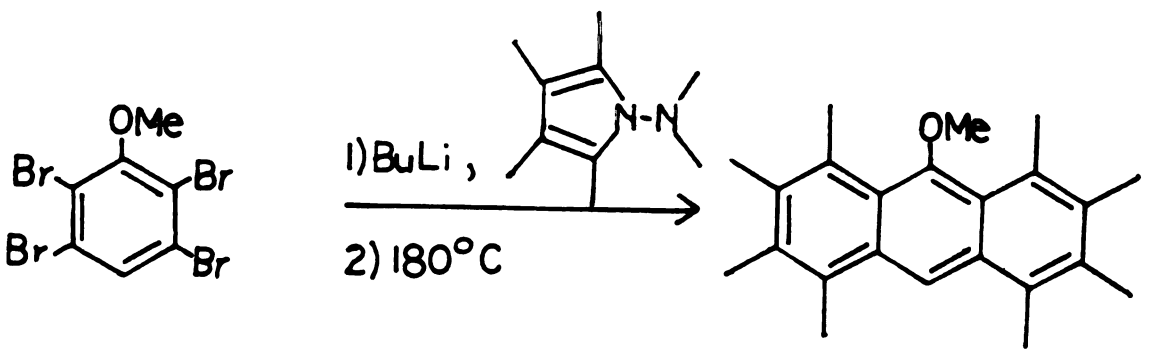
Table 1. Synthesis of 9,10-dialkoxyoctamethylanthracenes Using Di-aryne Equivalents.



Di-aryne precursor	Product (Yield)
19 R = Me	69 R = Me (60%)
70 R = Et	71 R = Et (50%)
72 R = i-Pr	73 R = i-Pr (60%)

then quenched with methanol. Workup involved extraction of the adduct with methylene chloride. Without further purification, the residual yellow-brown oil was heated to 180°C under vacuum (20-30 minutes) to remove the nitrogen bridges. The resulting black residue was purified by column chromatography and/or recrystallization, giving an overall yield for the two steps of 50-60%.

9-Methoxyoctamethylanthracene, 75, has two fewer peri-methyl-methoxy interactions than 68. The compound was synthesized in the same manner as described for 69, 71, and 73, from the di-aryne equivalent, 74.

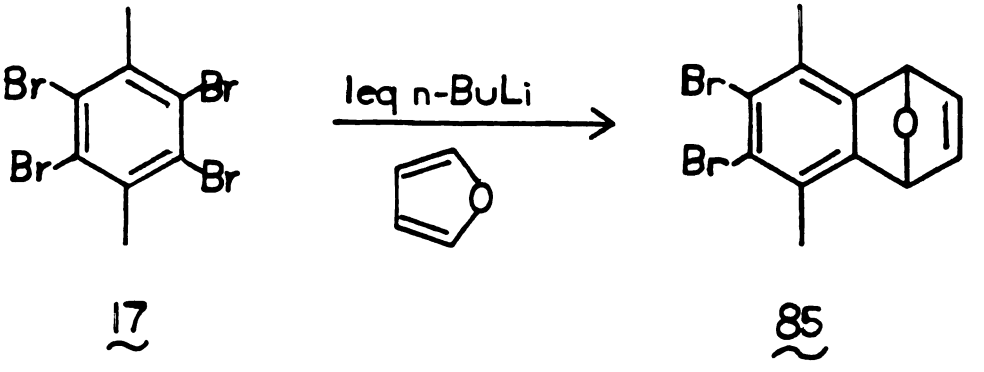


74 75 (20%)

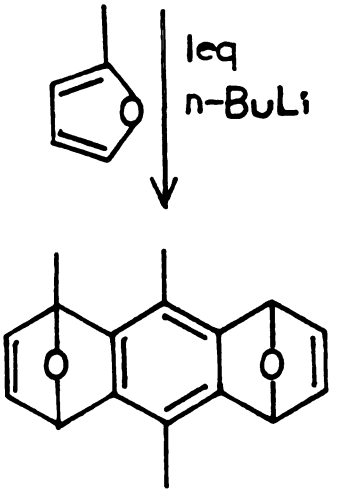
The photochemistry of many, much simpler anthracenes even those containing only one peri interaction is unknown in the literature. Consequently, it was decided to examine several such anthracenes. These were synthesized utilizing the two step bis-annelation scheme previously described. In the first step, di-aryne equivalents were reacted with

appropriately substituted furans to give the desired bis-adducts (see Table 2). Furans were used in place of pyrroles either because the furans containing the desired substitution were readily available, or the yield using the corresponding pyrrole was low. In general, the bis-annelation procedure was the same as that already described.

1,9,10-Trimethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide), 86, an unsymmetric bis-adduct, was synthesized in two steps from di-aryne equivalent 17 as shown.



17 85



86

Table 2. Bis-annelation Using Furans as Dienes.

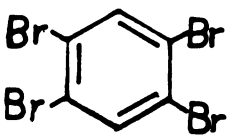
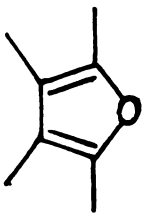
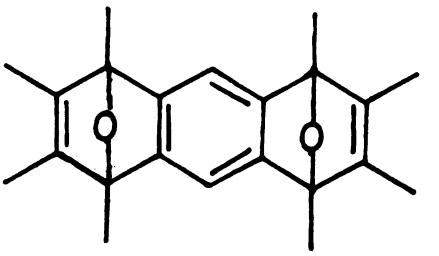
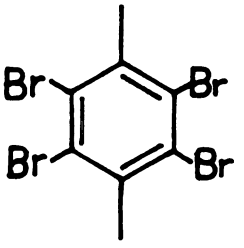
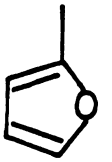
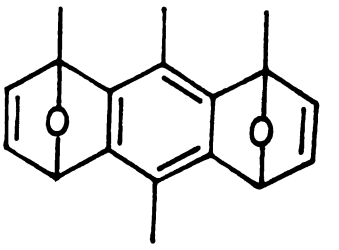
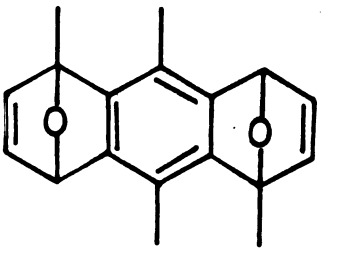
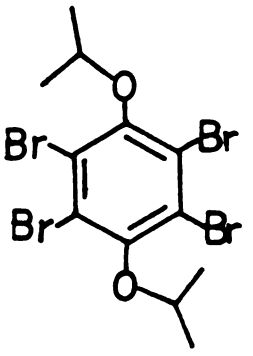
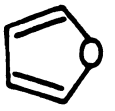
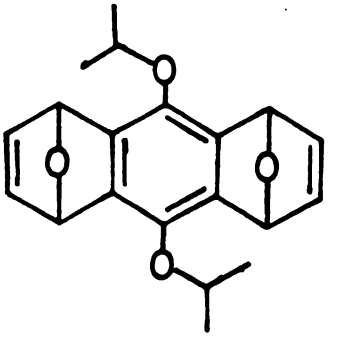
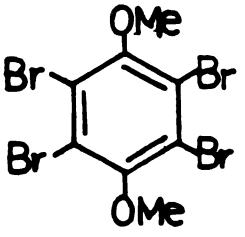
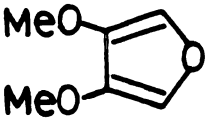
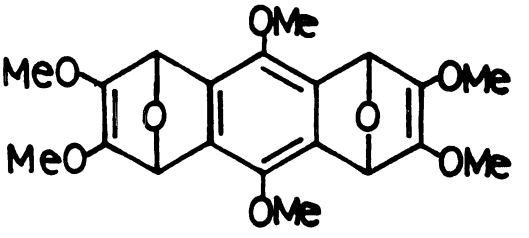
Di-aryne	Furan	Product (yield)
		
40	76	77 (71%)
		
17	78	79 (29%)
		+
		
		80 (34%)

Table 2. Continued.

Di-aryne	Furan	Product (yield)
		
72	81	82 (50%)
		
19	83	84 (65%)

Deoxygenation of the bis-adducts was carried out using low valent titanium by an improved method over that published by Hart and Nwokogu[8] (see Table 3). These authors used low valent forms of iron, tungsten, and titanium, generated by treatment of the metal chlorides with n-butyllithium. The yields were moderate to good, but the workup was generally quite tedius.

The improved deoxygenation method involved adding an excess of powdered zinc to a solution of titanium tetrachloride in tetrahydrofuran.[29] The resulting blue-gray suspension was brought to reflux, and the bis-epoxide in tetrahydrofuran was added. Reflux was generally continued for five hours, after which time the mixture was cooled and poured into dilute hydrochloric acid. Workup usually involved extraction of the yellow solid with methylene chloride. Evaporation of the solvent gave the desired anthracene in good yield (80-90%) and a high degree of purity.

Wege and co-workers[30] reported an additional method for deoxygenating 1,4-epoxy-1,4-dihydroarenes with enneacarbonyldiiron. The method involved formation of a tetracarbonyliron complex, such as 94, followed by decomposition of the complex to yield the arene. This method also gave clean product in consistently high yields. Unfortunately, no comparison of this method with the low valent titanium method can be made since the authors

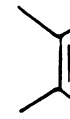


Table 3. Deoxygenation of Bis-adducts Using Low Valent Titanium.

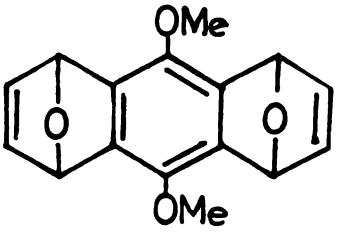
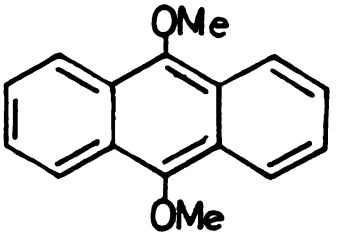
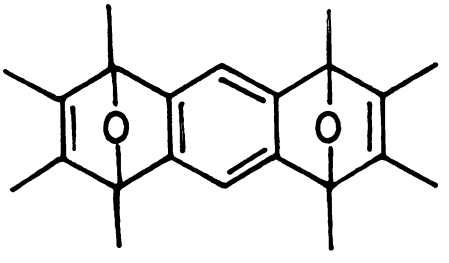
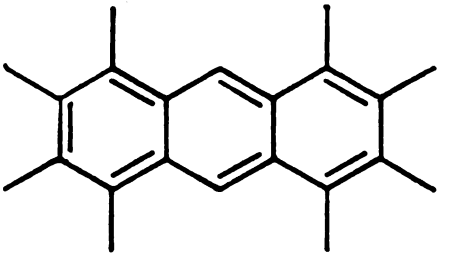
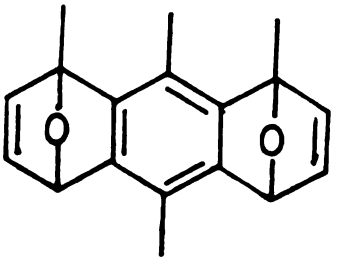
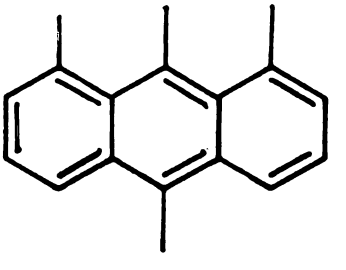
Bis-adduct	Product (yield)
 10	 22 (90%)
 77	 87 (80%)
 79	 88 (57%)

Table 3. Continued.

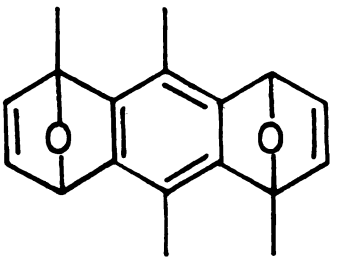
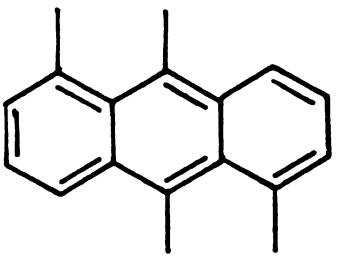
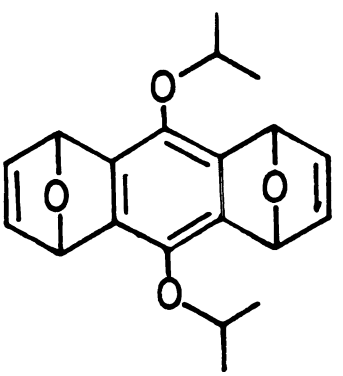
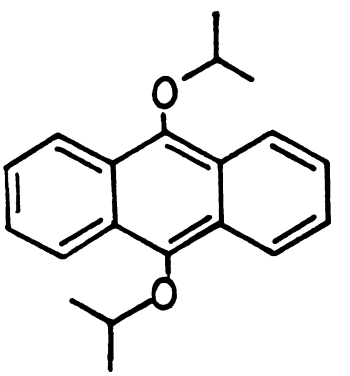
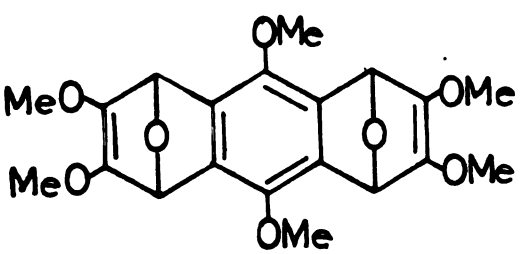
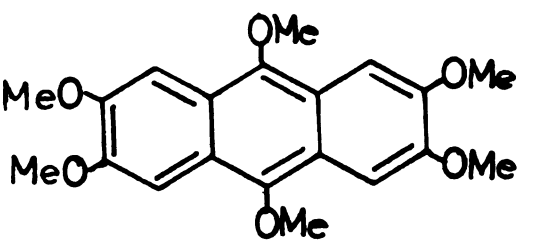
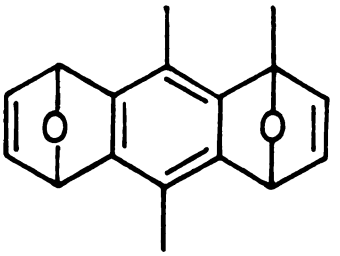
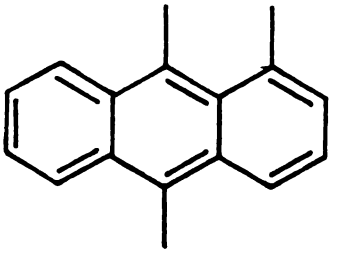
Bis-adduct	Product (yield)
 80	 89 (85 %)
 82	 90 (88 %)
 84	 91 (85 %)

Table 3. Continued.

Bis-adduct	Product (yield)
	
86	92(80 %)

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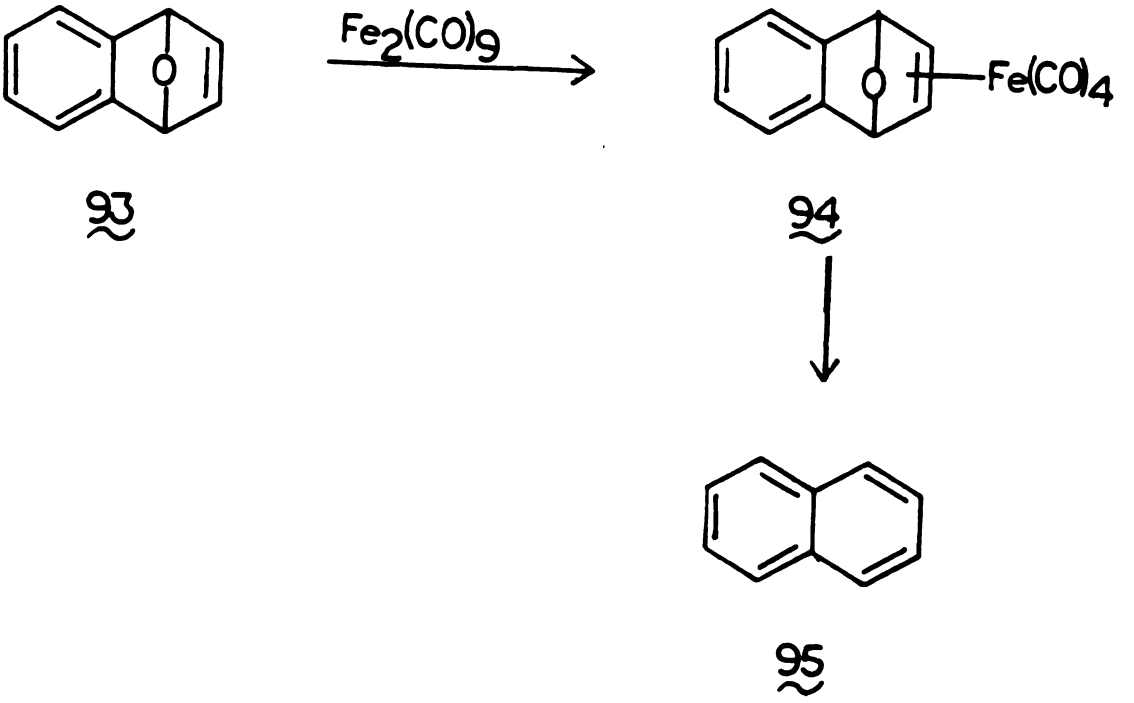

93 94 95

reported no results with bis-epoxides. However, in view of the high toxicity of iron carbonyl complexes, it is tempting to say that the zinc-titanium tetrachloride procedure is the method of choice for deoxygenating such compounds.

Highly substituted phenanthrenes also possess a high degree of steric strain, especially if substituted in the 4- and 5-positions.[31] Thus it was thought that 9,10-dimethoxyoctamethylphenanthrene, 98, and decamethylphenanthrene, 99, might undergo some photochemical valence isomerization.

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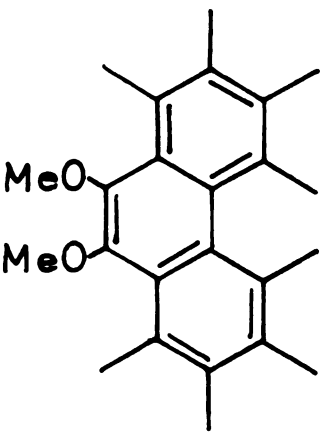
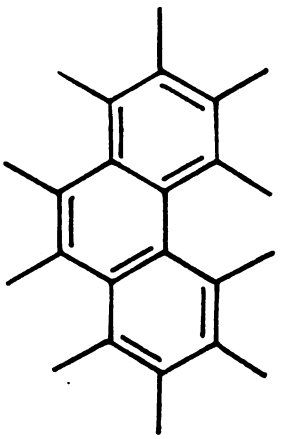
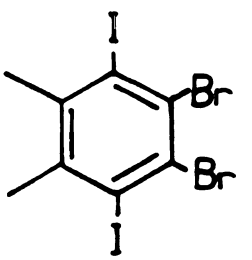


98

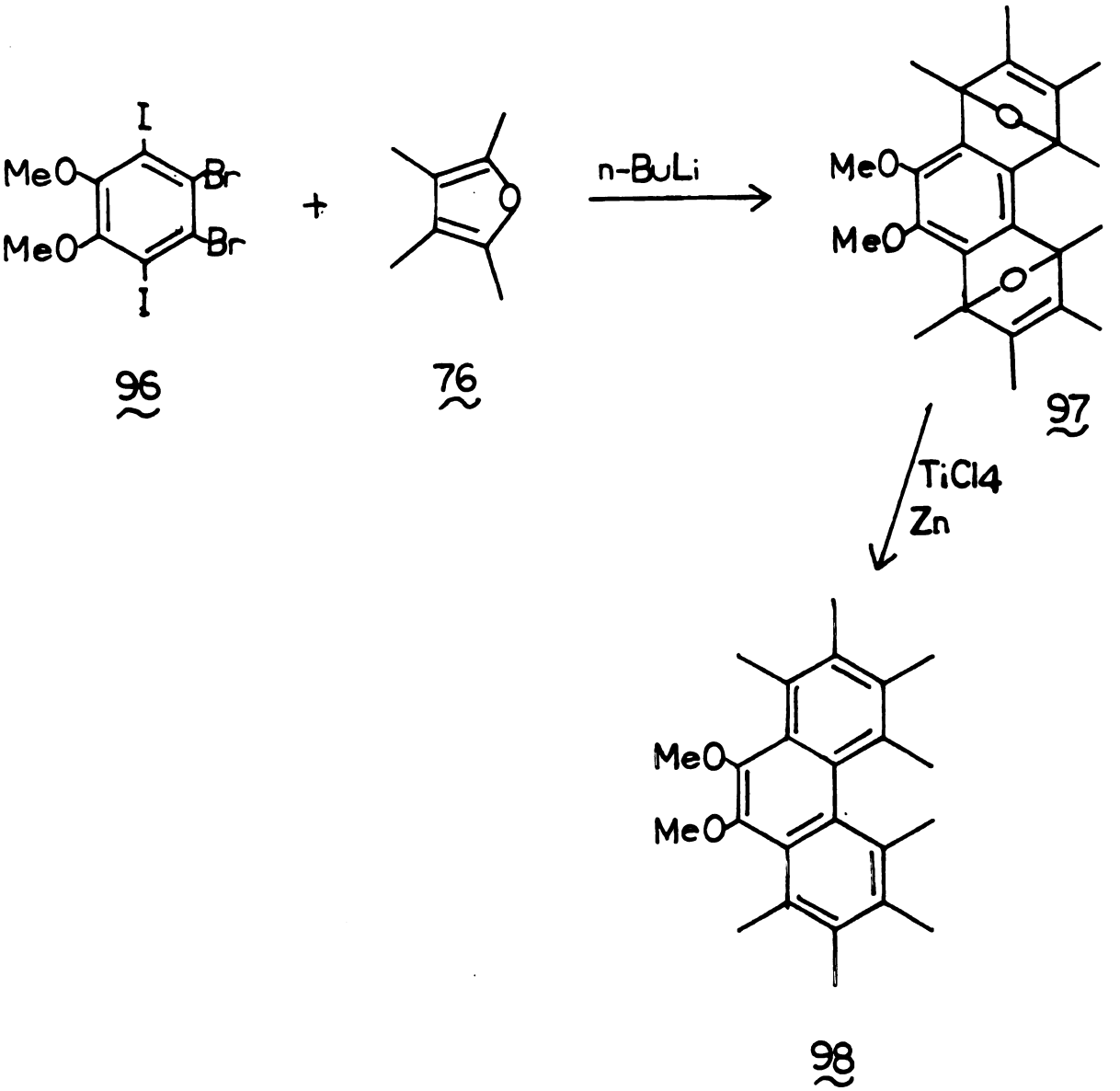


99

The 9,10-dimethoxy derivative, 98, was synthesized in two steps from di-aryne equivalent 96 and tetramethyl furan, 76, as shown in Scheme 5. Bis-adduct 97 could not be isolated, but the crude product was used directly for deoxygenation with low valent titanium. The overall yield for both steps was 20%. Decamethylphenanthrene, 99, was synthesized by Hart and Shamouilian in a similar manner from di-aryne precursor 26 in 40% overall yield.[9]



26



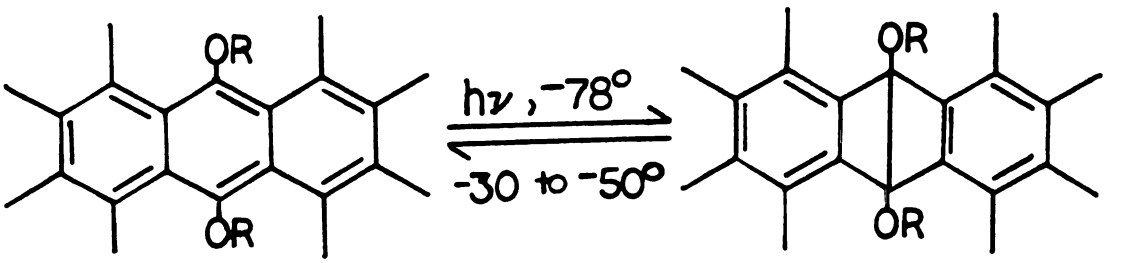
96 76 97 98

Scheme 5

B. Photochemistry

The photolysis of the arenes previously described was followed by NMR spectroscopy. In a typical procedure, a solution of 10-12 mg of the arene in 0.5 mL of benzene-d_6 (or toluene-d_8) was placed in a 5 mm NMR tube and flushed with nitrogen. Irradiation of the sample for 60-90 minutes using a Hanovia 450 W medium pressure lamp with Pyrex filter was carried out by taping the sample tube directly to the cooling jacket of the lamp. If low temperatures were required, the lamp and cooling jacket along with the sample were emersed in a dry ice-isopropanol bath, and dry nitrogen was passed through the cooling jacket.

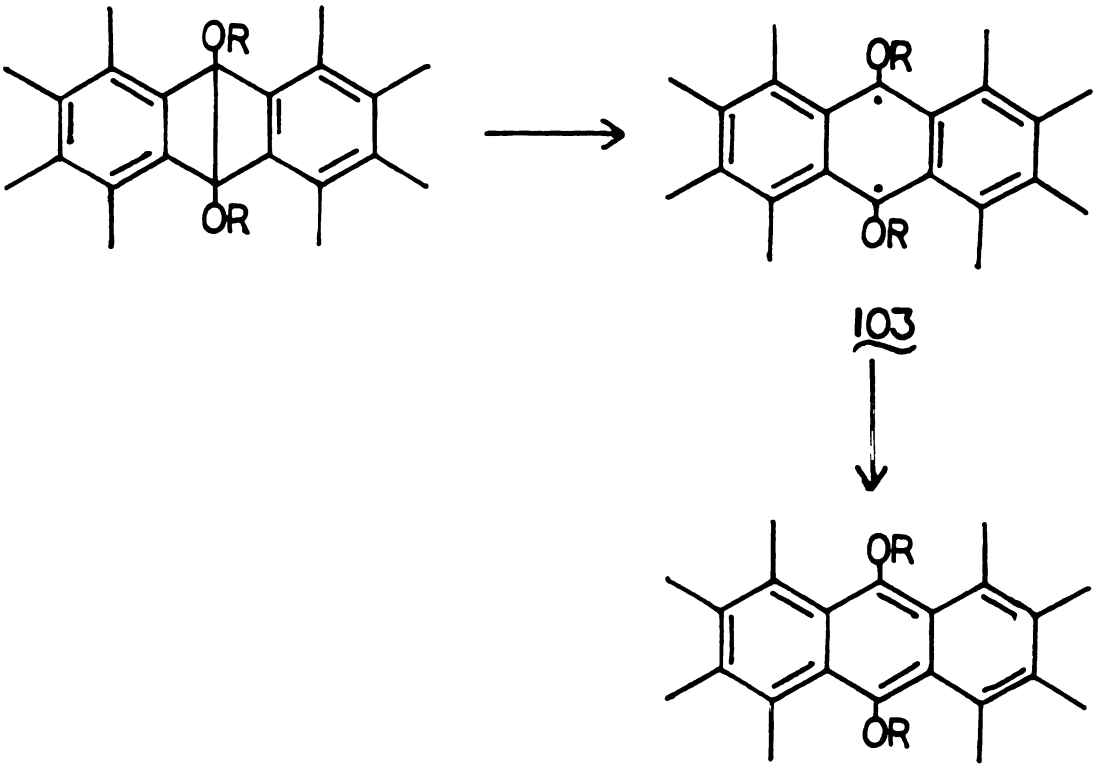
The series of 9,10-dialkoxyoctamethylanthracenes, 69, 71, and 73, were found to undergo photochemical valence isomerization to the 9,10-Dewar isomers, but these were



69 R = Me
71 R = Et
73 R = i-Pr

100 R = Me
101 R = Et
102 R = i-Pr

only stable at temperatures lower than -30°C. The most likely explanation for this decreased stability compared to decamethyl-9,10-Dewar-anthracene, 49, is that while formation of the Dewar isomers is a photochemically allowed concerted process, the thermal reversion must proceed through a diradical intermediate, i.e., 103. A structure such as

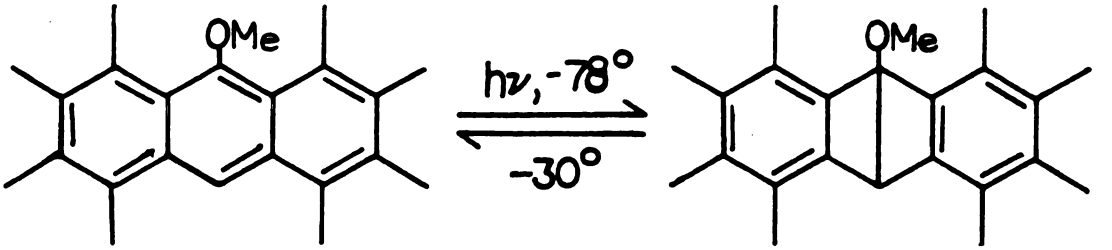


103 would be more stabilized by alkoxy groups than by methyl groups, as in decamethylanthracene, 45.

Interestingly, the stability of these 9,10-Dewar-anthracenes relative to their aromatic valence isomers does not increase with increasing size of the alkoxy groups.

9,10-Dimethoxy-9,10-Dewar-anthracene 100 reverts to 69 at -30°C with a half-life of approximately one hour. The diethoxy derivative, 101, rearranges to anthracene 71 at -50°C with a half-life of thirty minutes, and 9,10-di-isopropoxyoctamethylanthracene 102 rapidly reverts to 73 above -60°C. This must be because steric hindrance is also a factor in the stability of the Dewar isomers. Torsional strain in the Dewar isomers increases along the series di-methoxy<diethoxy<di-isopropoxy. The number of unhindered conformations would decrease along the same series resulting in an entropic destabilization.

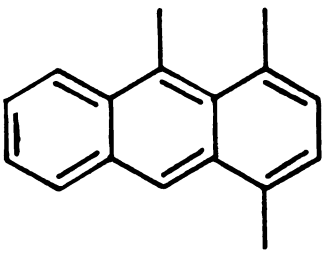
Low temperature photolysis of 9-methoxyoctamethyl-anthracene, 75, yields the 9,10-Dewar-anthracene 104, which reverts to starting anthracene at -30°C with approximately the same half-life as 9,10-Dewar-isomer 100. Thus, one less peri-substituent (i.e., less steric strain in the anthracene) must balance the effect of one less oxygen to stabilize the diradical intermediate in the thermal reversion.



75 104

The 9,10-Dewar-anthracenes discussed could not be isolated, but were identified by their proton and ^{13}C NMR spectra, as well as their ultraviolet spectra (see Table 4). A typical ultraviolet spectrum of a 9,10-Dewar-isomer is shown in Figure 2. The spectroscopic data are in good agreement with that for 9-t-butyl-9,10-Dewar-anthracene 59[18] and decamethyl-9,10-Dewar-anthracene 49.[14]

1,4,9-Trimethylanthracene, 105,[32] was irradiated in benzene at room temperature, giving a photoproduct that was stable even above 60°C.



105

The ^{1}H NMR spectrum (aliphatic region is shown in Figure 3) shows that the aromatic singlet for C-10 in anthracene 105 has been replaced by a singlet at δ4.27 (in $CDCl_3$). In addition, the methyl peaks have all shifted upfield by approximately 0.5 ppm. The ^{13}C NMR spectrum (also shown in Figure 3) has new peaks at δ62.27 and δ54.07, and shows an upfield shift by the methyl carbons. The spectra are consistent with that of the 9,10-Dewar isomer of 105 (the C-10 proton should appear at δ4-5, and the ^{13}C chemical shifts for C-9 and C-10 should be between δ50 and δ65). However, it is conceivable in this case, since 105 is unsymmetrically

Table 4. Spectroscopic Data for 9,10-Dewar-anthracenes.

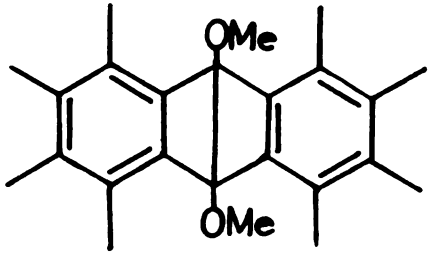
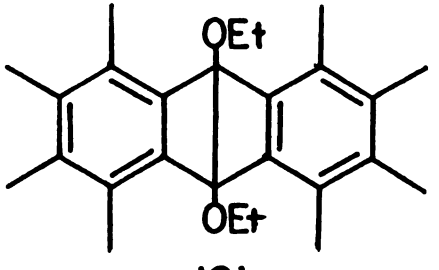
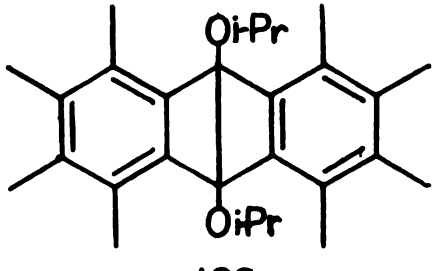
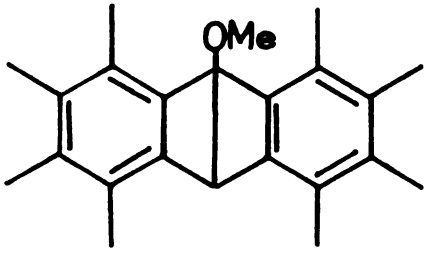
Entry	^{1}H NMR[a] (δ)	^{13}C NMR[a] (δ)	UV[b] (λ_{max})
 100	1.88 (s, 12H) 2.28 (s, 12H) 3.71 (s, 6H)	15.64, 15.87, 54.84 101.27, 129.65, 135.12, 144.05	270 nm
 101	1.37 (t,7Hz, 6H) 1.89 (s, 12H) 2.30 (s, 12H) 4.07 (q, 7Hz, 4H)	c	266 nm
 102	1.57 (d, 6Hz, 12H) 1.83 (s, 12H) 2.31 (s, 12H) 4.62 (sept, 6Hz, 2H)	c	c

Table 4. Continued.

Entry	^{1}H NMR[a] (δ)	^{13}C NMR[a] (δ)	UV[b] (λ_{max})
 104	1.90 (s, 6H) 1.93 (s, 6H) 2.13 (s, 6H) 2.35 (s, 6H) 3.46 (s, 3H) 4.94 (s, 1H)	15.34, 15.52, 15.61, 15.96, 54.57, 54.63, 99.53, 129.70, 133.64, 134.38, 136.93, 143.99, 144.05	272 nm

[a]Obtained after photolyzing the anthracenes in toluene-d_8 in an NMR tube at -78°C. Spectra were measured at -40° to -60°C.

[b]Samples were photolyzed in quartz Dewar-UV cell in hexane at -45°C. Spectra were obtained at the same temperature.

[c]9,10-Dewar-anthracene too unstable to obtain spectrum.

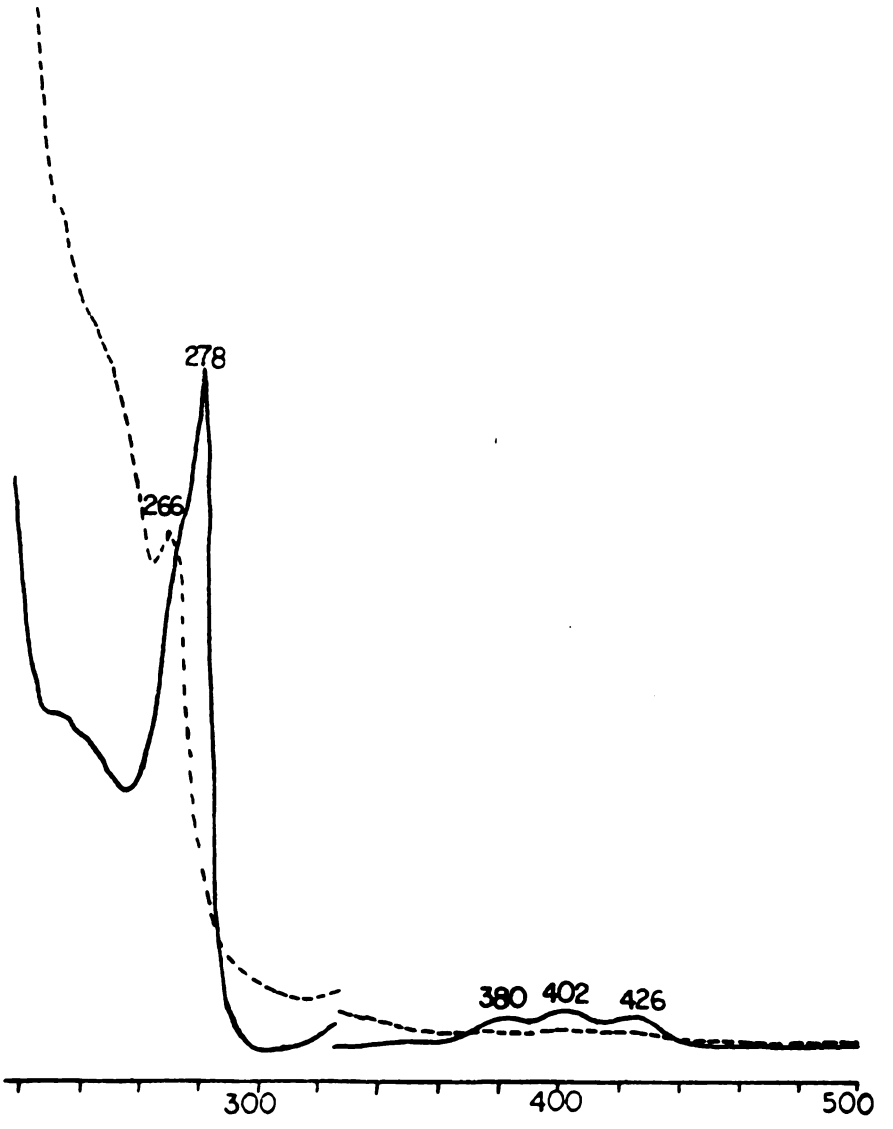


Figure 2. Ultraviolet spectrum of 9,10-diethoxyoctamethylanthracene 71 (solid line) and its 9,10-Dewar-isomer 101 (broken line) at -45°C in hexane.

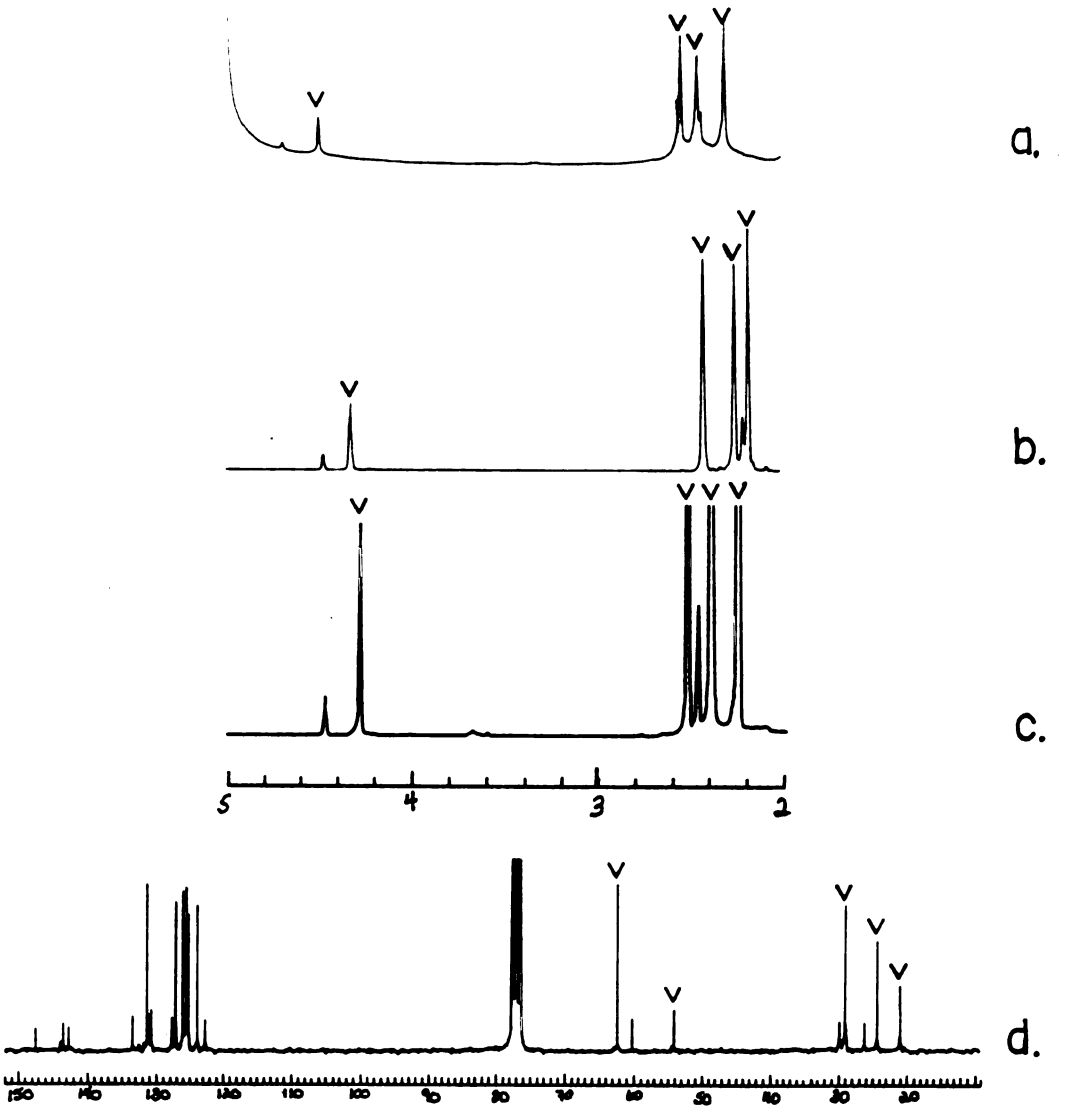
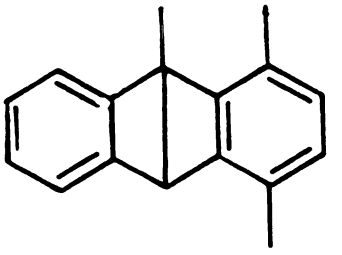


Figure 3. ^{1}H NMR spectra of products of the photolysis of 1,4,9-trimethylanthracene, 105, in three different solvents: a) pyridine-d_5; b) benzene-d_6; c) chloroform-d showing the region from δ2 to δ5; and d) the ^{13}C NMR in chloroform-d. (Arrows indicate peaks belonging to major photoproduct.)

substituted in the 9,10-positions, that a photodimer could also be produced.[23] The spectral data are consistent with that structure also.

Close inspection of the spectra reveals a minor product which appears to be isomeric with the major product. In the proton spectrum in $CDCl_3$, a second bridgehead proton peak is found at δ4.45, and there is an extra peak in the methyl region. Integration of the spectrum shows a 5:1 ratio between the two bridgehead peaks. There is also a 5:1 ratio between the methyl peaks at δ2.39 and δ2.50, and coincidental overlap of the other two methyls in both isomers at δ2.25 and 2.55 is consistent with the integration. The proton spectrum in pyridine-d_5 shows five separate methyl resonances (see Figure 3 as well as expanded methyl region shown in Figure 4). The ^{13}C NMR spectrum also shows a second C-10 bridgehead peak at δ50.20, (since C-9 is quaternary, it is reasonable that the concentration of minor isomer is too low to see this peak) and a total of five methyl peaks.

Since there is only one possible structure for the 9,10-Dewar-anthracene (106), and there are four possible structures for the photodimer (107 - 110), the two isomeric



106

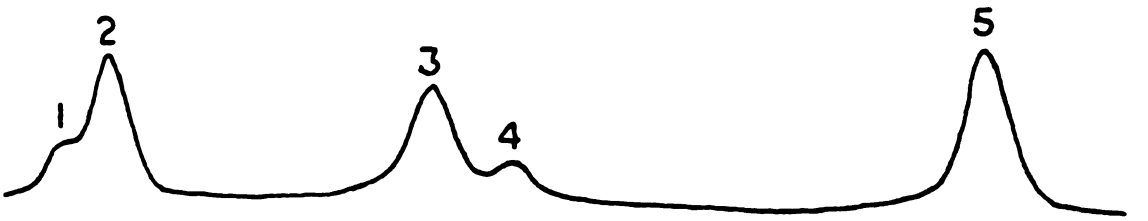
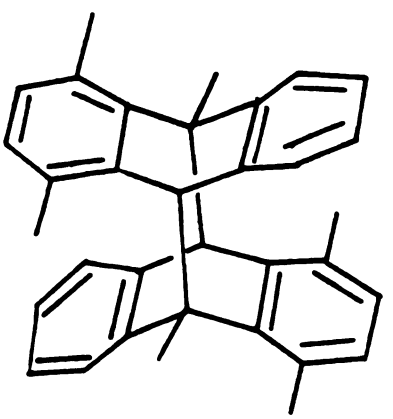
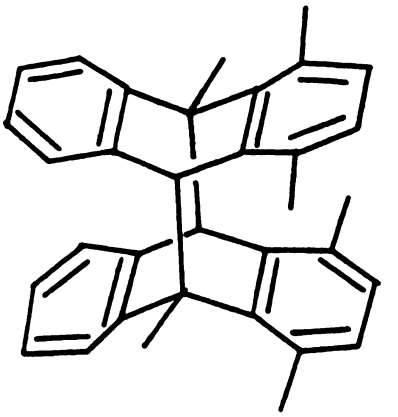


Figure 4. Methyl region from spectrum 3a, expanded to show five methyl peaks.

products must be the latter. Since photodimerization generally yields head-to-tail products, the isomers produced



107



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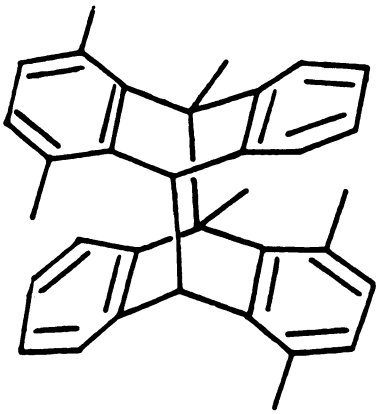

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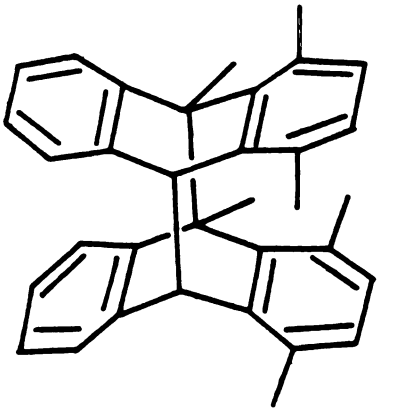
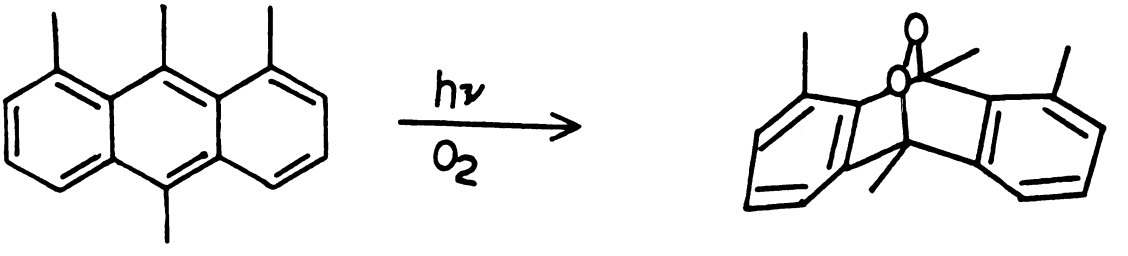


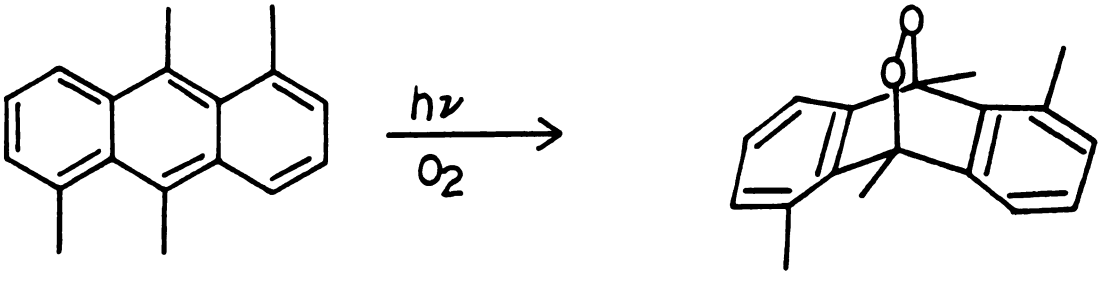
110

are probably 107 and 108. Photodimer 107 is most likely the major photoproduct, since it would be the least sterically hindered.

Unfortunately, none of the other anthracenes or phenanthrenes synthesized for this study underwent photochemical valence isomerization to Dewar isomers even at -78°C. However, both tetramethylanthracene derivatives, 88 and 89, reacted readily with singlet oxygen to give the endo-peroxides, 111 and 112, respectively. It is well established



88 111



89 112

that anthracenes give endoperoxides with singlet oxygen,[23] but with 88 and 89, the reaction was so facile that isolation of these hydrocarbons had to be carried out in the dark (i.e., fluorescent laboratory lights were sufficient to bring about their photo-oxidation).

C. Unusual Behavior of 1,2,3,4,5,6,7,8-Octamethylanthracene, 87

Octamethylanthracene, 87, when irradiated at -78°C in either degassed or undegassed samples, produces an unknown radical species as evidenced by its ESR signal (Figure 5) and the complete disappearance of its ^{1}H NMR spectrum.

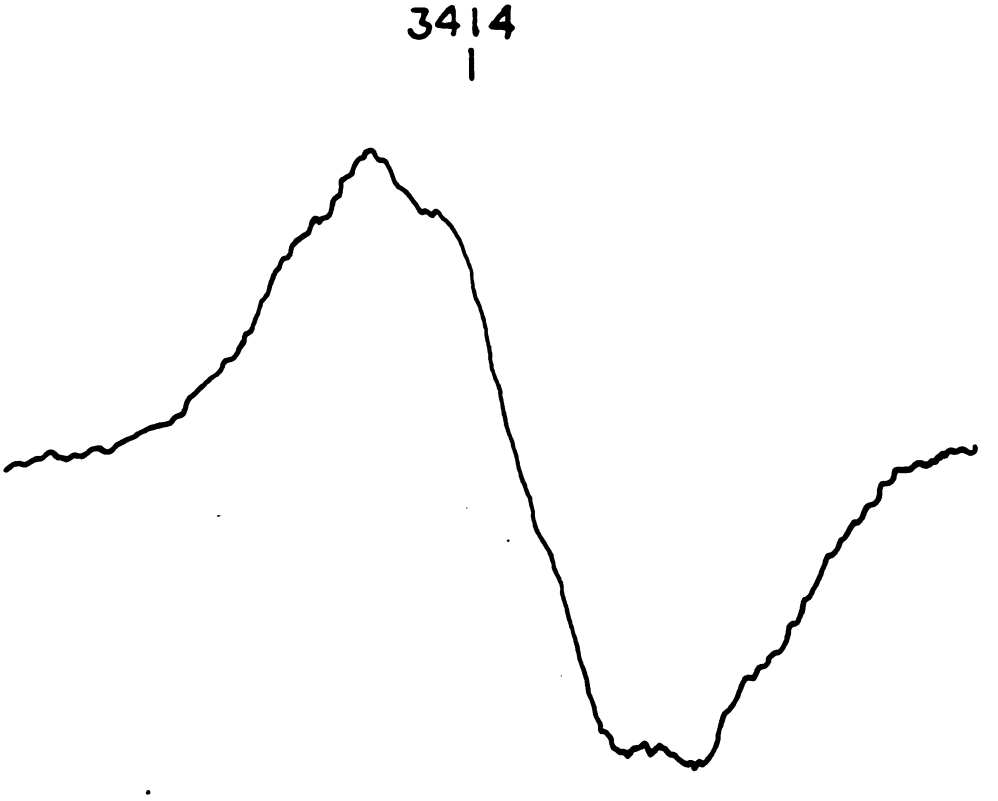
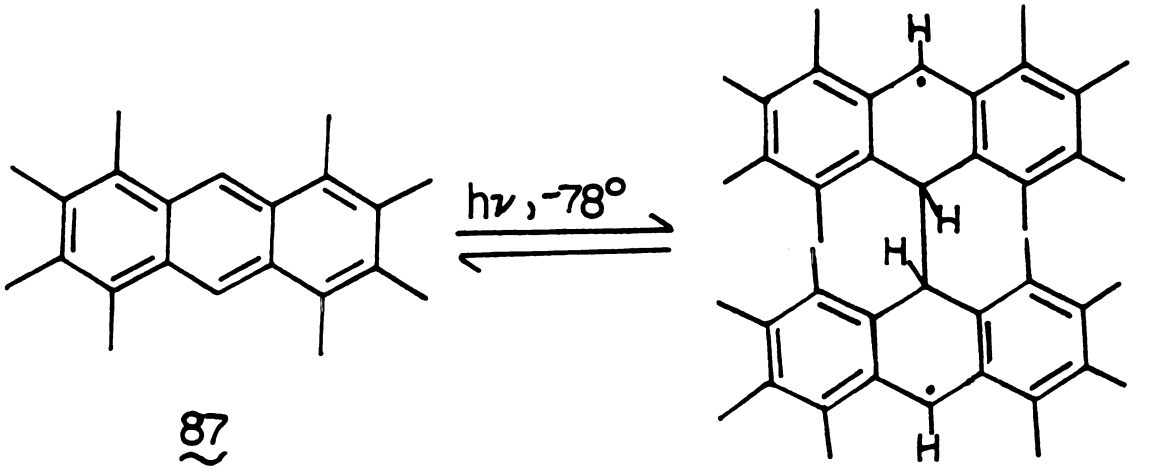


Figure 5. ESR spectrum of radical from the photolysis of octamethylanthracene, 87, in toluene at -100°C.

The radical species decayed above -30°C to give back octamethylanthracene, 87, unchanged.

Since its ESR spectrum does not show any hyperfine coupling, it is difficult to make any suggestions as to the nature of the radical species. One possibility, though, would be a diradical species, such as 113. Diradicals similar to 113 have been proposed as intermediates

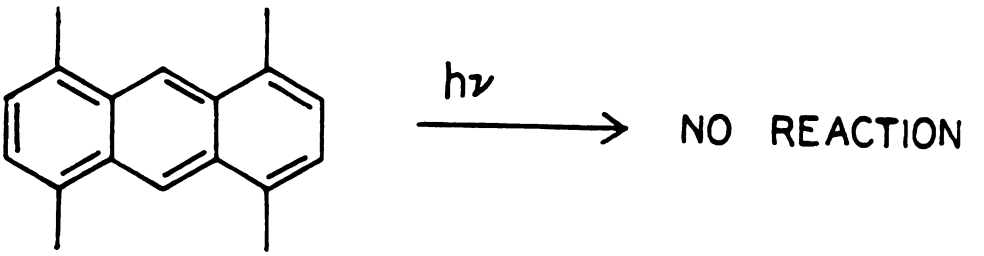


87 113

in the photodimerization of anthracenes.[23] In the present case, if 113 is formed, it may be too sterically hindered to close to the dimer and simply dissociates.

There is no precedent in the literature for such a diradical species, nor did any of the other compounds studied here exhibit similar behavior. Even 1,4,5,8-tetramethylanthracene, 114,[33] which should be about as sterically

hindered as 87, did not react under the same conditions of irradiation. Apparently, the radical species, whatever

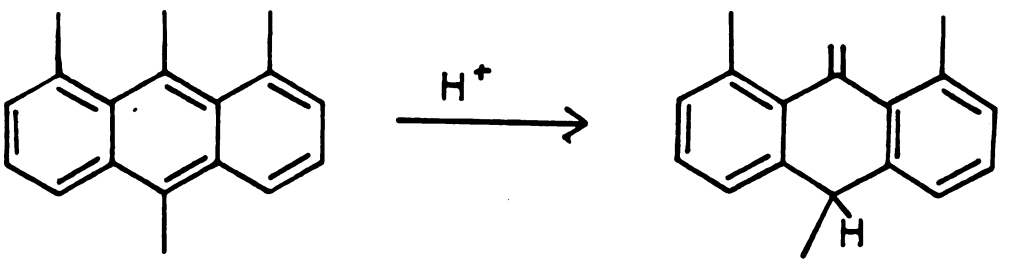


114

it is, is stabilized by the four additional methyl groups of 87.

D. Reactions of Anthracenes with Trifluoroacetic Acid

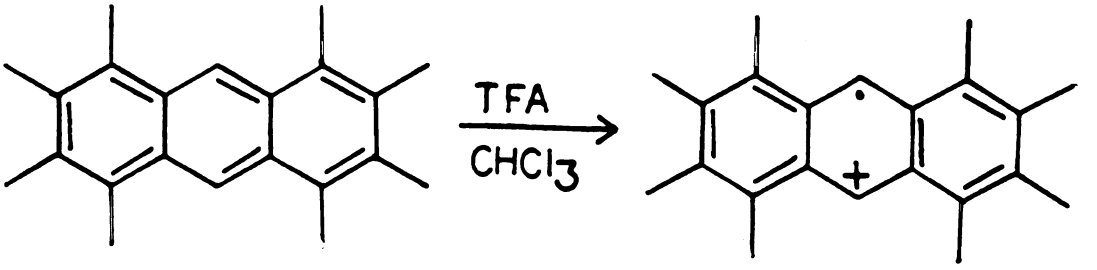
Peri-strained anthracenes substituted with methyl groups in the 9- and/or 10-positions rearrange in acid to give stable hydrocarbon analogues of 9-anthrones.[14,34] For example, 1,8,9,10-tetramethylanthracene, 88, in the presence of acid, rearranges to 115.[34] The reactions of



88 115

strong acid with peri-strained anthracenes containing hydrogens or alkoxy groups in the 9,10-positions is unknown.

Octamethylanthracene, 87, with trifluoroacetic acid in chloroform, is very easily oxidized to its radical cation as evidenced by the ESR signal (see Figure 6a). Although some 507 peaks are predicted, no fine structure



87 116

can be observed in its ESR spectrum even at -60°C. This radical cation, unlike the species produced photolytically, is very stable at room temperature, and on quenching with water gives back octamethylanthracene, 87.

Again, 1,4,5,8-tetramethylanthracene, 114, under the same reaction conditions, exhibits no ESR signal. This behavior is simply due to a difference in oxidation potentials.[35] The radical cation of anthracene itself can be produced by oxidation with thallium (III) trifluoroacetate in trifluoroacetic acid.[37] But there are only a few examples of anthracenes with a low enough oxidation

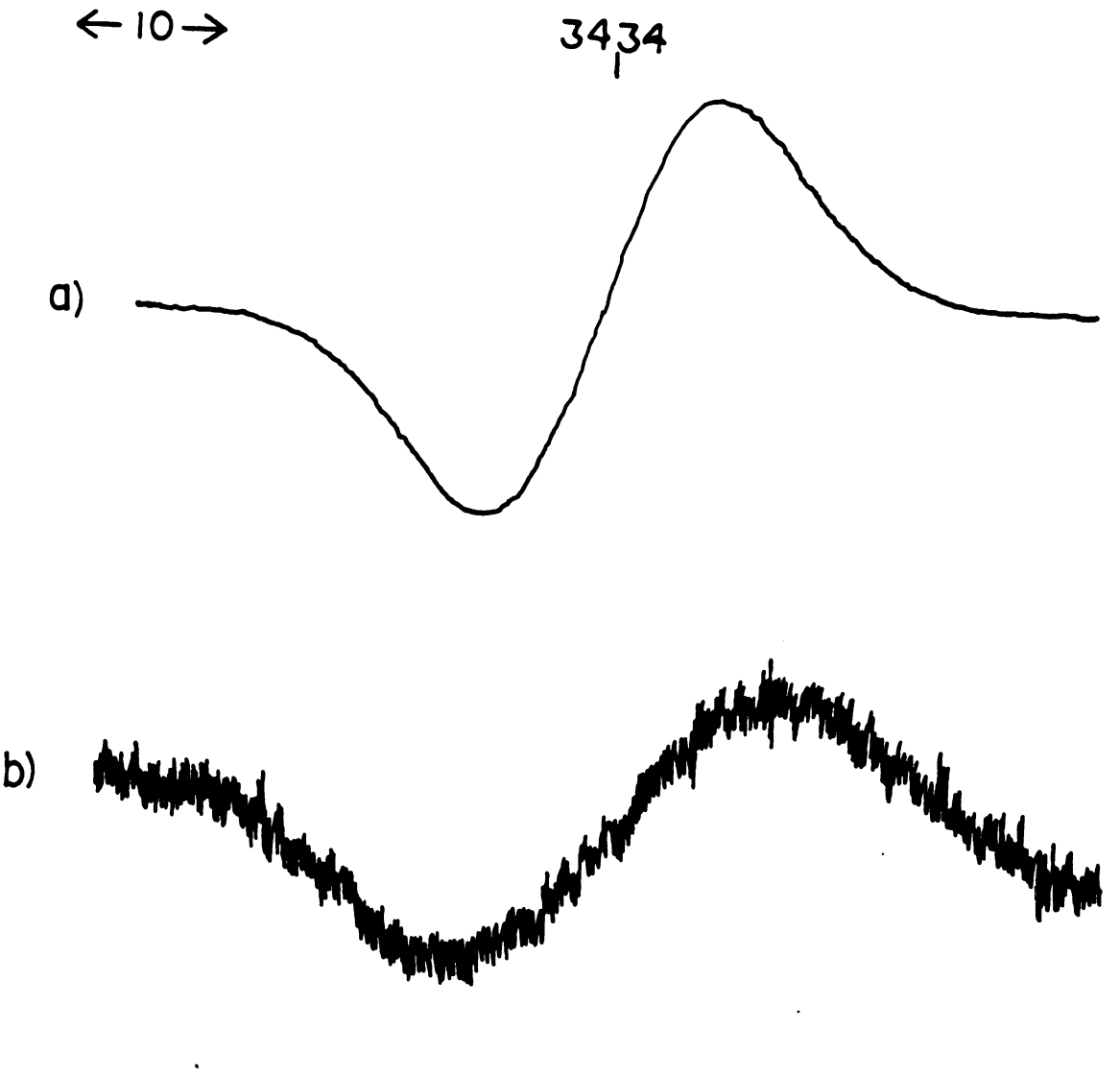
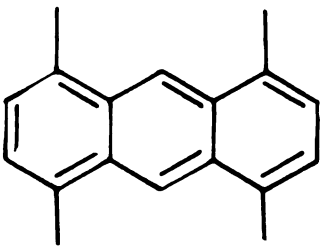


Figure 6. a) ESR spectrum observed on addition of 1 eq trifluoroacetic acid (1M in $CDCl_3$) to octamethylanthracene, 87, in $CDCl_3$ ($\sim 10^{-2}$M); b) ESR spectrum produced in similar manner from 9-methoxyoctamethylanthracene, 75.



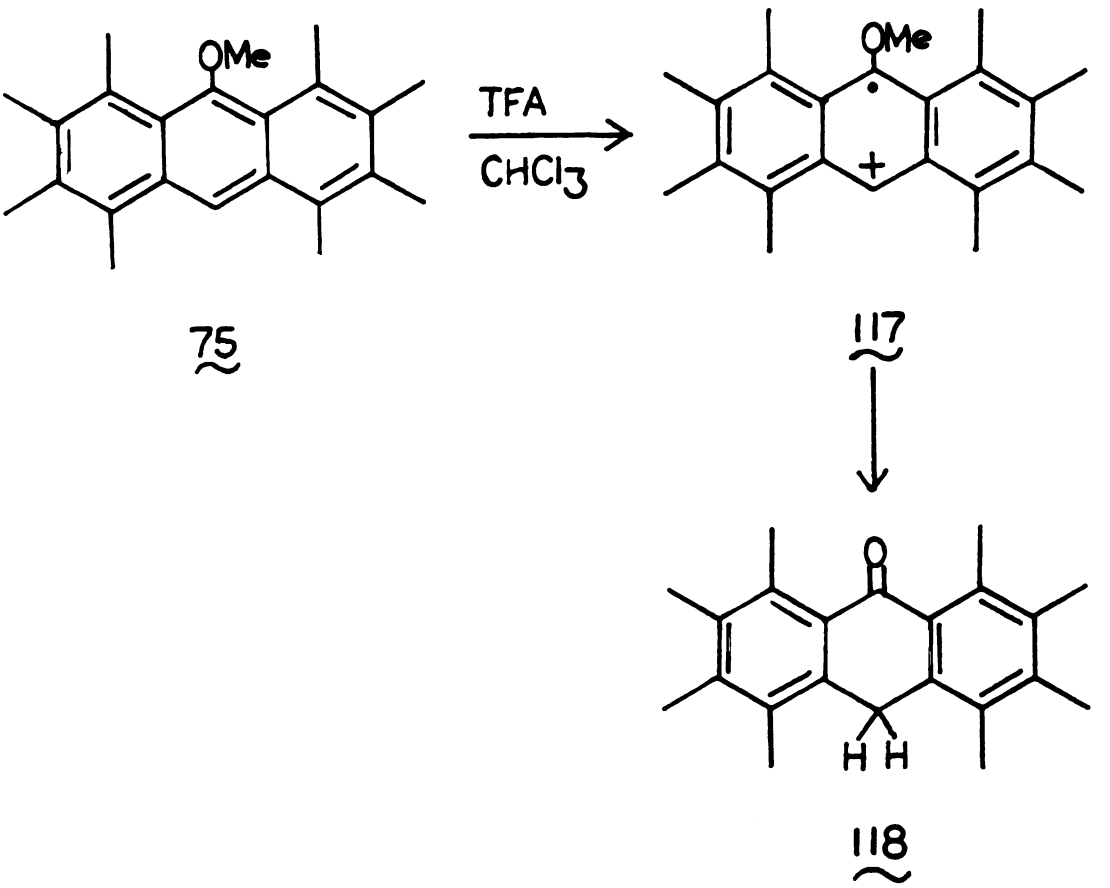
TFA
$CHCl_3$ → NO REACTION

114

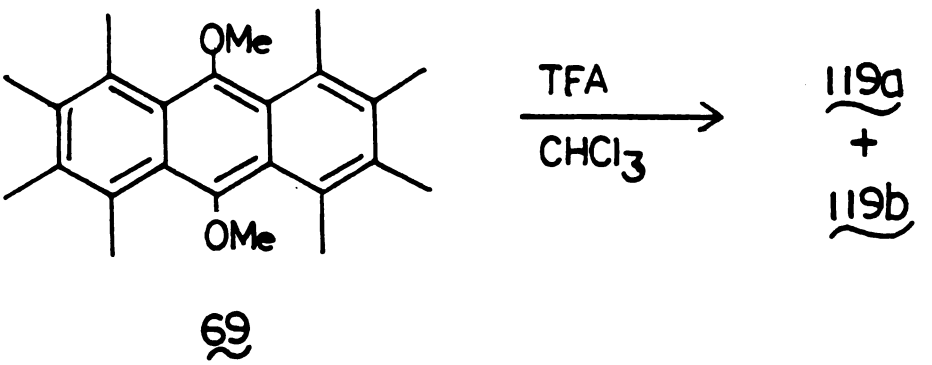
potential to give rise to the radical cation in the presence of trifluoroacetic acid.[38]

On addition of trifluoroacetic acid to a solution of 9-methoxyoctamethylanthracene 75 in chloroform, a weak ESR signal was obtained which appeared at the same position as that for octamethylanthracene, 87, giving evidence for formation of a radical cation (see Figure 6b). This signal decayed after several hours. On quenching with water and removing the solvent, a white solid was isolated, mp 245-248°C. The ^1H NMR spectrum of this solid consisted of five singlets (δ2.28, 2.31, 2.35, 2.54, 3.56) with an integration ratio of 3:3:3:3:1. The infrared spectrum showed strong bands at 1670 cm^{-1} and 1655 cm^{-1}, and the mass spectrum had a strong molecular ion peak at m/e 306 and a base peak at m/e 291. All of the spectral data of the product are consistent with the octamethylanthrone 118 (lit.[39] mp 251-252°C).

With 9,10-dimethoxyoctamethylanthracene 69 in chloroform, addition of trifluoroacetic acid caused the solution

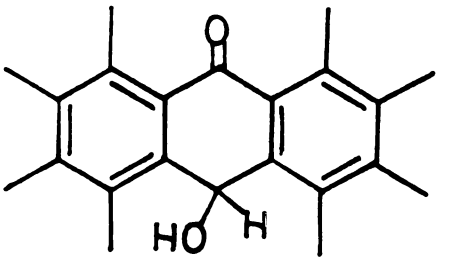


to turn dark blue, suggesting the formation of a radical cation. But the color faded in an instant to pink, and no



ESR signal could be observed. Quenching with water and removal of the solvent gave a pink residue. Fractional recrystallization of the residue with acetone gave two products, both white crystalline solids, in a 3:2 ratio.

The ^{1}H NMR of the minor product (119b), mp 290-292°C, consisted of five singlets (δ1.35, 1.94, 2.20, 2.49, 4.51) with an area ratio of 6:6:6:6:1. The infrared spectrum had strong bands at 1680 cm^{-1} and 3690 cm^{-1}, and the highest mass peak in the mass spectrum (also the base peak!) was m/e 305 (M^{+}-OH). These data suggest a structure like that shown for 119b.



119b

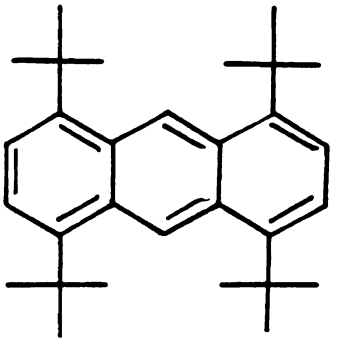
The major product (119a), mp 278-280°C, showed no carbonyl bands or hydroxy groups in the infrared spectrum. The ^{1}H NMR spectrum consisted of only two singlets (δ2.51, 2.28) in an integral ratio of 1:1. The ^{13}C NMR spectrum showed three aliphatic peaks (δ16.90, 17.19, 49.15) and four aromatic peaks. The mass spectrum had a strong peak at m/e 320 and a base peak of m/e 305. In spite of the

simplicity of the spectral data, no good suggestions can be made at this time as to the structure of this product.

Thus, it appears that both alkoxy and hydrogen substitution in the 9,10-positions give rise to radical cations in the presence of acid. The presence of alkoxy groups in these positions, however, leads to further reaction.

E. Conclusions

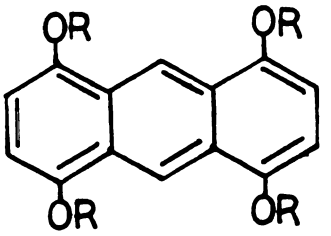
Although the success rate for designing anthracenes with photochemically accessible Dewar-isomers has not been very high, some conclusions can be drawn which may serve as a guide to future research. First, a large degree of steric strain is a factor, but there seems to be a balance between steric strain in the anthracene and that in the Dewar-isomer. For this reason, a compound such as 120 might be interesting. Although 120 should be



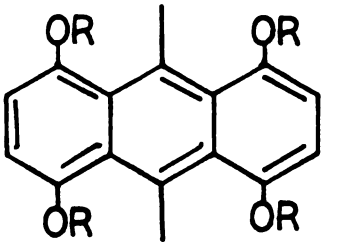
120

somewhat sterically hindered, the corresponding 9,10-Dewar-isomer should be relatively strain-free, and therefore, stable.

Second, 9,10-dialkoxy groups destabilize 9,10-Dewar-isomers relative to their corresponding anthracene valence isomers. However, alkoxy or other hetero-atom groups may not be a problem in other positions, as in compounds 121 and 122.



121

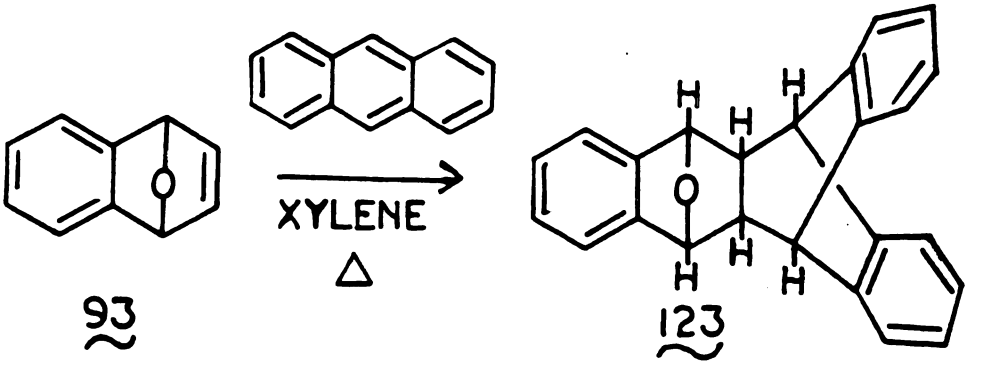


122

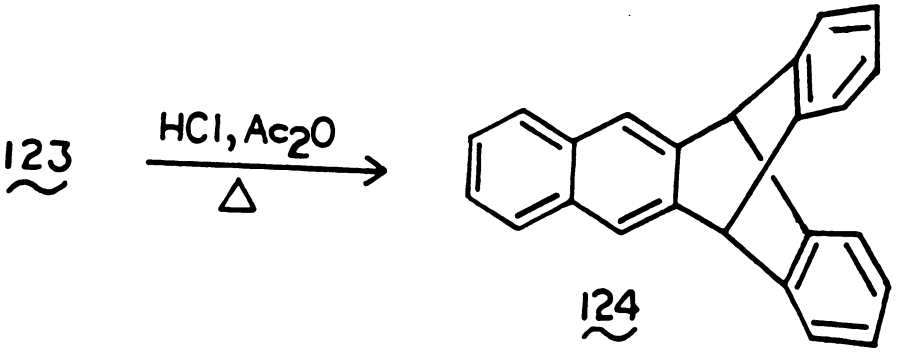
In any case, it must be pointed out that many anthracenes belong in a large gray area where they are too hindered to photodimerize, but not hindered enough to form a stable 9,10-Dewar-isomer.

Part II. Synthesis of Some Novel Iptycenes Using Diaryne Equivalents

Norbornene derivatives, such as 1,4-dihydronaphthalene-1,4-epoxide, 93, are effective dienophiles.[40,41] For example, Wittig showed that 93 reacts in high yield with anthracene and other polynuclear aromatic compounds to give novel cycloadducts such as 123.[40] The oxygen bridge



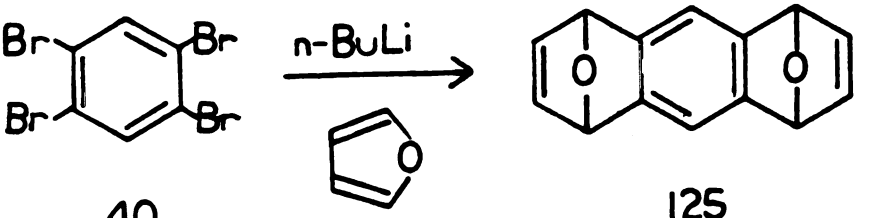
in 123 can be easily removed with hydrochloric acid in acetic anhydride to produce 5,12-benzeno-5,12-dihydronaphthacene, 124. Thus, many interesting compounds can



be made in two steps from the readily available epoxide 93.

A. Use of a 2,3;6,7-Anthradiyne Equivalent in Synthesis of a Novel Pentiptycene

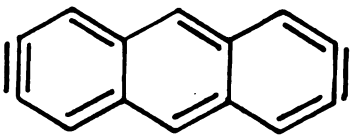
1,4,5,8-Tetrahydroanthracene-1,4;5,8-bis(epoxide) 125 can be synthesized from 1,2,4,5-tetrabromobenzene 40 and furan in 71% yield by a procedure similar to that described in Part I. The bis-epoxide 125 was isolated as a 50:50



40 125

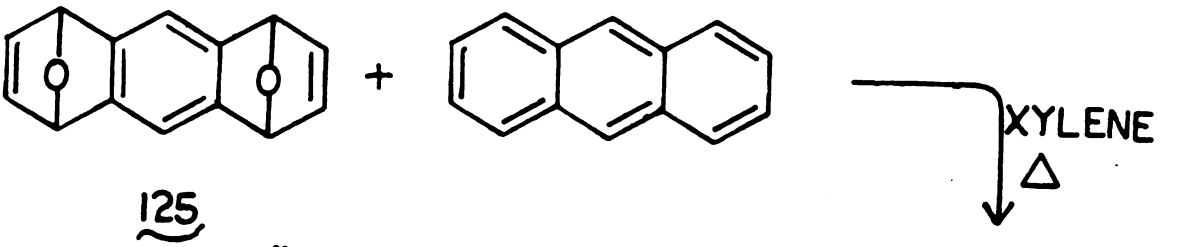
mixture of syn- and anti-isomers. These could be separated by trituration with methanol (the syn-isomer is soluble and the anti-isomer is not).

Bis-epoxide 125 should also react with a wide variety of dienes. And since the oxygen bridges in the resulting cycloadducts should be easily removed to give an aromatic product, 125 can be regarded as a synthetic equivalent of 2,3;6,7-anthradiyne 126.

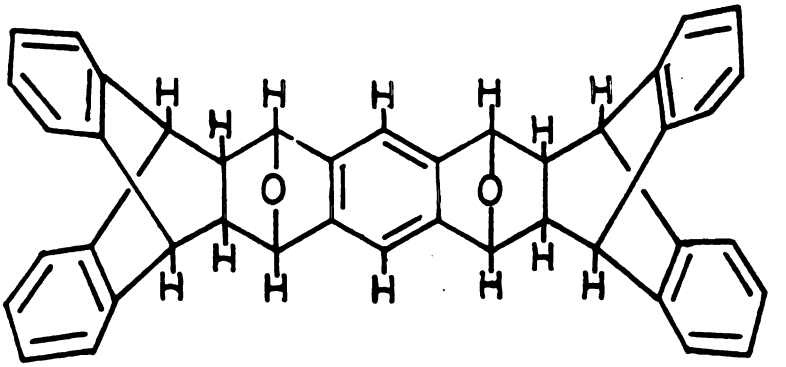


126

Reaction of bis-epoxide 125 with two equivalents of anthracene in refluxing xylene gave the bis-adduct 127. Anti-125 gave one isomer of 127 (mp 440°C, dec.), and syn-125 gave another isomer of 127 (mp 395°C, dec.). The two isomers were identified by their NMR spectra. The



125
(syn or anti)

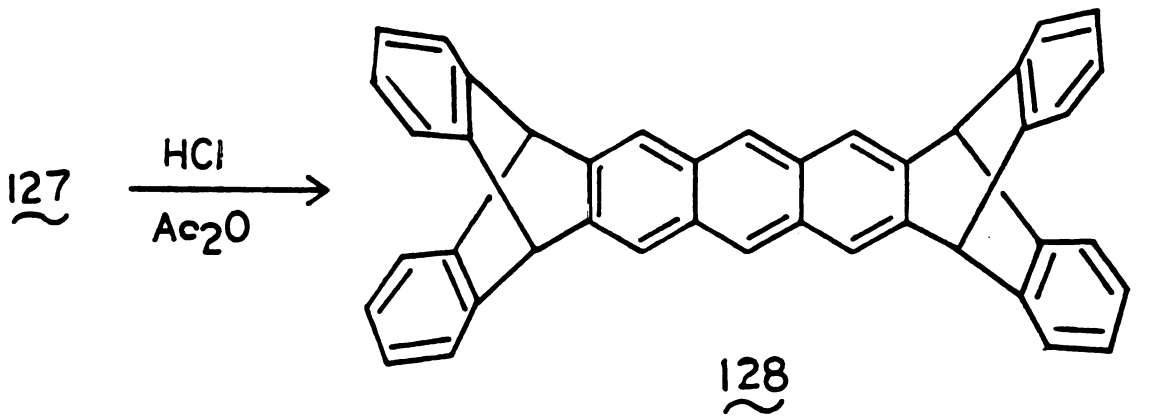


127

proton NMR spectrum of the isomer from syn-125 showed three four-proton singlets for the three sets of bridge-head hydrogens (δ2.13, 4.35, 4.80), and a singlet for the two uncoupled aromatic hydrogens (δ6.90), as well as four

aromatic multiplets for the remaining sixteen aryl hydrogens. The proton spectrum of the other isomer was almost identical. The ^{13}C NMR spectrum for each isomer showed only eleven signals (three aliphatic carbons and eight aromatic carbons), as required by symmetry.

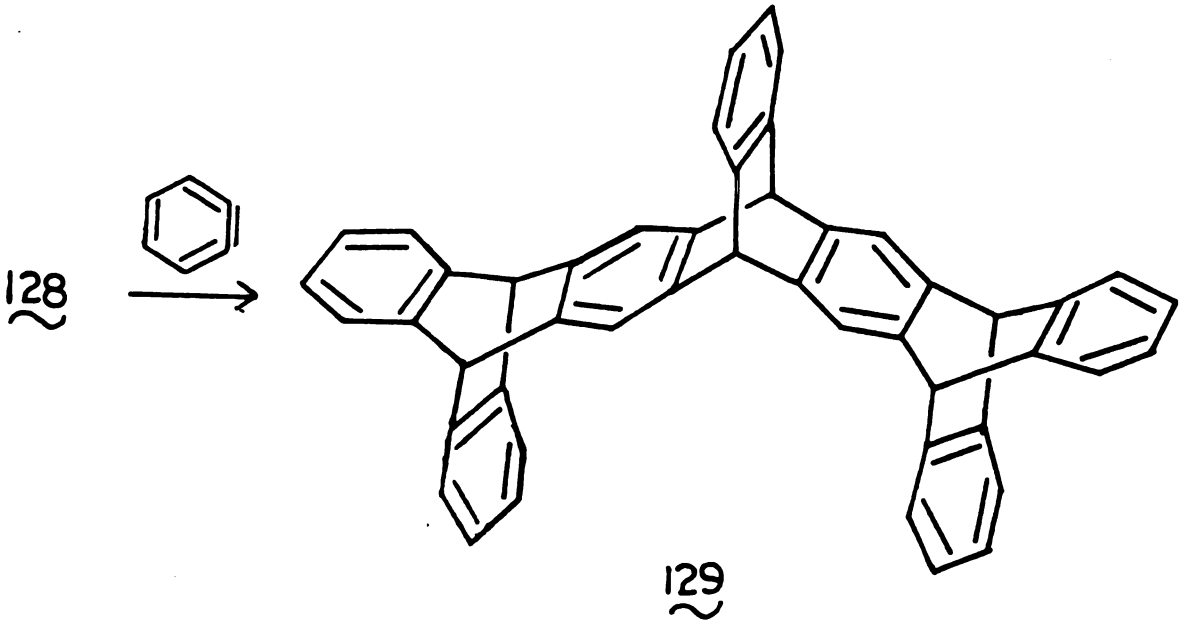
The oxygen bridges were removed from either isomer of 127 with hydrochloric acid in acetic anhydride to give pentiptycene 128. Again its structure was apparent from



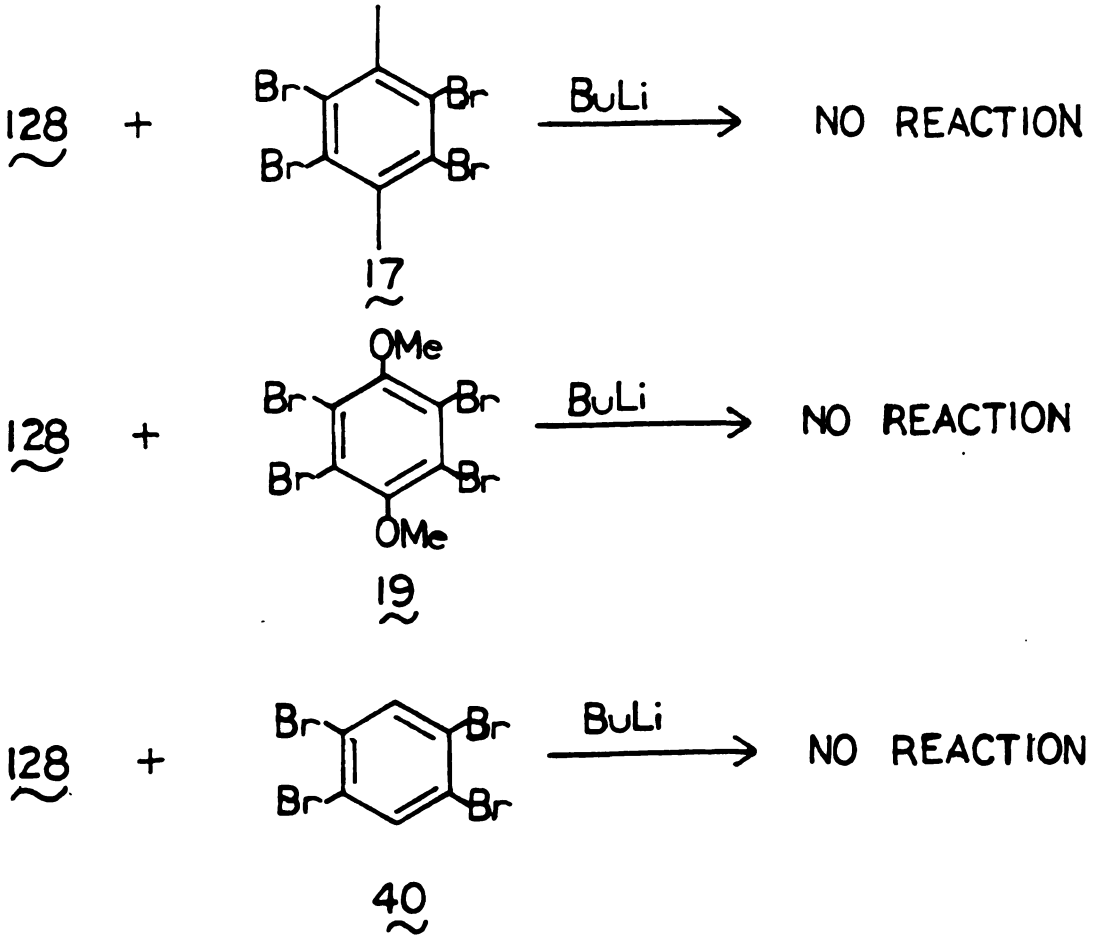
its spectra. The proton spectrum of 128 showed a four-proton singlet for the bridgehead hydrogens (δ5.50) and two singlets, area ratio 4:2, for the uncoupled protons of the central anthracene ring (δ7.81, 8.06), as well as two multiplets for the remaining sixteen aryl protons. The ^{13}C NMR spectrum of 128 showed only eight signals as required by symmetry. The ultraviolet spectrum of 128 in acetonitrile contained a wealth of absorption bands as a consequence of the central anthracene moiety, the longest

wavelength absorption appearing at 371 nm.

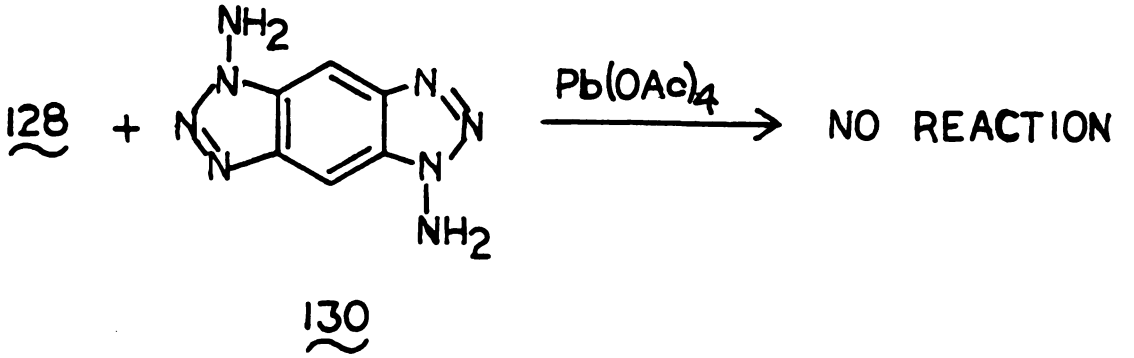
Reaction of pentiptycene 128 with o-benzyne (generated from o-benzenediazonium carboxylate) gave adduct 129.[42] The structure was assigned from the method of synthesis and from the spectral data.



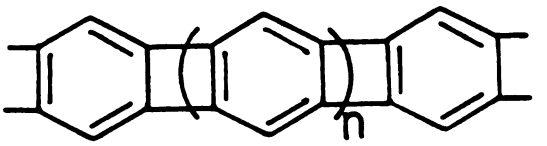
Attempts to react pentiptycene 128 with any di-aryne equivalents failed. With tetrabromobenzenes, 17, 19 and 40, the pentiptycene was recovered quantitatively. Apparently, the temperatures at which these n-butyllithium reactions must be run (-40°C to 0°C), were not high enough to allow the reaction to take place.



Pentiptycene 128 was also reacted with bis-triazole 130, a new di-aryne equivalent developed by Hart and Ok.[43]



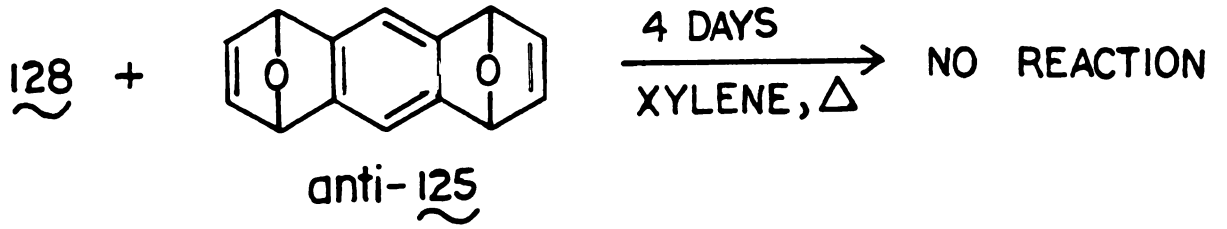
Again, all of the pentiptycene 128 was recovered, along with a white polymer thought to have structure 131. This polymer is obtained if the bis-triazole is oxidized by lead (IV)



131

tetraacetate in the absence of diene.[43]

The 2,3;6,7-anthradiyne equivalent, bis-adduct 125, was heated in refluxing xylene with pentiptycene 128. Even after four days, no product was formed. Here, the oxygen



anti-125

bridges in 125 may have a role in preventing the reaction. In the least hindered endo-approach, shown in Figure 7, there would still be a substantial non-bonding interaction between an oxygen bridge and one of the outer phenyl rings.

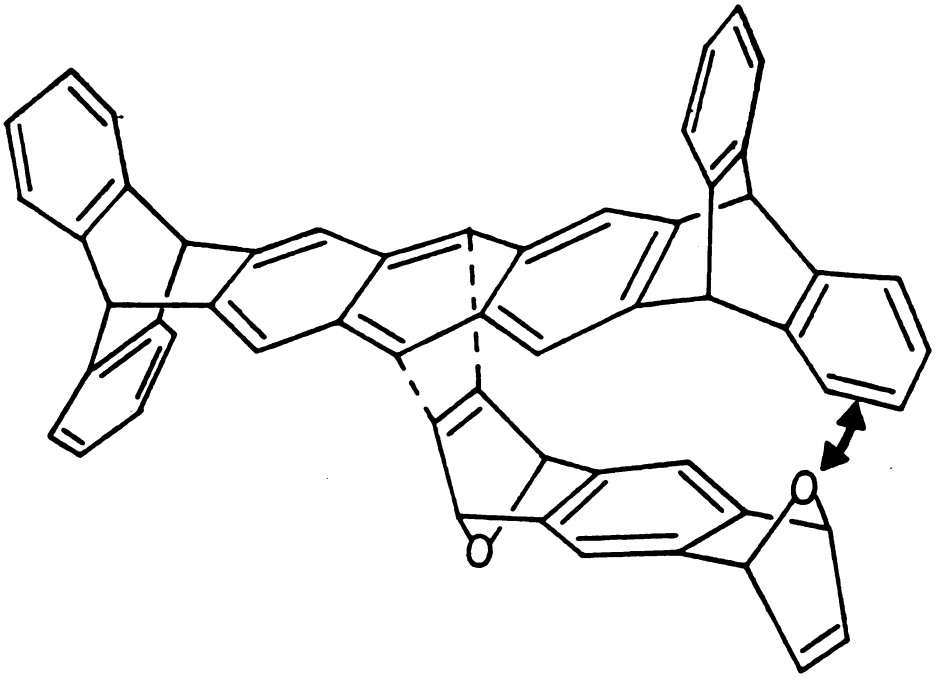
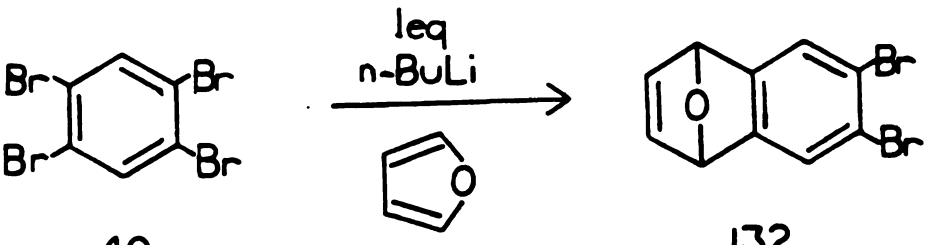


Figure 7. Endo-approach in Diels-Alder reaction between bis-epoxide 125 and pentiptycene 128.

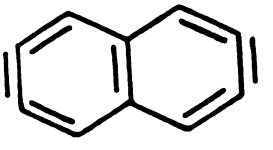
B. Synthesis of a Triptycene From a 2,3;6,7-Naphthadiyne Equivalent

6,7-Dibromo-1,4-dihydronaphthalene-1,4-epoxide, 132, synthesized from 1,2,4,5-tetrabromobenzene, 40, and furan using one equivalent of n-butyllithium, should also be an effective dienophile. Again, the oxygen bridge in the resulting cycloadducts should be easily removed to give an aromatic structure. And, since 132 is functionalized



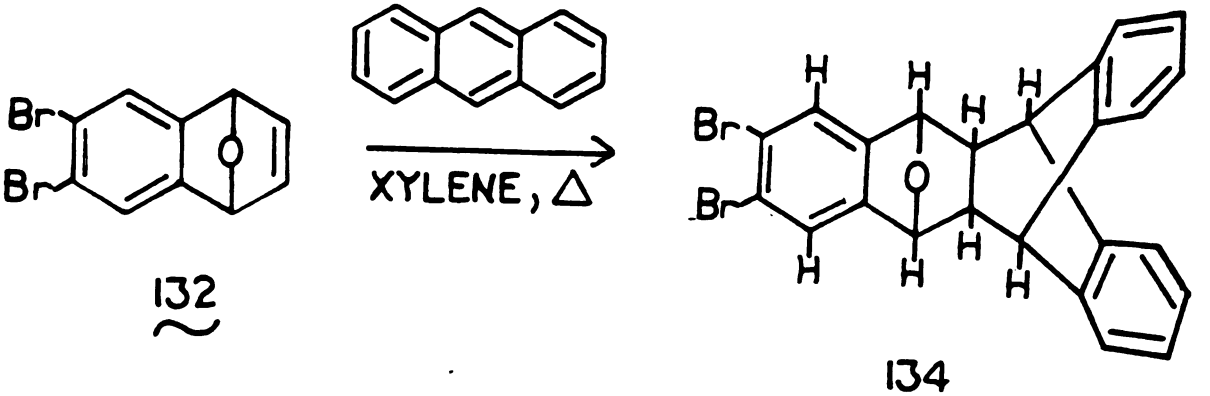
40 132

with bromines, it can be regarded as a synthetic equivalent of 2,3;6,7-naphthadiyne 133.



133

Reaction of epoxide 132 with one equivalent of anthracene in refluxing xylene gave the adduct 134 (mp 265-266°C)

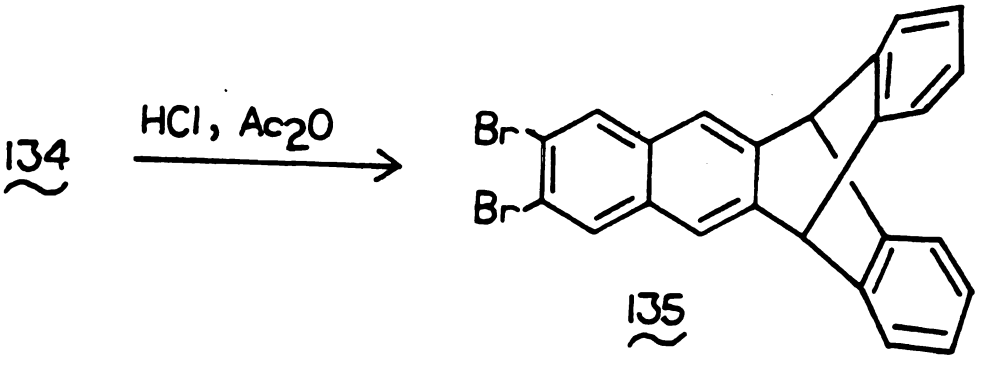


132 134

in 96% yield. The adduct was identified by its spectra. The proton NMR spectrum of 134 showed three two-proton

singlets for the three sets of aliphatic hydrogens (δ2.09, 4.26, 4.74), as well as aromatic peaks for the remaining ten aryl hydrogens. The ^{13}C NMR showed three aliphatic carbons and nine aromatic carbons, a total of twelve peaks as required by symmetry. The mass spectrum gave a molecular ion peak of m/e 480.

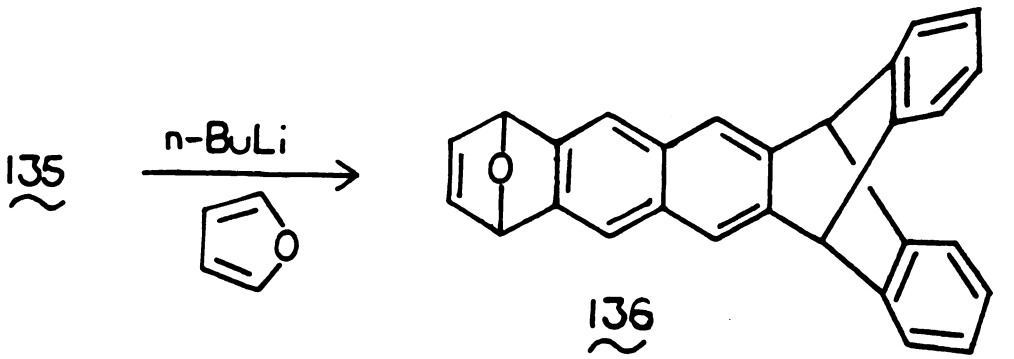
Adduct 134 was dehydrated with hydrochloric acid in acetic anhydride to give the dibromotriptycene 135. Again, the structure was apparent from the spectra. The ^{1}H NMR



spectrum of 135 showed a two-proton singlet (δ5.50) for the bridgehead hydrogens, two two-proton singlets for the uncoupled hydrogens of the naphthalene ring (δ7.60, 7.93), and two aromatic multiplets for the remaining eight aryl protons. The ^{13}C NMR showed only seven peaks. Two peaks due to quaternary carbons were missing because of the low solubility of the compound.

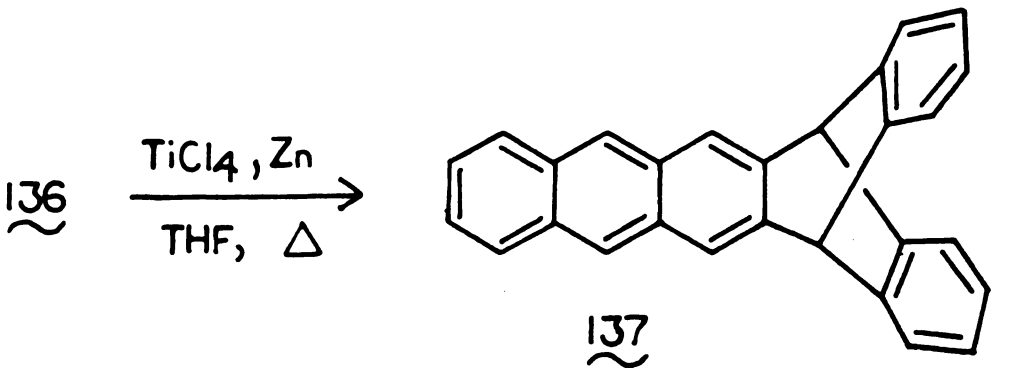
Reaction of 135 with furan using n-butyllithium to generate the aryne, was carried out in the manner described

for the dibenzyne reactions in Part I. As before, the structure of adduct 136 was apparent from its spectral data.



The ^{1}H NMR of 136 contained two two-proton singlets for the four bridgehead hydrogens (δ5.48, 5.72), and three two-proton singlets (δ6.88, 7.65, 7.76) for the three sets of uncoupled sp^2 hydrogens, as well as two aromatic multiplets for the remaining eight hydrogens. The ^{13}C NMR was simpler than predicted by symmetry, only eleven peaks, because of coincidental overlap of some of the aromatic peaks. The mass spectrum gave a molecular ion peak of m/e 370.

Deoxygenation of adduct 136 was carried out using low valent titanium in the same manner as described in Part I. The novel triptycene 137 (mp 221-222°C) was isolated in 79% yield. The spectral data are in agreement with the structure shown. The ^{1}H NMR spectrum of 137 consisted of a two-proton singlet (δ5.53) for the two bridgehead

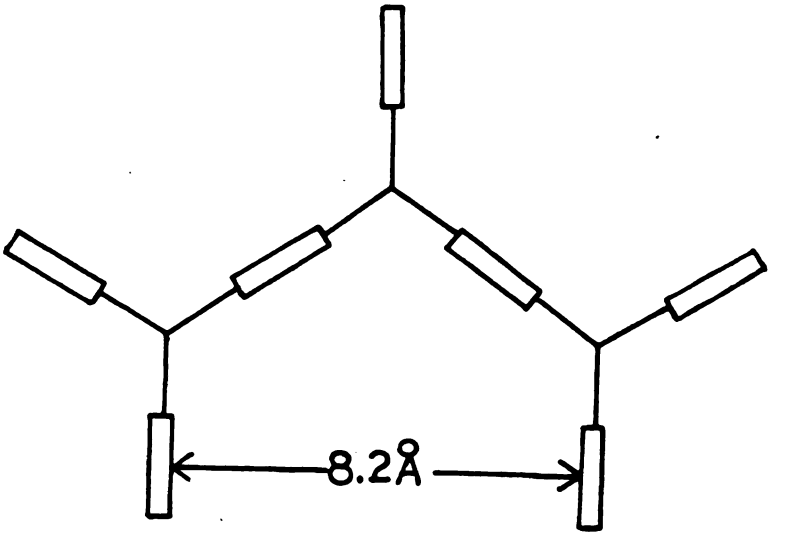


hydrogens, and two two-proton aromatic singlets for the two sets of uncoupled hydrogens of the anthracene moiety (δ7.87, 8.22), as well as four multiplets for the twelve remaining aromatic hydrogens. The ^{13}C NMR contained eleven peaks (one aliphatic, ten aromatic carbons) as required by symmetry. The mass spectrum gave a strong molecular ion peak at m/e 354.

C. Suggestions for Further Studies

Iptycenes are an intriguing class of compounds because they possess a high degree of symmetry, and they comprise planar aromatic systems in well-defined orientations to one another.[44,45]

Heptiptycene 129 has a geometry with several interesting structural features (see Figure 8). Four of the aryl rings are arranged in a horseshoe shape which creates a non-polar or lipophilic cavity with two parallel arene rings separated by approximately 8.2 Å. This cavity might

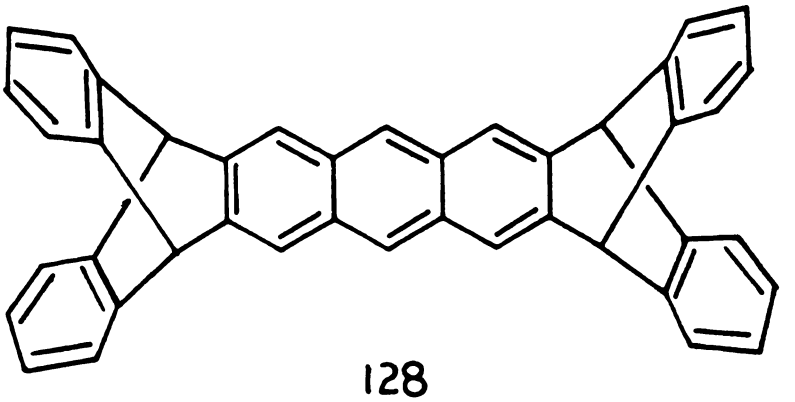


129

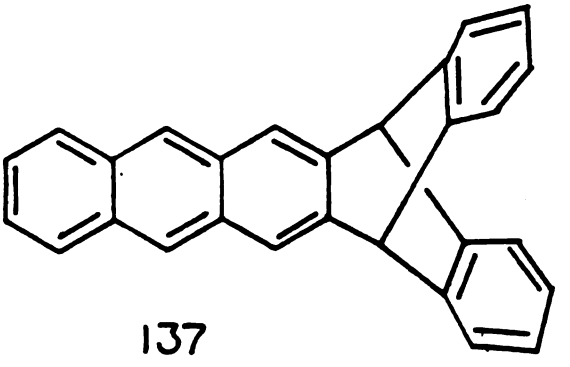
Figure 8. End on view of heptiptycene 129.

trap non-polar small molecules (especially if the three remaining rings were to carry polar, hydrophilic substituents), or may yield novel organometallic complexes. Also, with two additional arene rings, this cavity would be converted to three-dimensional hexagonal array of benzenoid rings.

Pentiptycene 128 and triptycene 137 supply easy entry into higher iptycene analogues since both contain an anthracene ring which can undergo Diels-Alder reactions with suitable dienophiles. If pentiptycene 128, for example, could react with a di-benzyne equivalent, the trideciptycene 138 would be produced. Here, five aryl rings on each side of the molecule are arranged so that

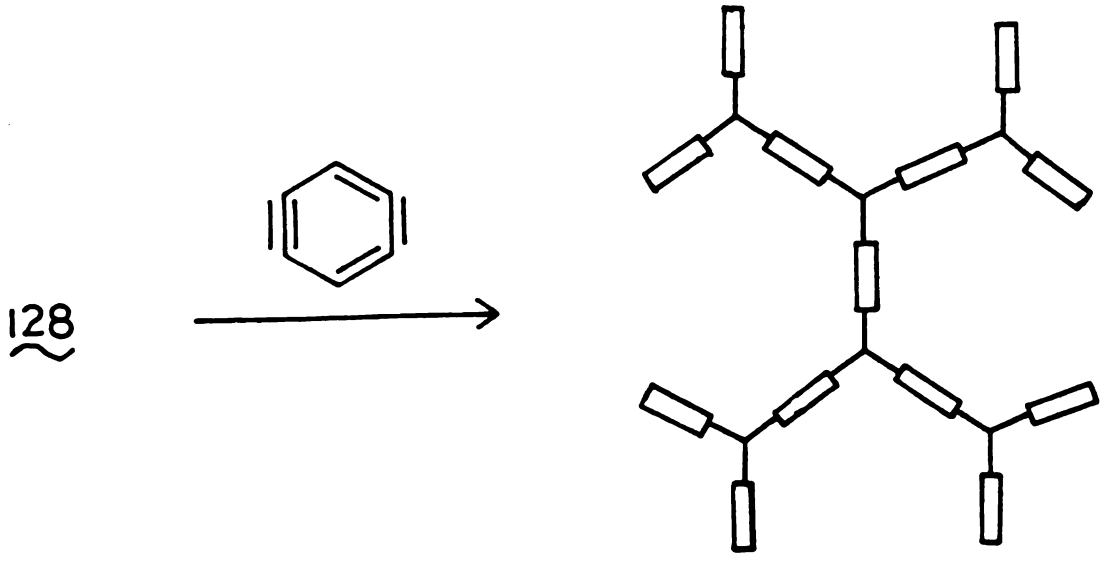


128



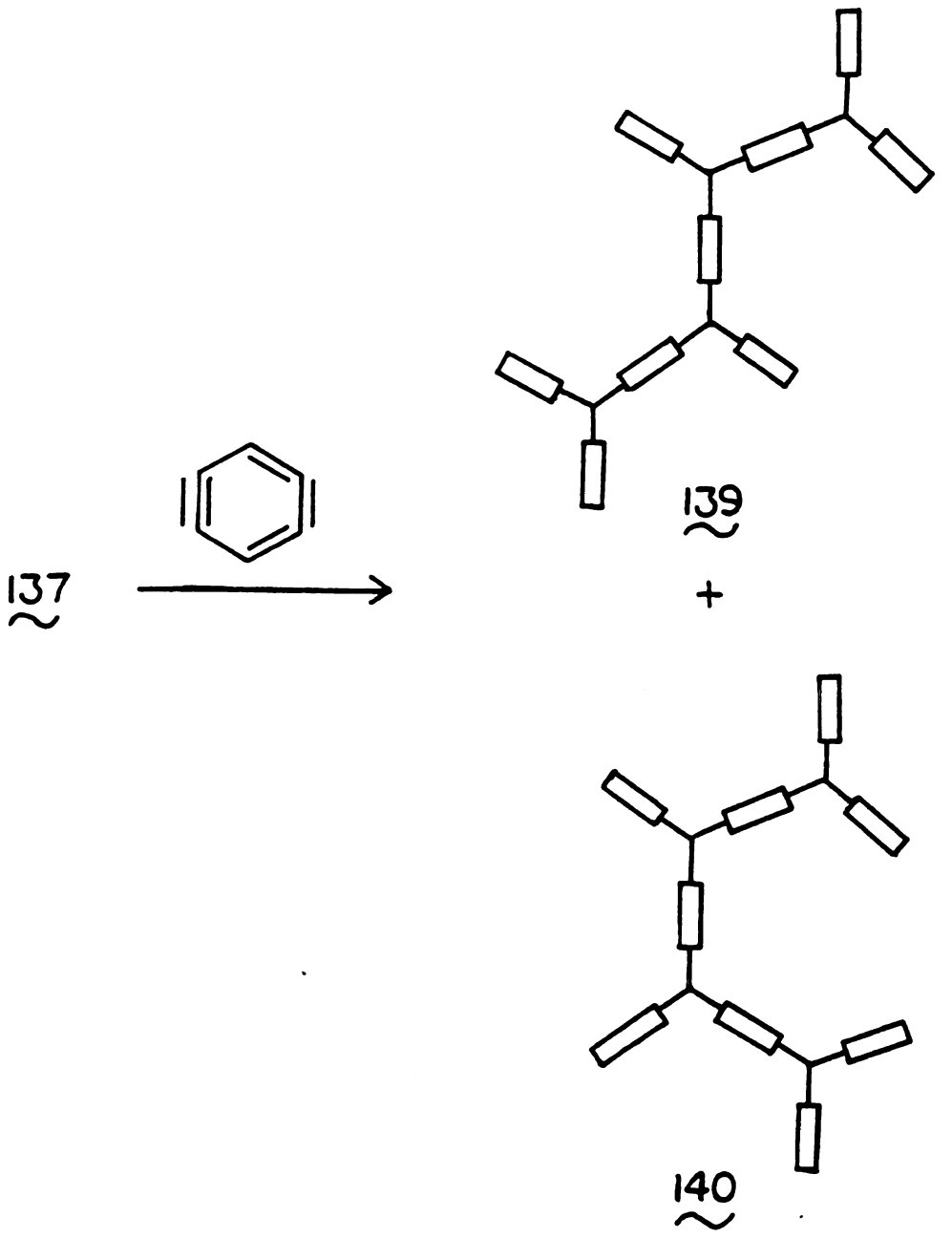
137

only one more arene ring would be needed to form a cyclic array. So far, as previously discussed, all attempts to react pentiptycene 128 with a di-benzyne equivalent have failed.



Triptycene 137 with a di-benzyne equivalent may yield two isomers of noniptycene, 139 and 140, one of which would possess the same arrangement of five aryl rings.

Finally, since pentiptycene 128 reacts with benzyne generated with o-benzenediazonium carboxylate to give heptiptycene 129, it should react in the same way with a derivative of o-benzenediazonium carboxylate, such as 141.[46] This would give dibromoheptiptycene 142, which could react further with anthracene or triptycene 137 and n-butyllithium to yield the novel iptycenes, 143 and 144, respectively (see Scheme 6).


137
139
+
140

EXPERIMENTAL

General Procedures

NMR spectra (^{1}H and ^{13}C) were recorded on either a Bruker WM 250 MHz or a Varian T-60 Nuclear Magnetic Resonance Spectrometer using tetramethylsilane (TMS) as the internal standard. ESR spectra were measured with a Varian E-4 EPR Spectrometer. IR spectra were recorded on a Perkin-Elmer Model 167 spectrometer. Mass spectra were measured at 70 eV by Mr. Ernest Oliver using a Finnigan 4000 spectrometer with the INCOS data system. Ultraviolet absorption spectra were recorded on a Varian Carey 219 spectrometer. Melting points were determined using a MEL-TEMP apparatus, modified when necessary for high temperatures, and are uncorrected. Anhydrous magnesium sulfate was used as the drying agent throughout, and the silica gel for chromatography was 230-400 mesh. Analyses were performed by either Spang Microanalytical Laboratory, Eagle Harbor, Michigan or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

9,10-Dimethoxyoctamethylanthracene, 69

To a solution of tetrabromo-p-dimethoxybenzene, 19,[28] (2.27 g, 5.0 mmol) and N,N-dimethylaminotetramethylpyrrole[28]

(2 g, excess) in 50 mL tetrahydrofuran under argon at -78°C was added n-butyllithium (12 mmol in 25 mL hexane) dropwise over two hours. The reaction was allowed to come slowly to room temperature, then 1 mL methanol was added, followed by 50 mL water. The product was extracted into methylene chloride, washed with water, dried, and the solvent removed.

A waxy, yellow solid remained, which was heated under vacuum at 180°C for thirty minutes. The black residue produced was eluted through 8 cm florisil with 1:1 chloroform-hexane, and recrystallized from ether-methanol to give 1.05 g (60%) bright yellow crystals, mp 216-218°C (lit.[28] 218-220°C). ^{1}H-NMR ($CDCl_3$): δ2.38 (s, 12 H), 2.76 (s, 12 H), 3.33 (s, 6 H). Mass spectrum m/e 350 (M^+), 335 (base peak).

Tetrabromohydroquinone, 145.

Bromine (64 mL, 1.2 mol) was added dropwise to a solution of hydroquinone (24.2 g, 0.2 mol) in 200 mL acetic acid cooled in an ice bath. The dark orange solution was left stirring overnight after which it was light orange and contained much white precipitate. A saturated sodium bisulfite solution was added until the reaction mixture was colorless, and 65 g (76%) white crystals collected, mp 242-244°C (lit.[48] 244°C). Mass spectrum m/e 426 (M^+ and base peak).

2,3,5,6-Tetrabromo-1,4-diethoxybenzene, 70

Ethyl bromide (5 mL, excess) was added all at once to a solution of 145 (10.65 g, 0.25 mol) and potassium hydroxide (2.8 g) in 30 mL methanol. The resulting solution was refluxed for twenty hours. Then the solvent was removed, and the residue was taken up in ether (100 mL) and 0.5 N sodium hydroxide, 0.1 N hydrochloric acid, and brine, and dried. Removal of the solvent left a tan solid which was recrystallized from methanol to give 7.2 g (60%) white needles, mp 150-151°C. Mass spectrum m/e (relative intensity) 482 (13), 454 (7), 426 (100), 131 (87). ^{1}H NMR ($CDCl_3$): δ1.45 (t, 6 Hz, 6 H), 4.00 (q, 6 Hz, 4 H).

9,10-Diethoxyoctamethylanthracene, 71

Synthesis was carried out analogous to 69 from 70 (2.4 g, 5 mmol) and N,N-dimethylaminotetramethylpyrrole[28] (2 g). Recrystallization of the crude product from methanol-water gave 0.95 g (50%) bright yellow needles, mp 171-172°C. ^{1}H NMR (toluene-d_8): δ1.26 (t, 7 Hz, 6 H), 2.32 (s, 12 H), 3.07 (s, 12 H), 3.48 (q, 7 Hz, 4 H). Mass spectrum m/e (relative intensity) 378 (33), 349 (60), 321 (100), 305 (10), 290 (10), 235 (9), 161 (12). Anal: Calcd for $C_{26}H_{34}O_2$: C, 82.46; H, 9.05. Found: C, 82.45; H, 9.09.

2,3,5,6-Tetrabromo-1,4-diisopropoxybenzene, 72

To a solution of 145 (21.3 g, 0.05 mol) and potassium hydroxide (5.61 g, 0.10 mol) in 75 mL methanol was added all at once isopropyl iodide (20.4 g, 0.12 mol). The brown reaction mixture was refluxed for forty hours after which the solvent was removed. The residue was taken up in ether (100 mL) and 0.5 N sodium hydroxide (50 mL). The organic layer was washed successively with 0.5 N sodium hydroxide, 0.1 N hydrochloric acid, and brine, and dried. Evaporation of the solvent gave a dark brown solid which was eluted through 8 cm florisil with 1:1 chloroform-hexanes. The resulting orange solid was recrystallized from methanol to give 10.4 g (41%) pale yellow needles, mp 104-105°C. ^{1}H NMR ($CDCl_3$): δ1.40 (d, 6 Hz, 12 H), 4.75 (sept, 6 Hz, 2 H). Mass spectrum m/e 510 (M^+), 43 (base peak).

9,10-Diisopropoxyoctamethylanthracene, 73

Synthesis was carried out analogous to 69 from 72 (2.55 g, 5.0 mmol) and N,N-dimethylaminotetramethylpyrrole[28] (2 g). Recrystallization of the crude product from acetone gave 1.2 g (60%) small, yellow crystals, mp 218-219°C. ^{1}H NMR (toluene-d_8): δ1.08 (d, 6 Hz, 12 H), 2.47 (s, 12 H), 3.19 (s, 12 H), 4.12 (sept, 6 Hz, 2 H); ^{13}C NMR ($CDCl_3$): δ17.1, 21.0, 22.0, 75.4, 127.7, 127.9, 133.6, 151.4. Mass

spectrum: m/e (relative intensity) 406 (8), 363 (5), 321 (100), 305 (7), 43 (50).

Anal. Calcd for $C_{28}H_{38}O_2$: C, 82.71; H, 9.42. Found: C, 82.76; H, 9.46.

2,3,5,6-Tetrabromo-4-(bromomethyl)anisole, 146

A solution of methyl tetrabromo-p-cresolate[49] (21.9 g, 0.05 mol) and bromine (16 g, 0.1 mol) in 1000 mL carbon tetrachloride was irradiated with a high intensity lamp, and refluxed for three hours. The solution was allowed to cool, washed with dilute sodium bisulfite, and the solvent removed. The off-white crystals remaining were recrystallized from ethanol to give 25.6 g (99+%) white needles, mp 162-164°C. ^{1}H NMR ($CDCl_3$): δ3.8 (s, 3 H), 4.8 (s, 2 H). Mass spectrum: m/e (relative intensity) 514 (1), 436 (65), 315 (21), 234 (30), 153 (40), 85 (37), 74 (100).

2,3,5,6-Tetrabromo-4-(acetoxymethyl)anisole, 147

To a solution of 146 (20.4 g, 0.04 mol) in 150 mL acetic anhydride was added potassium acetate (2 g). The reaction mixture was refluxed three hours, allowed to cool, then poured into an ice-2N sodium hydroxide mixture. The light brown precipitate which formed was filtered, and dissolved in methylene chloride (100 mL). The solution was

washed with dilute sodium bicarbonate, water, then dried. Removal of the solvent left a sandy solid which was recrystallized from methanol to give 19.7 g (99+%) white needles, mp 124-125°C. ^{1}H NMR ($CDCl_3$): δ2.1 (s, 3 H), 3.85 (s, 3 H), 5.55 (s, 2 H). Mass spectrum: m/e (relative intensity) no M^+, 437 (1), 415 (1), 375 (7), 357 (1), 74 (5), 43 (100).

2,3,5,6-Tetrabromo-4-(hydroxymethyl)anisole, 148

To a solution of 147 (20 g, 0.04 mol) in 150 mL ethanol was added 200 mL 1N potassium hydroxide. The solution was refluxed for four hours, then cooled in an ice bath. The white crystals which formed were collected by vacuum filtration and recrystallized from acetone to yield 16.7 g (92%) white needles, mp 172-173°C. ^{1}H NMR ($CDCl_3$): δ2.2 (br s, 1 H), 3.8 (s, 3 H), 5.15 (s, 2 H). Mass spectrum m/e (relative intensity) 454 (56), 373 (44), 330 (38), 266 (100), 223 (34), 141 (32), 74 (29).

2,3,5,6-Tetrabromoanisole, 74

A solution of tetra-n-butylammonium permanganate[50] (4.80 g, 13 mmol) in 50 mL pyridine under argon was added to 148 (4.54 g, 10 mmol) in 50 mL pyridine at room temperature. The resulting purple solution was heated to 40-50°C for six hours (solution turned brown). The reaction

mixture was cooled to room temperature and poured into dilute hydrochloric acid containing some sodium bisulfite. The white precipitate which formed was filtered and recrystallized from methanol to give 2.9 g (70%) small, white needles, mp 122-124°C (lit.[51] 120.5°C). ^{1}H NMR ($CDCl_3$): δ3.85 (s, 3 H), 7.7 (s, 1 H). Mass spectrum m/e (relative intensity) 424 (56), 409 (10), 381 (23), 328 (14), 221 (30), 81 (42), 61 (100).

1,2,3,4,5,6,7,8-Octamethyl-9-methoxyanthracene, 75

Synthesis was carried out analogous to 69 from 74 (2.17 g, 5 mmol) and N,N-dimethylaminotetramethylpyrrole[28] (2 g). The crude product was eluted through 10 cm silica gel with 10:1 hexane-chloroform then recrystallized from acetone-ether to give 0.2 g (20%) bright yellow crystals, mp 234-235°C. ^{1}H NMR (toluene-d_8): δ2.33 (s, 6 H), 2.36 (s, 6 H), 2.72 (s, 6 H), 3.04 (s, 6 H), 3.40 (s, 3 H), 8.58 (s, 1 H); ^{13}C NMR ($CDCl_3$): δ15.92, 17.57, 17.73, 19.33, 62.22, 114.36, 124.57, 127.72, 128.11, 131.17, 132.11, 133.78, 155.36. Mass spectrum m/e (relative intensity) 320 (80), 305 (100), 41 (100).

Anal. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81. Found: C, 86.17; H, 8.66.

1,2,3,4,5,6,7,8-Octamethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-bis(epoxide), 77

A solution of n-butyllithium (22 mmol) in 50 mL hexane was added dropwise over three hours to 1,2,4,5-tetrabromobenzene, 40,[52] (3.9 g, 10 mmol) and tetramethylfuran, 76,[49] (3 g) dissolved in 50 mL dry toluene under argon at -78°C. The reaction mixture was allowed to come slowly to room temperature, then 1 mL methanol was added. The organic layer was washed with water, dried, and the solvent removed. A waxy, yellow solid remained which was recrystallized from methanol to give 2 g (71%) small, pale yellow crystals, mp 290-296°C. ^{1}H NMR ($CDCl_3$): δ1.60 (s, 12 H), 1.78 (s, 12 H), 6.82 (s, 2 H). Mass spectrum m/e (relative intensity) 322 (14), 268 (2), 236 (10), 225 (100).

1,5,9,10-Tetramethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide), 80

To a solution of tetrabromo-p-xylene 17,[53] (8.44 g, 20 mmol) and 2-methylfuran, 78, (4.1 g, 50 mmol) in 200 mL dry toluene under argon at -23°C was added n-butyllithium (45 mmol in 100 mL hexane) dropwise over three hours. The reaction mixture was allowed to come slowly to room temperature and stirred overnight. Methanol (1 mL) was added, and the mixture was washed with water, dried, and

the solvent removed. The yellow waxy solid remaining was recrystallized with methanol to give 1.8 g (34%) off-white crystals, mp 248-252°C. ^{1}H NMR ($CDCl_3$): δ1.98 (s, 6 H), 2.25 (s, 6 H), 5.50 (d, 2 Hz, 2 H), 6.85 (br s, 2 H), 6.95 (br d, 2 Hz, 2 H). Mass spectrum m/e (relative intensity) 266 (25), 240 (12), 223 (43), 197 (100), 181 (69), 165 (43), 152 (23), 43 (95).

1,8,9,10-Tetramethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide), 79

After filtering the off-white crystals from the above, the mother liquor was evaporated to a yellow oil. Recrystallization from hexane gave 1.5 g (28%) white crystals, mp 174-180°C. ^{1}H NMR ($CDCl_3$) showed this to be a 3:2 mixture of syn and anti isomers. Major isomer: δ2.10 (s, 6 H), 2.30 (s, 3 H), 2.38 (s, 3 H), 5.65 (m, 2 H), 6.8-7.1 (m, 4 H); minor isomer: δ2.10 (s, 6 H), 2.40 (s, 3 H), 2.45 (s, 3 H), 5.65 (m, 2 H), 6.8-7.1 (m, 4 H). Mass spectrum: m/e (relative intensity) 266 (19), 240 (13), 223 (23), 197 (46), 181 (37), 165 (27), 152 (15), 85 (26), 43 (100).

9,10-Diisopropoxy-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide), 82

To a solution of 1,4-diisopropoxytetrabromobenzene, 72, (2.55 g, 5 mmol) and furan, 81, (1 g) in 50 mL dry toluene

at -78°C under argon was added dropwise over two hours n-butyllithium (12 mmol in 30 mL hexane). The reaction mixture was allowed to come slowly to room temperature at which time 1 mL methanol was added. The mixture was washed with water, dried, and the solvent removed. The yellow oil remaining was recrystallized from hexane to give 0.45 g (60%) white crystals, mp 184-188°C. ^{1}H NMR shows it to be a 1:1 mixture of syn and anti isomers which could not be separated: δ1.3 (dd, 7 Hz, 12 H), 4.2 (br sept, 7 Hz, 2 H), 5.8 (s, 4 H), 7.1 (s, 4 H). Mass spectrum m/e (relative intensity) 326 (21), 213 (15), 186 (100), 121 (27), 43 (48).

Diethyl Diglycollate, 149[54]

A solution of diglycollic acid (60.0 g, 0.045 mol) in 250 mL ethanol was treated with ten drops of concentrated sulfuric acid, and refluxed overnight. After removing the solvent, the oily residue was distilled under vacuum (97-100°C, 0.7 Torr) to give 70.3 g (83%) of a clear, viscous liquid. ^{1}H NMR ($CDCl_3$): δ1.30 (t, 7 Hz, 6 H), 4.23 (q, 7 Hz, 4 H), 4.23 (s, 4 H).

Diethyl 3,4-dihydroxyfuran-2,5-dicarboxylate, 150

To a freshly prepared solution of sodium ethoxide in ethanol (11.5 g sodium metal in 200 mL ethanol) was added

diethyl oxalate (17.5 g, 0.12 mol) and 149 (19.0 g, 0.10 mol). The solution was stirred at room temperature for two hours, then cooled in an ice bath. Neutralization with 2N hydrochloric acid gave 14 g (57%) white crystals, mp 185-6°C (lit.[54] 186°C).

Diethyl 3,4-dimethoxyfuran-2,5-dicarboxylate, 151

To a solution of 150 (19.6 g, 0.14 mol) in 100 mL acetone was added 28.0 g potassium carbonate and 30.4 g dimethyl sulfate. The mixture was refluxed with stirring for two hours, after which additional dimethyl sulfate (8 g) was added. Reflux was continued for fifteen more hours, then the hot solution was filtered. After removing the acetone from the filtrate, the remaining oil was cooled in an ice bath. Dilute ammonium hydroxide was added with stirring until a white, waxy precipitate formed. Filtration and recrystallization from hexane gave 18.4 g (85%) white needles, mp 82-84°C (lit.[54] 88-89°C). Mass spectrum: m/e 272 (M^+ and base peak).

3,4-Dimethoxyfuran-2,5-dicarboxylic acid, 152

To a solution of 151 (27.2 g, 0.1 mol) in 27 mL dioxane was added 60 mL 1N sodium hydroxide. After five hours of reflux the solution was cooled, and acidified with dilute hydrochloric acid. White crystals (19.9 g, 92%)

formed which were filtered and washed with water, mp 250°C (dec) (lit.[54] 255-7°C, dec).

3,4-Dimethoxyfuran, 83

Five separate reactions were set up as follows: copper (II) acetate (0.1 g) and powdered copper (2 g) were added to a solution of 152 (10 g, 0.046 mol) in 100 mL freshly distilled quinoline. The mixture was heated at 170°C for thirty minutes.

The five reaction mixtures were combined for vacuum distillation. At 110°C and 0.7 Torr, the first 200 mL were collected (no product was present in later fractions), and added to 200 mL ether. The organic solution was extracted five times with 50 mL portions of 2N sulfuric acid (cooled in an ice bath!!), two times with dilute sodium bicarbonate, then with water, and dried. The ether was removed and the remaining yellow liquid was distilled. The first fraction (61-2°C, 0.7 Torr) contained 15.0 g pure 83. The second fraction (110°C, 0.7 Torr), a 1:1 mixture of quinoline and 83, was redissolved in ether, extracted again, and redistilled to give an additional 5.0 g 83. The total yield was 20.0 g (68%) (lit.[55] 64%). ^{1}H NMR ($CDCl_3$): δ3.70 (s, 6 H), 6.90 (s, 2 H).

2,3,6,7,9,10-Hexamethoxy-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide), 84

To a stirred solution of tetrabromo-p-dimethoxybenzene 19,[28] (4.54 g, 10 mmol) and 83 (2.8 g, 22 mmol) in 100 mL dry toluene at -78°C under argon was added n-butyllithium (12 mmol in 30 mL hexane) dropwise over two hours. The reaction mixture was allowed to come slowly to room temperature after addition. Methanol (1 mL) was added, and the mixture was washed with water, dried, and the solvent removed. The remaining brown oil was treated with hexane to give 2.4 g (65%) small, white crystals, mp 140-155°C (a 1:1 mixture of syn and anti isomers). Washing the solid with methanol dissolved the syn isomer. The anti isomer was collected by vacuum filtration as small, white crystals, mp 220-222°C (dec). Removal of the methanol left an off-white oily solid (90% enriched sample of syn isomer) which could not be further purified. ^{1}H NMR ($CDCl_3$) (anti): δ3.65 (s, 12 H), 3.80 (s, 6 H), 5.4 (s, 4 H); (syn): δ3.70 (s, 12 H), 3.75 (s, 6 H), 5.4 (s, 4 H); ^{13}C NMR ($CDCl_3$) (anti): δ58.97, 60.76, 80.20, 139.31, 143.34, 145.69. Mass spectrum m/e (relative intensity) 390 (99), 375 (17), 347 (29), 301 (30), 287 (38), 273 (43), 257 (49), 245 (21), 45 (33).

6,7-Dibromo-5,8-dimethyl-1,4-dihydronaphthalene-1,4-epoxide, 85

To a solution of tetrabromo-p-xylene, 17,[49] (4.2 g, 10 mmol) and furan (3 mL) in 100 mL dry toluene under argon at -23°C was added n-butyllithium (14 mmol in 40 mL hexane) over two hours. The reaction mixture was allowed to come slowly to room temperature and stirred overnight. Methanol (1 mL) was added, and the mixture was washed with water, dried, and the solvent removed. The off-white solid was recrystallized from hexane, then methanol to give 1.6 g (50%) small white crystals, mp 140-142°C. ^{1}H NMR ($CDCl_3$): δ2.4 (s, 6 H), 5.7 (br s, 2 H), 6.95 (br s, 2H). Mass spectrum m/e (relative intensity) 330 (10), 304 (18), 221 (100), 141 (78), 115 (75).

1,9,10-Trimethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis(epoxide), 86

To a solution of 85 (1.65 g, 5 mmol) and 2-methylfuran (2 g, excess) in 50 mL dry toluene at -78°C under argon was added n-butyllithium (5 mmol in 20 mL hexane) dropwise over two hours. The reaction was allowed to come slowly to room temperature, and methanol (1 mL) was added. The mixture was washed with water, dried, and the solvent removed. The waxy yellow solid remaining (1 g, 80%) was a mixture of syn and anti isomers. Treatment with hexane gave one

isomer (*syn* ?) preferentially as small, off-white crystals, mp 190-195°C. Removal of the hexane left a yellow oil (90% enriched sample of other isomer) which could not be further purified. ^{1}H NMR of crystalline isomer ($CDCl_3$): δ1.90 (s, 3 H), 2.18 (s, 3 H), 2.21 (s, 3 H), 5.60 (br s, 3 H), 6.95 (br s, 4 H). Mass spectrum *m/e* (relative intensity) 252 (29), 226 (13), 209 (16), 197 (41), 181 (100), 165 (59), 152 (23), 43 (14).

9,10-Dimethoxyanthracene, 22

To a suspension of 1 mL titanium tetrachloride in 50 mL dry tetrahydrofuran under argon at 0°C was added 1.4 g zinc powder (excess). The steel gray suspension was heated to reflux, and a solution of bis-epoxide 10[49] (*syn*-*anti* mixture) (0.27 g, 1.0 mmol) in 50 mL tetrahydrofuran was added dropwise (15 minutes). The mixture was refluxed for eight hours, then cooled to room temperature, and poured into dilute hydrochloric acid. The resulting purple mixture was extracted with methylene chloride, and the organic layer was washed with water, and dried. The remaining yellow solid was recrystallized from chloroform to give 0.21 g (90%) yellow plates, mp 198-199°C (lit.[56] 202°C). ^{1}H NMR ($CDCl_3$): δ4.05 (s, 6 H), 7.30 (m, 8 H), 8.10 (m, 4 H).

1,2,3,4,5,6,7,8-Octamethylanthracene, 87

Deoxygenation of 77 was carried out in the same manner and scale as 10. The crude product was recrystallized from chloroform - hexane to give 0.25 g (80%) small yellow crystals, mp 292-294°C (lit.[39] 299-300°C). ^{1}H NMR (toluene-d_8): δ2.30 (s, 12 H), 2.71 (s, 12 H), 8.83 (s, 2 H). Mass spectrum m/e (relative intensity) 290 (100), 275 (9).

1,8,9,10-Tetramethylanthracene, 88[57]

Deoxygenation of 79 was carried out in the same manner and scale as 10, except the reaction was worked up in the dark. Removal of the solvent left a yellow oil which was recrystallized from methanol-ether to give 135 mg (57%) yellow flakes, mp 80-82°C. ^{1}H NMR (toluene-d_8): δ2.66 (s, 6 H), 2.71 (s, 3 H), 2.79 (s, 3 H), 7.16-7.25 (m, 4 H), 8.02 (d, 2 H). Mass spectrum m/e (relative intensity) 234 (97), 219 (100), 202 (29), 189 (14), 101 (29), 94 (16).

1,5,9,10-Tetramethylanthracene, 89

Deoxygenation of 80 was carried out in the same manner and scale as 10, except the reaction was worked up in the dark. The crude product was recrystallized from methanol to give 0.20 g (85%) yellow needles, mp 71-72°C. ^{1}H NMR (toluene-d_8): δ2.65 (s, 6 H), 2.87 (s, 6 H), 7.14-7.24

(m, 4 H), 8.01 (d, 9 Hz, 2 H). Mass spectrum m/e (relative intensity) 234 (100), 219 (62), 202 (16), 108 (28).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.84.

9,10-Diisopropoxyanthracene, 90

Deoxygenation of 82 was carried out in the same manner and scale as 10. The crude product was recrystallized from methanol to give 0.26 g (83%) yellow needles, mp 122-124°C. ^{1}H NMR (toluene-d_8): δ1.29 (d, 6.1 Hz, 12 H), 4.49 (sept. 6.1 Hz, 2 H), 7.35 (m, 2.5 Hz, 4 H), 8.45 (m, 2.5 Hz, 4 H). Mass spectrum m/e (relative intensity) 294 (15), 252 (2), 209 (100), 180 (8), 152 (15), 43 (15).

2,3,6,7,9,10-Hexamethoxyanthracene, 91

Deoxygenation of 84 was carried out in the same manner and scale as 10. Removal of the solvent left 0.31 g (85%) of a yellowish solid which was recrystallized from methanol, mp 261-62°C. ^{1}H NMR ($CDCl_3$): δ4.05 (s, 12 H), 4.04 (s, 6 H), 7.45 (s, 4 H). Mass spectrum m/e (relative intensity) 358 (48), 343 (100), 328 (9), 313 (8), 179 (3).

Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.03; H, 6.19. Found: C, 67.11; H, 6.35.

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2,3,6,7-Tetrahydroxyanthroquinone, 153

A solution of 91 (0.3 g, 0.8 mmol) in 12 mL methylene chloride was added to boron tribromide (1.5 g, 6 mmol) in 10 mL methylene chloride under argon at -78°C. The solution was allowed to come slowly to room temperature, stirred for an additional four hours, then cooled in an ice bath. Ice-water (~10 mL) was added cautiously, and the brown-orange crystals which formed were filtered. Recrystallization from ethanol gave 0.14 g (67%) bright orange crystals, mp <330°C (dec.) (lit.[59] <330°C, dec.). Mass spectrum m/e (relative intensity) 272 (45), 258 (100), 240 (16), 229 (37), 212 (22), 184 (18).

1,9,10-Trimethylanthracene, 92[34]

Deoxygenation of 86 was carried out in the same manner and scale as 10, except work-up was carried out in the dark. The crude product was sublimed at 30°C and 0.7 torr to give 0.17 g (80%) yellow needles, mp 76-78°C. ^{1}H NMR ($CDCl_3$): δ2.75 (s, 3 H), 2.8 (s, 3 H), 2.95 (s, 3 H), 7.2 (m, 4 H), 7.8 (m, 3 H). Mass spectrum m/e (relative intensity) 220 (100), 205 (47), 189 (11), 178 (8), 101 (8).

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4,5-Dibromo-3,6-diiodoveratrole, 96

A solution of 4,5-dibromoveratrole[58] (18 g, 0.61 mol) and mercuric oxide (42 g) in 160 mL trifluoroacetic acid was heated to reflux for four hours. The reaction mixture was cooled in an ice bath, and the white solid (4,5-dibromo-3,6-di-(trifluoroacetatomercurio)veratrole) which formed was filtered.

The crude solid was heated at 70-75°C with iodine (60 g) and potassium iodide (40 g) in 200 mL water (mechanical stirrer) for eight hours. After the reaction mixture was cooled, the solid was filtered, and taken up into chloroform. The organic solution was washed successively with 10% sodium thiosulfate, dilute sodium bicarbonate, and water, dried, and the solvent removed. The off-white solid remaining was recrystallized from chloroform-methanol to give 26.4 g (79% from 4,5-dibromoveratrole) white needles, mp 144-145°C. Mass spectrum m/e (relative intensity) 532 (25), 504 (21), 489 (14), 405 (5), 390 (15), 254 (13), 203 (53), 155 (61), 127 (100), 104 (42), 76 (54).

9,10-Dimethoxyoctamethyl-1,4,5,8-tetrahydrophenanthrene-1,4;5,8-bis(epoxide), 97

To a solution of 96 (1.37 g, 2.5 mmol) and tetramethylfuran, 76,[49] (1 g, 8 mmol) in 50 mL dry ether was added n-butyllithium (9 mmol in 50 mL hexane) dropwise over four

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hours. The reaction mixture was allowed to come to room temperature and stirred overnight. Methanol (1 mL) was added, and the mixture was washed with water, dried, and the solvent removed. A light yellow oil remained which could not be purified. ^{1}H NMR ($CDCl_3$): δ1.65 (s, 6 H), 1.80 (s, 6 H), 1.85 (s, 6 H), 1.86 (s, 6 H), 3.75 (s, 6 H). Mass spectrum m/e (relative intensity) 382 (10), 339 (100), 328 (29), 296 (86), 285 (50), 281 (79), 165 (45), 123 (87), 71 (89).

9,10-Dimethoxyoctamethylphenanthrene, 98

Deoxygenation of the crude oil, 97, was carried out in the same manner as 10. The crude product was recrystallized from methanol to give 0.22 g (25% from 96) light yellow needles, mp 187-188°C. ^{1}H NMR ($CDCl_3$): δ2.30 (s, 6 H), 2.36 (s, 6 H), 2.41 (s, 6 H), 2.80 (s, 6 H), 3.86 (s, 6 H); ^{13}C NMR ($CDCl_3$): 16.78, 16.98, 18.05, 20.82, 60.10, 118.50, 127.20, 131.31, 131.94, 134.08, 146.20. Mass spectrum m/e (relative intensity) 350 (53), 307 (100), 292 (16), 277 (12), 175 (16), 160 (18), 131 (19).

Anal. Calcd. for $C_{24}H_{30}O_2$: C, 82.24; H, 8.62. Found: C, 82.12; H, 8.75.

General Procedure for Photolysis of Anthracenes and Phenanthrenes

The arene to be photolyzed (10-12 mg) was dissolved in 0.5 mL benzene-d_6, placed in a 5 mm NMR tube and flushed with nitrogen. Irradiation of the sample for 60-90 minutes using a Hanovia 450 W medium pressure lamp with Pyrex filter was carried out by taping the sample tube directly to the water-cooled jacket of the lamp.

All of the anthracenes and phenanthrenes discussed were irradiated first at room temperature, then at -78°C. For the low temperature runs, toluene-d_8 was substituted for benzene-d_6 as solvent. The lamp and cooling jacket along with the sample were immersed in a dry ice-isopropanol bath, and dry nitrogen was passed through the cooling jacket.

After irradiation, the sample tube was immediately transferred to the WM 250 NMR spectrometer, pre-set at a suitable temperature between -60°C and room temperature, and the spectrum was recorded. The results are presented in the text.

Irradiation of 1,5,9,10-tetramethylanthracene, 89, in the Presence of Oxygen

The reaction was carried out in the same manner as described for the room temperature photolyses of arenes,

except the sample was undegassed. After irradiating for 30 minutes, the endoperoxide 112 was produced. ^{1}H NMR (benzene-d_6): δ1.96 (s, 6 H), 2.09 (s, 6 H), 6.75-7.01 (m, 6 H); ^{13}C NMR (benzene-d_6): δ18.56, 21.87, 81.24, 119.66, 126.91, 131.53, 131.88, 143.80 (a sixth aromatic peak must fall coincidentally under the solvent peak). Mass spectrum m/e (relative intensity) 266 (4), 234 (100), 219 (32), 85 (22), 40 (16).

Irradiation of 1,8,9,10-tetramethylanthracene, 88, in the Presence of Oxygen

Photolysis of an undegassed sample of 88 for thirty minutes produced endoperoxide 111. ^{1}H NMR (benzene-d_6): δ1.79 (s, 3 H), 1.99 (s, 3 H), 2.07 (s, 6 H), 6.71-7.06 (m, 6 H). Mass spectrum m/e (relative intensity) 266 (4), 251 (9), 234 (100), 219 (36), 85 (20).

Reaction of Octamethylanthracene 87 with TFA

To a solution of octamethylanthracene 87 (6 mg, 0.02 mmol) in 0.5 mL chloroform-d was added 0.02 mL of 1M trifluoroacetic acid in chloroform-d. Immediately, the solution turned a deeper shade of yellow. The ^{1}H NMR spectrum of 87 disappeared, and an ESR signal (shown in Figure 6a) was observed. After no change in the spectra of the sample for one hour, the solution was quenched with water. The ^{1}H NMR of octamethylanthracene 87 reappeared unchanged.

Reaction of 9-methoxyoctamethylanthracene 75 with TFA

The experiment was carried out in the same manner and scale as 87. Initially, the ^{1}H NMR spectrum was wiped out, and a weak ESR signal (Figure 6b) appeared. After several hours, a new ^{1}H NMR spectrum appeared. After quenching with a few drops of water, the solvent was removed, leaving an off-white residue. This was recrystallized from methanol to give 4 mg (70%) white solid, mp 245-248°C. The spectral data of this solid are consistent with that of the octamethylanthrone 118 (lit.[39] mp 251-252°C). ^{1}H NMR ($CDCl_3$): δ2.28 (s, 6 H), 2.31 (s, 6 H), 2.35 (s, 6 H), 2.54 (s, 6 H), 3.56 (s, 2 H). IR spectrum ($CHCl_3$): 820 cm^{-1} (m), 1160 cm^{-1} (w), 1320 cm^{-1} (m), 1450 cm^{-1} (m), 1580 cm^{-1} (m), 1655 cm^{-1} (s), 1670 cm^{-1} (s), 2960 cm^{-1} (s). Mass spectrum m/e (relative intensity) 306 (86), 291 (100).

Reaction of 9,10-dimethoxyoctamethylanthracene 69 with TFA

The experiment was carried out in the same manner as 87. On addition of trifluoroacetic acid, the solution turned dark blue. But the color faded in an instant to pink, and a new ^{1}H NMR spectrum appeared. Quenching with water, and removal of the solvent gave a pink residue. Fractional recrystallization of the residue with acetone gave first 119b (mp 278-280°C), then 119a (mp 290-292°C), both as white crystalline solids. (The yield of each product determined

by integration of the ^{1}H NMR was 60% 119a and 40% 119b. Much product was lost in the isolation).

For 119a - ^{1}H NMR ($CDCl_3$): δ2.28 (s, 1 H), 2.51 (s, 1 H); ^{13}C NMR ($CDCl_3$): δ16.90, 17.19, 49.15, 133.29, 134.14, 136.79, 140.73. IR spectrum ($CHCl_3$): 880 cm^{-1} (m), 1240 cm^{-1} (s), 1410 cm^{-1} (m), 3025 cm^{-1} (m). Mass spectrum: m/e 320 (32), 305 (100), 290 (24), 277 (10).

For 119b - ^{1}H NMR ($CDCl_3$): δ1.35 (s, 6 H), 1.94 (s, 6 H), 2.20 (s, 6 H), 2.49 (s, 6 H), 4.51 (s, 1 H). IR spectrum: 1280 cm^{-1} (m), 1340 cm^{-1} (m), 1680 cm^{-1} (s), 2940 cm^{-1} (s), 3690 cm^{-1} (br). Mass spectrum m/e (relative intensity) 305 (100), 291 (7).

1,4,5,8-Tetrahydroanthracene-1,4;5,8-bis(epoxide), 125

To a stirred solution of 1,2,4,5-tetrabromobenzene, 40,[52] (3.94 g, 10 mmol) and furan (10 ml) in dry toluene (200 mL) at -23°C under argon was slowly added (4 h) n-butyllithium (7.7 mL, 12 mmol, of a 1.55 M solution in hexane diluted with 200 mL of dry hexane). After addition the mixture was slowly allowed to warm to room temperature. Methanol (1 mL) was added cautiously and the mixture was stirred for a few minutes. The organic layer was washed with water and dried. Solvent removal under reduced pressure gave a gummy yellow solid which partially dissolved on addition of methanol (10 mL). The off-white crystals which remained (0.7 g) were recrystallized from acetone to

give small white plates of the anti isomer, mp (dec) 245°C. The methanol solution was evaporated to dryness and the residue was recrystallized from ethyl acetate-hexane, then from methanol to give the pure syn isomer (0.8 g), mp 191-193°C. The total yield of both isomers was 71%. ^{1}H NMR ($CDCl_3$) (anti): δ5.62 (s, 4 H), 7.01 (s, 4 H), 7.18 (s, 2 H); ^{13}C NMR ($CDCl_3$) (anti): δ82.23, 113.75, 143.30, 147.69; the NMR spectra of the syn isomer were virtually identical with those of the anti isomer (differences of 0.01 in the proton spectrum and 0.10 in the carbon spectrum). Mass spectrum (anti) m/e (relative intensity) 210 (43), 184 (26), 181 (13), 156 (34), 155 (63), 154 (31), 153 (100), 152 (73), 151 (18), 128 (22), 127 (13), 126 (10), 87 (12), 85 (29). Anal. (anti): Calcd. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.76. Found: C, 79.95; H, 4.87.

Adduct of Anthracene and bis-epoxide 125 (127)

A solution of bis-epoxide 125 (anti isomer) (2.1 g, 10 mmol) and anthracene (3.6 g, 20 mmol) in xylene (100 mL) was heated at reflux for 48 h. The reaction mixture was cooled to room temperature and the resulting white precipitate was collected (4.6 g, 80%) as a mixture of 127 and a trace amount of unreacted anthracene. The latter was removed by sublimation to give pure 127, mp 440°C (dec). ^{1}H NMR ($CDCl_3$): δ2.13 (s, 4 H), 4.36 (s, 4 H), 4.82 (s, 4 H), 6.90 (s, 2 H), 6.98 (m, 4 H), 7.11 (m, 4 H), 7.19 (m, 4 H), 7.26 (m, 4 H); ^{13}C NMR ($CDCl_3$): δ47.48, 48.80,

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81.09, 110.08, 123.50, 123.68, 125.70, 125.97, 141.49, 144.25, 145.61; mass spectrum, m/e (relative intensity) 566 (6), 530 (21), 375 (50), 370 (65), 326 (17), 339 (15), 203 (13), 191 (43), 178 (100), 44 (43).

Analogous reaction of syn-125 with anthracene gave a stereoisomer of 127 in 60% yield; mp 395°C (dec); ^{1}H NMR ($CDCl_3$): δ2.13 (s, 4 H), 4.35 (s, 4 H), 4.80 (s, 4 H), 6.90 (s, 2 H), 6.98 (m, 4 H), 7.12 (m, 4 H), 7.18 (m, 4 H), 7.26 (m, 4 H); ^{13}C NMR: δ47.47, 49.07, 81.18, 110.04, 123.42, 123.70, 125.66, 126.0, 141.34, 144.19, 145.79.

Pentiptycene, 128

A suspension of 127 (syn or anti) (800 mg, 1.4 mmol) in acetic anhydride (20 mL) and concentrated hydrochloric acid (4 mL) was heated at reflux for 8 h. The cooled reaction mixture was poured into 200 mL of ice-water and the resulting light yellow crystals were extracted with chloroform. The organic layer was washed successively with water and saturated sodium bicarbonate, and dried. Removal of the solvent gave a light yellow residue which was recrystallized from tetrahydrofuran and methanol to give 300 mg (41%) of pentiptycene as small, white plates, mp >500°C. ^{1}H NMR ($CDCl_3$): δ5.50 (s, 4 H, bridgehead protons), 7.02 (m, 8 H), 7.40 (m, 8 H), 7.81 (s, 4 H), 8.06 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ53.81, 121.34, 123.81, 125.11, 125.71, 130.58, 140.80, 144.40; UV (CH_3CN): λ_{max}

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371 nm (ε 6540), 353 (8830), 336 (7150), 320 (4240), 306 (2030), 284 (212, 000), 272 (81,270), 266 (60,500), 260 (61,600), 243 (23,200). Anal. Calcd for $C_{42}H_{26}$: C, 96.98; H, 4.90. Found: C, 96.46; H, 4.98.

Attempted Reaction of Pentiptycene 128 with 1,2,4,5-tetrabromobenzenes, 17, 19 and 40

To a solution of 128 (0.7 g, 1.3 mmol) and 17, 19 or 40 (1 mmol) in 200 mL dry tetrahydrofuran at -23°C under argon was added n-butyllithium (1 mmol in 20 mL hexane) dropwise over two hours. The reaction mixture was allowed to come slowly to room temperature, and methanol (1 mL) was added. The mixture was washed with water, dried and the solvent removed. The white solid remaining (∿0.7 g) in all cases was found to be unreacted pentiptycene 128.

Attempted Reaction of Pentiptycene 128 with Diaryne Precursor 130

Lead (IV) tetraacetate (265 mg, 0.6 mmol in 50 mL tetrahydrofuran) was added all at once to a solution of pentiptycene 128 (350 mg, 0.66 mmol) and bis-triazole 130 (57 mg, 0.3 mmol) in 50 mL tetrahydrofuran under argon at room temperature. The reaction mixture was stirred for thirty minutes at room temperature. A white solid (50 mg) formed which was filtered. This solid was insoluble

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in all normal organic solvents as well as water, and did not melt below 500°C.

The mother liquor was diluted with water (50 mL) and extracted into ether. The organic layer was washed with water and brine, and dried. Removal of the solvent left 320 mg pentiptycene 128.

Attempted Reaction of Pentiptycene 128 with Bis-epoxide 125 (anti)

A solution of pentiptycene 128 (53 mg, 0.1 mmol) and anti-125 (12 mg, 0.05 mmol) in 20 mL xylene was stirred at reflux for four days. Removal of the solvent left a white residue (65 mg) shown by ^{1}H NMR to be a mixture of unreacted 125 and 128.

6,7-Dibromo-1,4-dihydronaphthalene-1,4-epoxide, 132

To a stirred solution of 1,2,4,5-tetrabromobenzene, 40,[52] (8 g, 10 mmol) and furan, 81, (10 mL) in 200 mL dry toluene at -23°C under argon was added n-butyllithium (22 mmol in 200 mL hexane) dropwise over three hours. The reaction mixture was allowed to come slowly to room temperature after addition. Methanol (1 mL) was added, and the mixture was washed with water, dried, and the solvent removed. The remaining yellow, oily solid was treated with hexane to give 4.1 g (70%) small crystals, mp 115-117°C

(methanol). ^{1}H NMR ($CDCl_3$): δ5.64 (s, 2 H), 6.98 (s, 2 H), 7.45 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ81.76, 120.61, 125.43, 142.68, 150.19. Mass spectrum m/e (relative intensity) 302 (9), 276 (19), 193 (100), 113 (46), 87 (21), 63 (25).

Adduct of 132 and Anthracene (134)

A solution of epoxide 132 (1.5 g, 5 mmol) and anthracene (1 g, 5.6 mmol) in 50 mL xylene was heated at reflux for 72 hr. The reaction mixture was cooled, and 50 mL hexane was added. A light tan solid formed which was collected and washed with hexane. Recrystallization of the solid from tetrahydrofuran and methanol gave 2.3 g (96%) small, off-white crystals, mp 265-266°C. ^{1}H NMR ($CDCl_3$): δ2.09 (s, 2 H), 4.26 (s, 2 H), 4.74 (s, 2 H), 7.02 (m, 2 H), 7.06 (m, 2 H), 7.11 (m, 6 H); ^{13}C NMR ($CDCl_3$): δ47.21, 48.45, 80.82, 123.61, 123.81, 124.17, 125.31, 125.9, 126.17, 128.17, 141.10, 143.84. Mass spectrum m/e (relative intensity) 480 (4), 462 (1), 302 (2), 289 (7), 276 (9), 203 (26), 191 (100), 178 (53).

3,4-Dibromo-[2^{b}1.1]triptycene, 135

A suspension of 134 (200 mg, 0.4 mmol) in acetic anhydride (10 mL) and concentrated hydrochloric acid (2 mL) was heated at reflux for 24 hrs. The cooled reaction mixture was poured into 200 mL ice-water, and the resulting

light brown solid was extracted with methylene chloride. The organic layer was washed successively with water and saturated sodium bicarbonate, and dried. Removal of the solvent gave a light brown residue which was recrystallized from tetrahydrofuran and methanol to give 110 mg (57%) of 135 as small, off-white crystals, mp 386-388°C (dec.). ^{1}H NMR ($CDCl_3$): δ5.50 (s, 2 H), 7.02 (m, 4 H), 7.41 (m, 4 H), 7.60 (s, 2 H), 7.93 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ53.62, 120.58, 123.84, 125.78, 131.64, 144.02, 155.16 (lacks two peaks due to quaternary carbons because of low solubility of compound).

Adduct of 135 and Furan (136)

To a stirred solution of 135 (250 mg, 0.54 mmol) and furan, 81, (2 mL) in 100 mL dry tetrahydrofuran at -78°C under argon was added n-butyllithium (2 mmol in 100 mL hexane) dropwise over two hours. The reaction mixture was allowed to come slowly to room temperature after addition. Methanol (1 mL) was added, and the mixture was extracted with methylene chloride, washed with water, dried, and the solvent removed. The remaining yellow residue was recrystallized from methanol to give 140 mg (71%) small, light yellow crystals, mp 188-190°C. ^{1}H NMR ($CDCl_3$): δ5.48 (s, 2 H), 5.72 (s, 2 H), 6.88 (s, 2 H), 7.01 (m, 4 H), 7.41 (m, 4 H), 7.65 (s, 2 H), 7.76 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ53.92, 81.88, 118.37, 121.64, 122.17, 123.70, 125.52, 125.61,

127.43, 141.75, 145.82. Mass spectrum m/e (relative intensity) 370 (1), 341 (1), 303 (1), 170 (2), 149 (4), 84 (5), 40 (100).

[3^{b}1.1]-Triptycene, 137

Deoxygenation of 136 was carried out in the same manner and scale as 10. The crude product was recrystallized from tetrahydrofuran and methanol to give 280 mg (79%) small off-white crystals, mp 221-222°C (dec). ^{1}H NMR ($CDCl_d$): δ5.53 (s, 2 H), 7.04 (m, 4 H), 7.38 (m, 2 H), 7.44 (m, 4 H), 7.87 (s, 2 H), 7.91 (m, 2 H), 8.22 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ53.65, 121.31, 123.81, 124.96, 125.61, 125.75, 127.99, 130.52, 131.69, 141.10, 144.19. Mass spectrum m/e (relative intensity) 354 (100), 353 (66), 278 (3), 176 (69).

BIBLIOGRAPHY

BIBLIOGRAPHY

1. For a review, see Hoffmann, R. W. Dehydrobenzene and Cycloalkynes, Academic Press, New York (1967).

2. Fields, E. K.; Meyerson, S. Adv. Phys. Org. Chem. 1968, 6, 18-21.

3. Wittig, G.; Harle, H. Justus Liebigs Ann. Chem. 1959 623, 17.

4. Cragg, G. M. L.; Giles, R. G. F.; Roos, G. H. P. J. Chem. Soc., Perkin I 1975, 1339.

5. Stringer, M. B.; Wege, D. Tetrahedron Lett. 1980, 21, 3832.

6. Hart, H.; Lai, C.-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. J. Am. Chem. Soc. 1980, 102, 6649.

7. Sy, A.; Hart, H. J. Org. Chem. 1979, 44, 7.

8. Hart, H.; Nwokogu, G. J. Org. Chem., 1981, 46, 1251.

9. Hart, H.; Shamouilian, S. J. Org. Chem. 1981, 46, 4874.

10. Lehoullier, C. S.; Gribble, G. W. J. Org. Chem. 1983, 48, 1682.

11. Hart, H.; Shamouilian, S.; Takehira, Y. J. Org. Chem. 1981, 46, 4427.

12. Skvarchenko, V. R.; Shalev, V. K. Dokl. Akad. Nauk. SSSR, Ser. Khim. 1974, 216, 110.

13. Cadogan, J. I. G.; Harger, M. J. P.; Sharp, J. T. J. Chem. Soc. B 1971, 602.

14. Hart, H.; Ruge, B. Tetrahedron Lett. 1977, 18, 3143.

15. van Tamelen, E. E.; Pappas, S. P. J. Am. Chem. Soc. 1962, 84, 3789.

16.

17

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16. Franck, R. W.; Mandella, W. L.; Falci, K. J. J. Org. Chem. 1975, 40, 327.

17. Maier, G.; Schnieder, K.-A. Angew. Chem. Int. Ed. Engl. 1980, 19, 1022.

18. Gusten, H.; Mintas, M. J. Am. Chem. Soc. 1980, 102, 7936.

19. Applequist, D. E.; Searle, R. J. Am. Chem. Soc. 1964, 86, 1389.

20. Pritschins, W.; Grimme, W. Tetrahedron Lett. 1979, 20, 4545.

21. Pritschins, W.; Grimme, W. Tetrahedron Lett. 1982, 23, 1151.

22. Yang, N. C.; Carr, R. V.; Li, E.; Mcvey, J. K.; Rice, S. A. J. Am. Chem. Soc. 1974, 96, 2297.

23. Cowan, D. O.; Drisko, R. L., Elements of Organic Photochemistry, Plenum Press, New York (1976), pp. 37-74.

24. Fritsche, J. J. Prakt. Chem. 1867, 101, 333; 1869 106, 274.

25. Calas, R.; Lalande, R. Bull. Soc. Chim. Fr. 1959, 763; 1959, 776; 1960, 144.

26. Chapman, O. C.; Lee, K. J. Org. Chem. 1969, 34, 4166.

27. Hart, H., unpublished results.

28. Lai, C.-Y., Ph.D. Thesis, Michigan State University, 1981.

29. Low valent titanium produced from zinc and titanium tetrachloride has been used successfully to reductively couple carbonyl compounds: Makaiyama, T.; Sato, T.; Hanna, J. Chem. Lett. 1973, 1041; and to reduce sulfoxides: Drabowicz, J.; Mikolajczyk, M. Synthesis, 1978, 138.

30. Best, W. M.; Collins, P. A.; McCulloch, R. K.; Wege, D. Aust. J. Chem. 1982, 35, 843.

31. For papers dealing with strain in 4,5-dimethylphenanthrenes, see: Frisch, M. A.; Barker, C.; Margrave, J. L.; Newman, M. S. J. Am. Chem. Soc. 1963, 85, 2356; Karnes, H. A.; Kybett, B. D.; Wilson, M. H.; Margrove, J. L.; Newman, M. S. Ibid 1965, 87, 5554

32.

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3

Dougherty, R. C.; Bertorello, H. E.; deBertorello, M. M. Org. Mass. Spectrom. 1971, 5, 1321; Allinger, N. L.; Kao, J. J. J. Am. Chem. Soc. 1977, 99, 975; Bushmelev, V. A.; Shakirov, M. M.; Derendyaev, B. G.; Koptyug, V. A. Zh. Org. Khim. 1979, 15, 1934; J. Org. Chem. USSR (Engl. Transl.) 1979, 15, 1747.

32. Jiang, J. B.-C., Ph.D. Thesis, Michigan State University, 1975.

33. Synthesized by Y. Takehira, unpublished results.

34. Bowden, B. F.; Cameron, D. W. J. Chem. Soc., Chem. Comm. 1977, 77.

35. Reduction potentials of series of anthracenes increase almost linearly with the amount of alkyl substitution regardless of the position.[36] Although there is no similar compilation of oxidation half-wave potentials, it follows that the $E_{1/2}$ would decrease similarly along the same series.

36. Klemm, L. H.; Kohlik, A. J.; Desai, K. B. J. Org. Chem. 1963, 28, 625.

37. Sullivan, P. D.; Menger, E. M.; Reddoch, A. H.; Paskovich, D. H. J. Phys. Chem. 1978, 82, 1158.

38. Nemoto, F.; Ishizu, K. Chem. Phys. Lett. 1981, 84, 44; Gerson, F.; Kaupp, G.; Ohya-Nishigichi, H. Angew. Chem. Int. Ed. Engl. 1977, 16, 657.

39. Backer, H. J.; Strating, J.; Hiusman, L. H. H. Rec. Trav. Chim. 1969, 58, 761.

40. Wittig, G.; Harle, H.; Krauss, E.; Niethammer, K. Chem. Ber. 1960, 93, 951.

41. See also: Wolthius, E. J. Org. Chem. 1961, 26, 2215; Wittig, G.; Steinhoff, G. Chem. Ber. 1962, 95, 203; Fieser, L. F.; Haddadin, M. J. J. Am. Chem. Soc. 1964, 86, 2081; Parham, M. E.; Frazer, M. G.; Bradsher, C. K. J. Org. Chem. 1972, 37, 358; Sasaki, T.; Kanematsu, K.; Hayakawa, K. J. Chem. Soc., Perkin I, 1972, 1951; Sasaki, T.; Kanematsu, K.; Hayakawa, K.; Uchide, M. Ibid 1972, 2750; Wittig, G.; Reuther, W. Liebigs Ann. Chem. 1972, 761, 20; Sasaki, T.; Kanematsu, K.; Hayakawa, K.; Kondo, A. J. Org. Chem. 1973, 38, 4100; Bremmer, J. B.; Hwa, Y.; Whittle, C. P.; Aust. J. Chem. 1974, 27, 1597; Sasaki, T.; Kanematsu, K.; Iizuka, K.; Ando, I. J. Org. Chem. 1976, 41, 1425;

Sasaki, T.; Kanematsu, K.; Iizuka, K.; Izumichi, N. Tetrahedron 1976, 32, 2879; Tochtermann, W.; Malchow, A.; Timm, H. Chem. Ber. 1978, 111, 1233; Mori, M.; Hayamizu, A.; Kanematsu, K. J. Chem. Soc., Perkin I 1981, 1259.

42. Independent results by N. Raju.

43. Hart, H.; Ok, D., unpublished results.

44. Lipczynska-Kochany, E.; Iwamura, H. Chem. Lett. 1982, 1075.

45. Godfrey, R. J. Chem. Soc., Perkin II, 1978 1019.

46. Attempts in this laboratory to synthesize 141 have to date failed! A report in the literature claiming to have made 2-amino-4,5-dibromobenzoic acid (from which 141 can be made) by direct bromination of anthranilic acid is in error.[47]

47. J. Indian Chem. Soc. 1979, 56, 1237.

48. Sarauw, Justus Liebigs Ann. Chem. 1878, 209, 125.

49. Nwokogu, G. Ph. D. Thesis, Michigan State University, 1981.

50. Sala, T.; Sargent, M. V. Chem. Commun. 1978, 253; Morris, J. A.; Mills, D. C. Chem. Brit. 1978, 326.

51. McOmie, W. F. W.; Harrisons, C. R. J. Chem. Soc. (C) 1966, 997.

52. Scheufelen, A. Justus Liebigs Ann. Chem. 1885, 231 152; Cox, B.; Kubler, D. G.; Wilson, C. A. J. Chem. Educ. 1977, 54, 379.

53. Shamouilian, S., Ph. D. Thesis, Michigan State University, 1981.

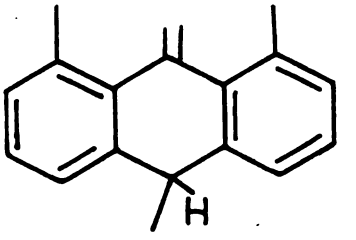
54. McDonald, E.; Suksamrarn, A.; Wylie, R. J. Chem. Soc., Perkin I, 1972, 1893.

55. Iten, P.; Hofmann, A.; Eugster, C. Helv. Chim. Acta, 1978, 61, 430.

56. Meyer, K. H. Liebigs Ann. Chem. 1911, 379, 37.

57. Attempts to synthesize 88 by another group failed.[34] The authors reported that they were only able to

isolate tautomer 115.



115

Tautomer 115 (20%) was detected by NMR in crude 88 in the method of synthesis reported here.

58. Underwood, H. W.; Baril, O. L.; Toone, G. C. J. Am. Chem. Soc. 1930, 52, 4087.

59. Boldt, P. Chem. Ber. 1967, 100, 1270.