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TETRAHALOBENZENES AS DI-ARYNE EQUIVALENTS IN POLYCYCLIC ARENE SYNTHESIS

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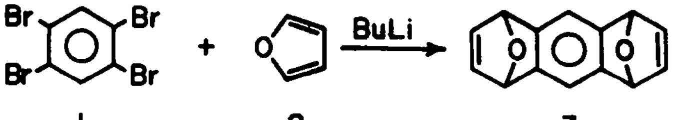
ABSTRACT: *1,2,4,5-Tetrabromobenzenes and analogous naphthalenes react with one or two equivalents of n-butyllithium and various dienes (furans, pyrroles, cyclopentadienes, fulvenes) to form mono- or bis-cycloadducts. Highly substituted arenes can be obtained by removing the oxygen or nitrogen bridges from the furan or pyrrole adducts. By choice of conditions, two identical or two different rings can be fused to the di-aryne equivalent. Improved short syntheses of permethylnaphthalene, -anthracene and -naphthacene are described. A new triphenylene synthesis is presented.*

INTRODUCTION

1,2,4,5- and 1,2,3,4-Tetrahalobenzenes can be used as 1,4- and 1,3-benzadiyne equivalents, respectively. During the past several years, we have described three ways in which such intermediates can be synthetically useful: (1) through cycloadditions to furans or pyrroles, followed by elimination of the oxygen or nitrogen bridges, they can be used to prepare highly substituted arenes of the anthracene or phenanthrene type;[1] (2) through cycloadditions to anthracenes or other dienes, they can provide short routes to iptycenes;[2] (3) through regioselective addition of carbon nucleophiles, they can be used to synthesize *m*- and *p*-terphenyls, as well as other highly substituted aryl, vinyl and ethynyl benzenes.[3]



1 **2** **3**

Although experimental details have been described in full for most of our efforts in the second and third of the above categories, we have neglected to describe those details for many of our results in the first category. It is the purpose of this paper to provide those details for the examples listed in our preliminary communication,[1b] and for a number of related previously unpublished arene syntheses.

RESULTS AND DISCUSSION

Cycloadditions to Furans

1,2,4,5-Tetrabromobenzene reacts with excess furan and *n*-butyllithium (BuLi) to give an excellent yield of the syn- and anti-bis-adducts 3.[2b,4] By using substituted 1 and 2, a variety of

Table I Bis-Adducts from Tetrahaloarenes and Furans

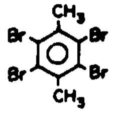
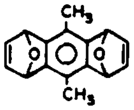
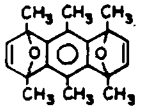
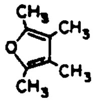
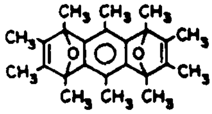
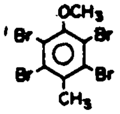
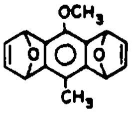
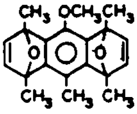
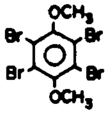
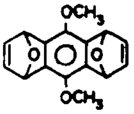
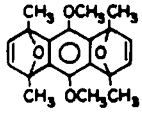
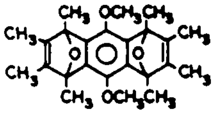
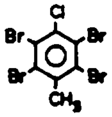
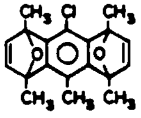
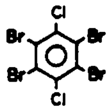
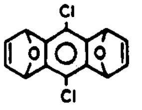
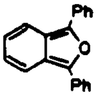
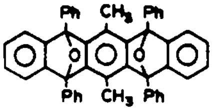
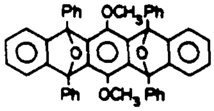
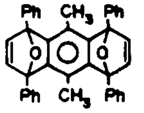
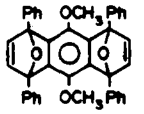
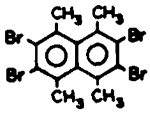
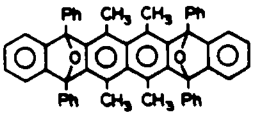
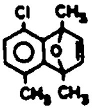
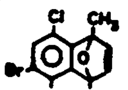
Tetrahalo-arene	Furan	Adduct (anti/syn)	Yield, %^{a} (solvent)^b	mp, °C^c
1	2	3[2b]	65(T)	245 (anti) 191-193 (syn)
 4	2	 5 (50/50)	89(T)	(205-265)
4	 6	 7 (57/43)	73(E), 93(T)	283-284 (anti)
4	 8	 9 (64/36)	57(E), 78(T)	(264-274)
 10	2	 11 (50/50)	87(THF)	220-222
10	6	 12	56(E), 71(T)	172-173
 13	2	 14[19]	86(THF)	203-205
13	6	 15	72(THF)	(270-277)
13	8	 16 (60/40)	78(THF)	(280-290)
 17	6	 18	>16(THF)^d	253-256

Table I. Bis-Adducts from Tetrahaloarenes and Furans continued:

 19[17]	2	 20	6(THF)	227-231
4	 21	 22	67(T)	>360
13	21	 23	42(T)	355-357
4	 24	 25	52(T)[g]	320-321
13	24	 26	50(T)[e,f]	303-305
 27[1a]	21	 28	82(T)	357-358

[a] Combined yield for syn and anti isomers. [b] E=ether, T=toluene, THF=tetrahydrofuran. [c] mp range in ( ) is for the syn/anti mixture; other mp's are for one pure isomer. [d] Mono-adducts  and  were also formed. [e] 20% and 71% of 24 was recovered, respectively, in the preparation of 25 and 26; yields are based on consumed 24. [f] 9% of reduced mono-adduct (5,8-dimethoxy-1,4-diphenyl-1,4-dihydronaphthalene-1,4-endoxide), mp 182-184°C, was also isolated.

substituted analogs of 3 have been prepared (Table 1). Except for 3, 5 and 14, all of the adducts listed are new. Their structures were clear from the method of synthesis, from spectra (given in the experimental section), and in some cases from their deoxygenation to substituted anthracenes.[1c]

The bis-cycloadducts were usually obtained as a syn/anti mixture. In some instances, one of the isomers (usually the major isomer, and most likely the less soluble anti-isomer) crystallized from the reaction mixture or from chromatography. X-ray structures of the predominant isomer of 3[9b] and 7 (Figure 1) showed that the oxygens were anti.

In the two examples with low yields (18, 20), considerable polymeric product, as well as some

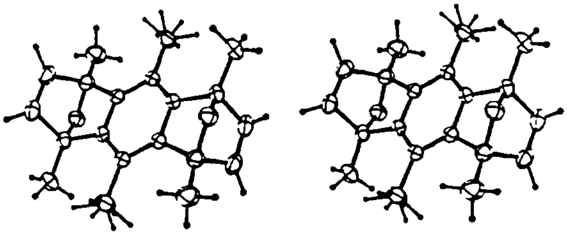
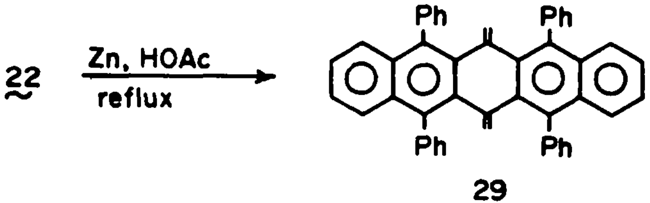


Figure 1. Stereodrawing of anti-7 (the hydrogens on the aryl methyl groups are disordered).

mono-adduct, was formed. Another contaminant, in all cases, can result from addition of BuLi to the aryne intermediates; this type of by-product is usually minimized in toluene (vis-a-vis ether or THF).

Deoxygenation of certain of these bis-endoxides (*i.e.*, 5, 7, 14 and 15) to the corresponding anthracenes with low-valent transition metals (Fe, W, Ti) was highly successful as reported earlier.[1c] In some cases (*i.e.*, 9), however, deoxygenation was incomplete or accompanied by side reactions, and in others (*i.e.*, 15, 16), methoxyls were also removed. Attempts to deoxygenate 22 with low-valent iron[1c] gave recovered starting material. With zinc in refluxing acetic acid, however, 22 gave the stable quinonedimethide 29 in quantitative yield. This product was



29

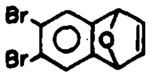
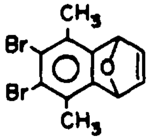
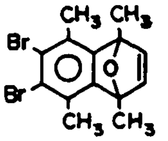
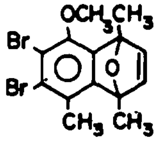
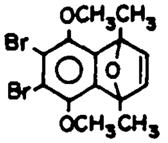
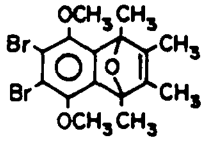
characterized by its spectra, particularly the vinyl proton singlet at δ 4.86. With the same reagent, the dimethoxy analog 23 gave what appeared to be the expected pentacene in high yield, though purification of the blue-green product proved difficult due to its high reactivity with air.

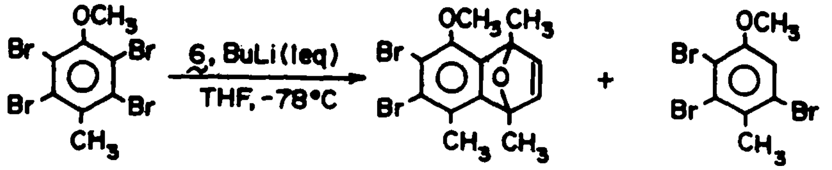
Mono-cycloadducts from Tetrahalobenzenes and Furans

It may be desirable, on occasion, to carry out the two cycloadditions to a 1,4-benzadiyne equivalent stepwise so that, instead of obtaining product with two identical appended rings (Table 1), the two rings can be different. This goal can be achieved by using only one equivalent each of BuLi and furan, but the choice of solvent may be critical for a given tetrahaloarene. For example, treatment of 1 or 4 with one equivalent each of furan and BuLi in ether or THF as solvent gave only bis-adduct (and recovered tetrahaloarene). This result can be attributed to the low solubility of 1 and 4 in oxygenated solvents at low temperatures, and the considerably greater solubilities of the mono-cycloadducts, which are consequently selectively metalated.

These difficulties can be overcome in either of two ways. If the tetrahaloarene carries solubilizing substituents, mono-adducts can be obtained, even in oxygenated solvents. For example, treatment of 10 and 6 with 1 eq. of BuLi in THF at -78°C gave, after workup, 42% of mono-adduct 30 (and an equal yield of 31, from proton quench of the intermediate lithio compound[8]). Similarly, 13

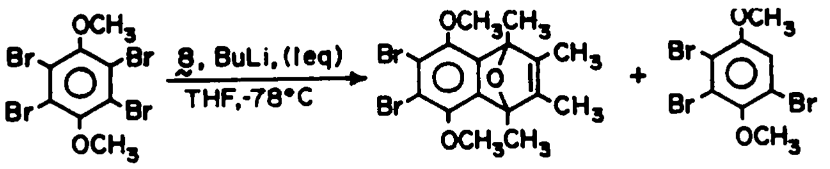
Table 2. Mono-adducts from Tetrahalobenzenes and Furans

Tetrahalo-benzene	Furan	Mono-adduct	Yield, %	mp, °C
1	2	 34[2c]	70	115-117
4	2	 35	75	155-157
4	6	 36	98	146-147
10	6	 30	53	149-151
13	6	 37	44	162-165
13	8	 32	51	94-96



10 30 (42%) 31 (42%)

and 8 gave mono-adduct 32.


13
32 (51%)
33 (35%)

A more general solution to monoadduct formation is to use the less polar toluene as a solvent. Table 2 shows examples of mono-adducts prepared in this way. Except for 34[2c] and 36, the yields were not optimized and can probably be improved. The structures of the mono-adducts are based on their spectra. An example of their use to fuse two differently substituted rings to a given tetrahalobenzene is given later in this paper.[6]

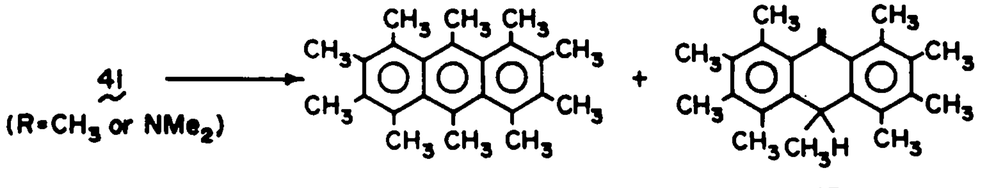
Cycloadditions to Pyrroles

One use to which bis-cycloadditions of furans to di-aryne equivalents can be put is the synthesis of highly substituted arenes with multiple peri-interactions (for example, the synthesis of 1,4,5,8,9,10-hexamethylanthracene by deoxygenation of 7[1c]). Sometimes, however, deoxygenation is accompanied by undesired side-reactions.[1c] This difficulty may be overcome by using 1,4-imines in place of 1,4-endoxides, nitrogen bridge removal being accomplished by oxidation[7] or pyrolysis.[8] Consequently, we carried out a number of bis-cycloadditions of N-substituted pyrroles to 1,4-benzadiyne equivalents (Table 3).

The reactions were generally carried out by adding BuLi (usually in hexane, but in some cases in THF or ether) at -78°C to a 1:2 mixture of the tetrahaloarene and pyrrole in toluene, followed by warming to room temperature and workup. The products were anti/syn mixtures from which the predominant isomer could usually be obtained pure through trituration, crystallization or chromatography.

Although cycloaddition was successful for phenyl-substituted pyrroles 42 and 44, it failed with *N*-methyl-2,5-diphenylpyrrole and with *N*-methyl-tetraphenylpyrrole. These failures appear to be a consequence of electronic rather than steric factors. The bulk of the R group on nitrogen (see compounds 41) has only a slight effect on the cycloaddition yield.

Some of the bis-adducts in Table 3 were converted to the corresponding fused-ring arenes by removal of the nitrogen bridges. For example, oxidation of 43 (R=CH_3) with *m*-chloroperbenzoic acid (*m*-CPBA)[9] or pyrolysis or *m*-CPBA oxidation of 41 (R=NMe_2) gave decamethylanthracene 52[10]


52
53

contaminated with varying amounts of its 9-methylene-9,10-dihydro isomer 53 (see experimental for details). The best method allows a two-step 46% overall yield synthesis of 52 from readily

Table 3. Bis-Adducts from Tetrahaloarenes and Pyrroles

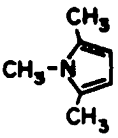
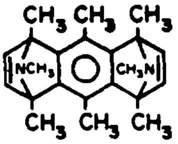
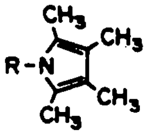
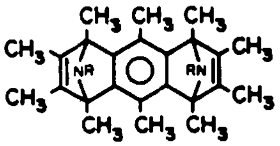
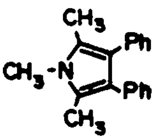
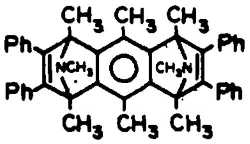
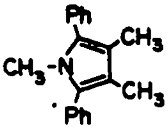
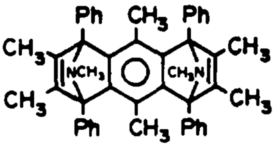
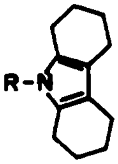
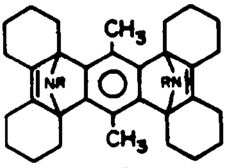
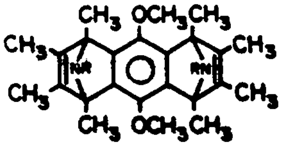
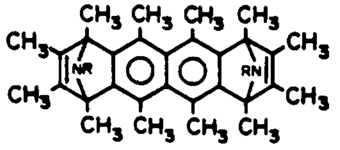
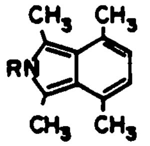
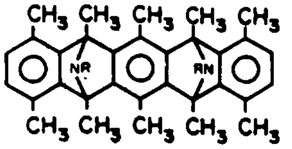
Tetrahalo-arene	Pyrrole	Adduct (anti/syn)	Yield, %[a]	mp, °C[b]
4	 38	 39 (73/27)	73	242-244
4	 40	 41 (R=CH_3)	79	256-258
		(R=n-Bu)	64	204-205
		(R=iPr)	65	243-245
		(R=Bn)	61	268-270
		(R=Ph)	51	293-294
		(R=NMe_2)	33	203-206
			31	190-191
4	 42	 43	59	230-232
4	 44	 45	57	270-271
4	 46		76[d]	282-284
		47 (R=CH_3)	76[d]	282-284
		(R=NMe_2)	37[e]	155-163[c] (dec)
13	40 (R=NMe_2)	 48	69[d]	166-169

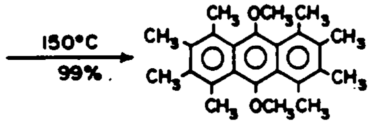
Table 3 Bis-Adducts from Tetrahaloarenes and Pyrroles continued:

Tetrahalo-arene	Pyrrole	Adduct (anti/syn)	Yield, %[a]	mp, °C[b]
27	40 (R=NMe$_2$)	 49	62[d]	180-182
4	 50 (R=NMe$_2$)	 51	56	285-286

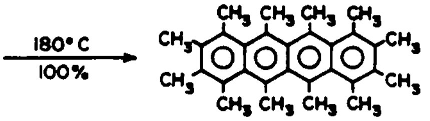
[a] Combined yield for syn and anti isomers, except for 41 (R=NMe$_2$), where both isomers were isolated pure; the solvent was toluene and, except where noted, the BuLi was in hexane. [b] Mp is for one pure isomer. [c] Becomes yellow and is converted to the corresponding anthracene, which melts at 367-369°C. [d] BuLi in THF. [e] BuLi in ether.

available starting materials, a substantial improvement over our first 7-step 8% overall route from 4,7-dimethylisatin.[10]

When the methyl groups in the central ring of 41 are replaced by methoxyls, the isomerization problem is avoided. Thus, pyrolysis of 48 gave a quantitative yield of 54, whose ^{1}H NMR spectrum showed only three methyl singlets at δ 2.38, 2.76 and 3.33 (areas 12:12:6).

48 

54

49 

55

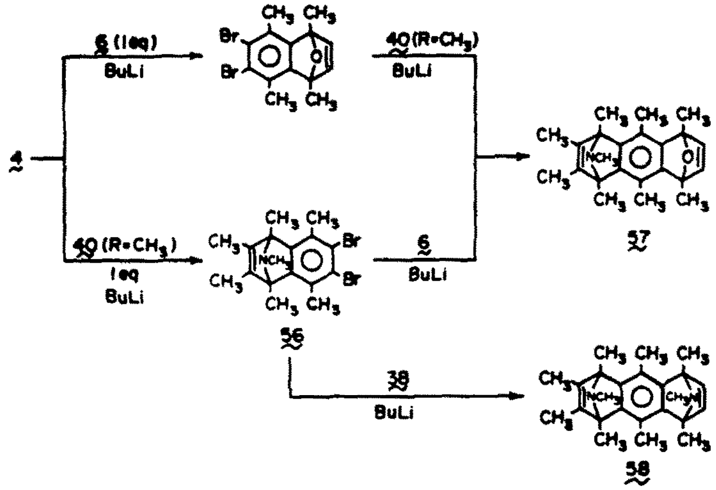
Pyrolysis of 49 at 180°C similarly gave the known[1a] dodecamethylnaphthacene 55. This 2-step synthesis of 55 (overall yield 62%) from 27 and 40 (R=NMe$_2$) represents a substantial improvement over the original procedure[1a] (8% overall). It is noteworthy that isomerization is not a problem in this synthesis of 55, whereas it is in the synthesis of 52.

Analogous attempts to aromatize 51 (R=NMe$_2$) were not entirely successful. Although the pyrolysis appeared to proceed, the insolubility of the product prevented its complete characterization.

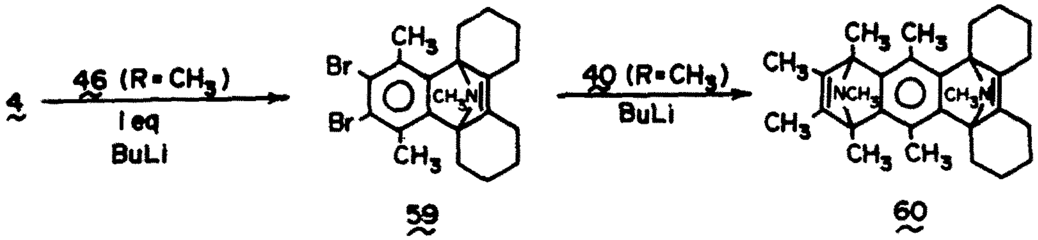
Stepwise Bis-annulations

Stepwise cycloaddition to a 1,4-benzadiyne equivalent allows annulation with two differently substituted arene rings. To illustrate this methodology, the following examples were carried out.

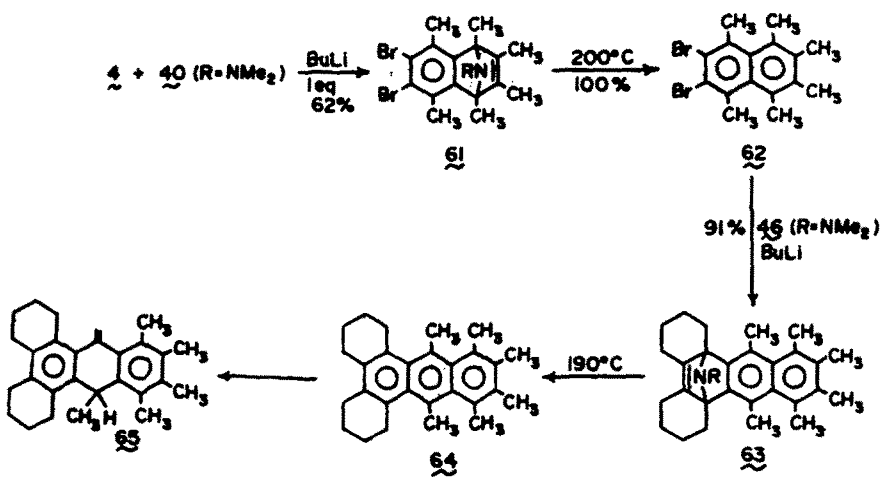
Mono-adduct 36 (Table 2) reacted with 1 eq. of 40 (R=CH$_3$) and BuLi to give the mixed di-adduct 57 in 42% yield. The same mixed adduct was obtained via 56 by performing the two cycloadditions in the reverse order. The syn/anti ratio in 57 was similar but not identical for the two paths. The imine analog of 57 (*i.e.*, 58) was similarly obtained via 56.



The unsymmetric di-adduct 60 was similarly prepared by stepwise annulation of 4.



Mono-adducts may be aromatized prior to the second cycloaddition. For example, mono-adduct 61 was converted quantitatively at 200°C to dibromohexamethylnaphthalene 62. This two-step synthesis



of 62 (overall > 60%) is superior to an earlier route[10] (6 steps, 39% from 4,7-dimethylisatin). A second cycloaddition, now with pyrrole 46 (R=NMe$_2$) affords 63 in 91% yield. Pyrolysis of 63 gave 64 in nearly quantitative yield, but the product could not be obtained pure due to facile isomerization to 65. Compound 64 seems to be more susceptible than 52 to this type of dearomatization. Thus, treatment of 64 with a trace of trifluoroacetic acid gave 65 (room temperature, 5 min, 100%).

Table 4 Aryne Adducts of Various Dienes

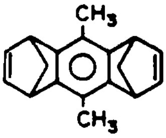
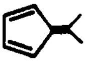
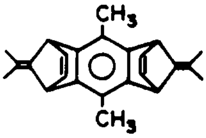
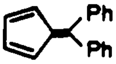
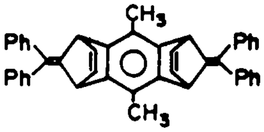
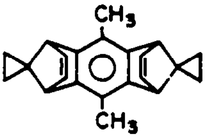
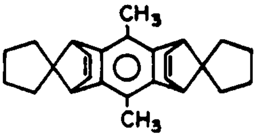
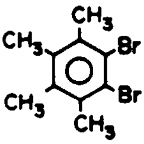
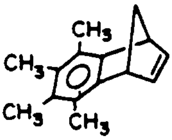
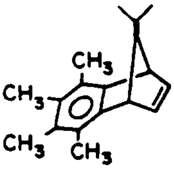
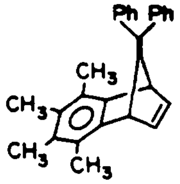
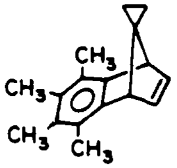
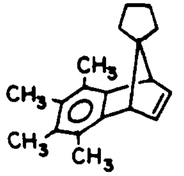
Aryne Equivalent	Diene	Adduct	Yield, % (solvent)[a]	mp,°C
4	 66	 71	97 (E)	105-107
4	 67	 72	70 (THF)	270-272
4	 68	 73	36 (THF)	>350
4	 69	 74	80 (T)	223-225
4	 70	 75	58 (T)	222-225
 76	66	 77	97 (E)	50-52
76	67	 78	57 (THF)	96-98

Table 4 Aryne Adducts of Various Dienes continued

Aryne Equivalent	Diene	Adduct	Yield, % (solvent)[a]	mp,°C
76	68	 79	62 (THF)	177-178
76	69	 80	52 (T)	106-107
76	70	 81	73 (T)	95-97

[a] E=ether, THF=tetrahydrofuran, T=toluene.

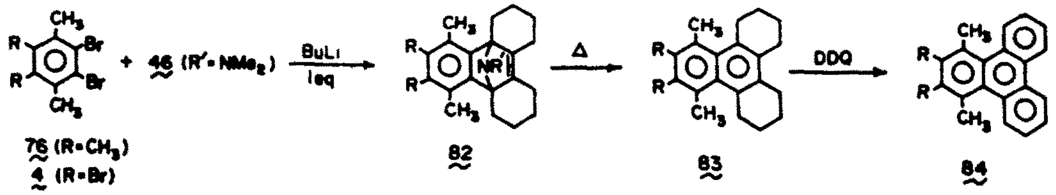
Other Aryne Cycloadditions

Dienes other than furans and pyrroles have also been added to 1,4-benzadiyne equivalent 4. Examples are given in Table 4, which also includes analogous tetramethyl mono-aryne adducts 77-81, derived from 76 and BuLi as the tetramethylbenzyne source. As previously, bis-adducts 71-75 were usually a mixture of syn/anti isomers, though one of the two isomers (mp given) often predominated and was easily isolated in pure crystalline form via chromatography. The structures of the cycloadducts are based on their method of synthesis and spectra.

Mechanistic experiments showed that cyclopentadiene itself, and not the cyclopentadienide anion, cycloadds to the aryne intermediates from 4. For example, treatment of diyne equivalent 4 (1 eq) and cyclopentadiene (2 eq) in ether at -78°C with BuLi (2 eq) gave a nearly quantitative yield of bis-cycloadduct 71. When the amount of BuLi was increased to 4 eq (presumably converting some of the cyclopentadiene to its anion), the yield of 71 dropped to 37%. Finally, when equimolar amounts of cyclopentadiene and BuLi were first allowed to react completely at -78°C (the cyclopentadienide precipitates from solution), followed by successive addition of 4 (2 eq) and BuLi (2 more eq), workup gave only polymeric product and dicyclopentadiene; no 71 was formed. These results also suggest that when the reaction is carried out in the usual way, BuLi undergoes metal-halogen exchange with the diyne equivalent faster than it abstracts a proton from cyclopentadiene.

Miscellaneous Results

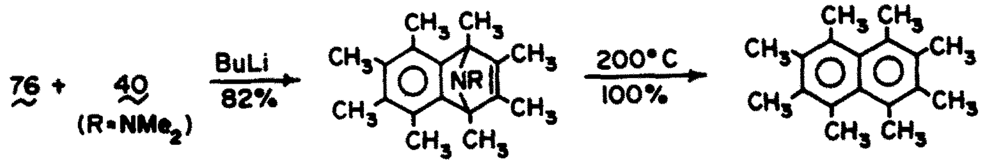
A new triphenylene synthesis was developed, using aryne technology. Treatment of 76 with octahydrocarbazole derivative 46 (R′=NMe₂) and 1 eq of BuLi gave adduct 82 (62%) which, on heating



76 (R=CH₃)
4 (R=Br)
82
83
84

to 250°C, gave naphthalene 83 (R=CH₃) in quantitative yield. Dichlorodicyanoquinone (DDQ) dehydrogenation of 83 gave triphenylene 84 (R=CH₃) in 68% yield. A similar sequence starting with 4 gave 84 (R=Br) in 55% overall yield for the three steps. The two bromine substituents in 84 (R=Br) could of course be used to further elaborate the triphenylene framework.

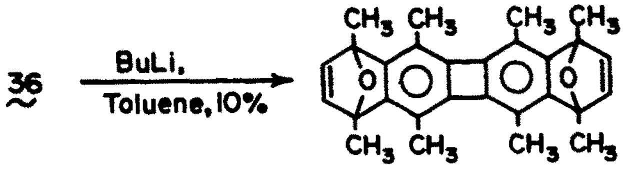
A new octamethylnaphthalene synthesis was also developed, taking advantage of the pyrolytic aromatization of *N*-dimethylaminopyrrole cycloadducts. Thus, treatment of 76 with 40 (R=NMe₂) and BuLi gave in 82% yield the adduct 85 which was quantitatively pyrolyzed to 86. This two-step route



85
86

is somewhat better than our previous route,[11] which used 40 (R=CH₃) and *m*-CPBA oxidation for the second step (overall 65%).

Finally, we call attention to the possibility that mono-cycloadducts of benzadiyne equivalents, because of the presence of two remaining bromines, are potential biphenylene precursors. The conversion of 62, for example, to the corresponding biphenylene has already been described.[11] This reaction type may even be performed with the adducts themselves, prior to bridge elimination. For example, although the yield is low, mono-adduct 36 (Table 2) was converted to biphenylene 87 with retention of the endoxide functionality.



87

To summarize, tetrahaloarenes function as useful di-aryne equivalents. Cycloadditions with furans, pyrroles and other dienes proceed in good to excellent yields, allowing one to readily mono- or bis-annulate an existing arene ring. Since the intermediates (arynes) are high-energy species, the cycloadditions are exothermic and, hence, allow one to prepare a variety of sterically strained compounds easily and efficiently.

EXPERIMENTAL

General Procedures

^1H NMR spectra were measured in $CDCl_3$ unless otherwise stated, using $(CH_3)_4Si$ as an internal standard, on a Varian T-60 or Bruker WM-250 spectrometer and are given in δ units. ^{13}C NMR spectra were determined on a Varian CFT-20 spectrometer. IR spectra were determined on a Perkin Elmer Model 167 spectrometer, UV spectra on a Unicam SP-800, Cary 219 or Cary-1756 spectrometer, and mass spectra on a Finnigan 4000 spectrometer with the INCOS data system. High resolution mass spectra were obtained on a Varian CH5 spectrometer. Melting points, taken on a Thomas Hoover Unimelt or Fisher Electrothermal MP apparatus, are uncorrected. Analyses are by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Tetrabromo-*p*-xylene (4)[12]

To a solution of *p*-xylene (21 g, 0.23 mol) in 100 mL of CCl_4 was added, dropwise at rt with stirring, 6 eq of bromine. After overnight reflux, satd. aq. $NaHSO_3$ was added to the cooled mixture to decolorise the excess bromine. The precipitate was recrystallised from chloroform-methanol to give 79.5 g (94%) of 4, mp 249-251°C (lit[12] 251-252°C); ^{1}H NMR: δ 2.78 (s).

2,3,5,6-Tetrabromo-4-methoxytoluene (10)[13]

p-Cresol (20 g, 0.185 mol) was added dropwise to 60 mL (1.16 mol) of bromine containing 1 g Fe filings at room temperature. Small portions of $CHCl_3$ were added from time to time to permit stirring. After 6 h, HBr evolution subsided. The residue was dissolved in hot $CHCl_3$, washed successively with aq. $NaHSO_3$, $NaHCO_3$ and evaporated to give 73 g (93%) of tetrabromo-*p*-cresol, mp 195-196°C (lit[14] 196°C).

Potassium hydroxide (10 g) in 50 mL of H_2O was added to 32.3 g of tetrabromo-*p*-cresol and the hot suspension was treated with 20 g of dimethyl sulfate. Chloroform (20 mL) was added to the resulting milky-white cake, and the mixture was stirred for 6 h at rt, then heated at reflux for 4 h. Cooling, extraction with $CHCl_3$ and evaporation of the extract to dryness gave 32.5 g (97%) of 10 as white needles, mp 136-138°C (lit[13] 135°C).

2,3,5,6-Tetrabromo-1,4-dimethoxybenzene (13)

A suspension of 2,5-dibromo-1,4-dimethoxybenzene[15] (29.6 g, 0.1 mol) and 48 g of Br_2 in CCl_4 (50 mL) containing 0.5 g of I_2 was heated overnight at reflux. Excess bromine was destroyed with aq. $NaHSO_3$. The precipitate was recrystallized from chloroform-methanol to give 37.4 g (83%) of 13, mp 193-195°C (lit[16] 194°C). ^{1}H NMR: δ 3.76 (s).

2,3,5,6-Tetrabromo-4-chlorotoluene (17)

4-Chlorotoluene (10.5 g, 83.3 mmol) was added dropwise at rt over 15 min to 50 mL (0.97 mol) of bromine containing 2 g of Fe filings. When HBr evolution subsided (6 h), the excess Br_2 was destroyed by successive washing with aq $NaHSO_3$ and $NaHCO_3$. The solid was extracted with $CHCl_3$, dried and evaporated to give 26.4 g (72%) of 17, mp 264-265°C. ^{1}H NMR: δ 2.77 (s); mass spectrum, *m/e* (rel. intensity) 442 (31), 363 (29), 203 (55), 122 (57), 87 (100). *Anal.* Calcd for $C_7H_3Br_4Cl$: C, 19.01; H, 0.68. Found: C, 19.05; H, 0.68.

Typical Procedure for Bis-Cycloaddition of Furans (Table 1). 1,4,5,8,9,10-Hexamethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-bis-endoxide (7)

To a suspension of 4 (4.22 g, 10 mmol) and 2,5-dimethylfuran (6) in toluene (100 mL) at -78°C, under argon was added dropwise 11 mL (22 mmol) of BuLi (2M in hexane) that had been further diluted with 100 mL of hexane. After stirring for 2 h at -78°C, the mixture was allowed to warm slowly to room temperature and was quenched with methanol (1 mL), then water. The organic layer was dried ($MgSO_4$) and evaporated. Trituration of the crude product with hexane gave 2.79 g (93%) of 7 as an anti/syn mixture (57:43 by NMR). Successive washing with ether gave pure anti-7, mp 283-284°C. Alternatively, chromatography over neutral alumina (Activity II) was used to purify the product. ^{1}H NMR: δ 1.94 (s, 12 H), 2.29 (s, 6 H), 6.78 (s, 4 H); mass spectrum, *m/e* (rel. intensity) 294 (9), 251 (37), 225 (81), 209 (22), 193 (21), 178 (26), 43 (100). *Anal.* Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.51; H, 7.50. The anti/syn mixture had the following spectra: ^{1}H NMR: δ 1.94, 1.96 (s, 12 H), 2.29, 2.34 (s, 6 H), 6.79 (br s, 4 H); ^{13}C NMR: δ 13.81 and 14.39, 18.69 and 19.00, 89.44 and 89.73, 121.72 and 122.09, 147.46, 149.74 and 150.09.

With ether in place of toluene, the yield of 7 was 2.19 g (73%). With only 10 mmol of BuLi and ether as the solvent, there was obtained 3.26 g of crude product. Chromatography (alumina; hexane eluent) gave 1.35 g (32%) of recovered 4. Further elution (3:1 hexane:CH_2Cl_2) gave 1.58 g (47%) of 7; no monoadduct 36 was formed.

Spectroscopic Properties of Furan Bis-adducts (Table 1)

For 5[19] (s/a mixture): mp (dec) 205-265°C (lit[18] 210-300); ^{1}H NMR: δ 2.239, 2.245 (s, 6 H), 5.701, 5.704 (s, 4 H), 7.022, 7.027 (s, 4 H); ^{13}C NMR: δ 14.56, 81.15, 121.44 and 121.63, 143.39 and 143.25, 146.46; mass spectrum, *m/e* (rel. intensity) 238 (M^+, 28), 212 (11), 183 (100), 165 (51), 152 (24).

For 9 (s/a mixture): ^{1}H NMR: δ 1.598, 1.667 (s, 12 H), 1.866, 1.832 (s, 12 H), 2.356, 2.302 (s, 6 H); ^{13}C NMR: δ 10.84 and 10.88, 14.21 and 15.14, 17.23 and 17.58, 89.46 and 89.89, 120.50 and 121.08, 145.40 and 145.80, 149.56 and 150.00; UV ($CDCl_3$) λ_{max} (ε) 257 nm (993), 290 (978); mass spectrum, *m/e* (rel. intensity) 350 (M^+, 18), 308 (22), 296 (24), 264 (53), 253 (100). *Anal.* Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.28; H, 8.53.

For 11 (s/a mixture): ^{1}H NMR: δ 2.214, 2.228 (s, 3 H), 3.855, 3.866 (s, 3 H), 5.673 (br s, 2 H), 5.888 (br s, 2 H), 7.016 (br s, 4 H); ^{13}C NMR: 14.34, 59.74 and 60.03, 80.82, 81.11, 118.64 and

118.43, 135.64 and 135.52, 142.98 and 143.34, 143.17, 146.58, 149.39; mass spectrum, *m/e* (rel. intensity) 254 (M$^+$, 15), 228 (6), 199 (100), 183 (45), 167 (37), 152 (37). *Anal.* Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.73; H, 5.48.

For 12 (s/a mixture): ^{1}H NMR: δ 1.955 (s, 6 H), 1.971 (s, 6 H), 2.310, 2.361 (s, 3 H), 3.588, 3.672 (s, 3 H), 6.835 (br s, 4 H); mass spectrum, *m/e* (rel. intensity) 310 (M$^+$, 8), 267 (33), 241 (84), 225 (100). *Anal.* Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.32; H, 7.17.

For 14[19]: ^{1}H NMR (one isomer): δ 3.77 (s, 6 H), 5.72 (s, 4 H), 6.87 (s, 4 H); ^{13}C NMR (s/a mixture): δ 60.61 and 60.31, 80.77, 138.72, 142.97 and 143.15, 145.97 and 144.12; mass spectrum, *m/e* (rel. intensity) 270 (M$^+$, 43), 215 (100), 199 (77), 183 (25), 139 (30).

For 15: ^{1}H NMR: δ 1.981 (s, 12 H), 3.676 (s, 6 H), 6.840 (s, 4 H); mass spectrum, *m/e* (rel. intensity) 326 (M$^+$, 8), 283 (47), 257 (100), 241 (92), 227 (26). *Anal.* Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.70; H, 6.82.

For 16 (s/a mixture): ^{1}H NMR: δ 1.681, 1.728 (s, 12 H), 1.882, 1.861 (s, 12 H), 3.751, 3.696 (s, 6 H); mass spectrum, *m/e* (rel. intensity) 382 (M$^+$, 6), 339 (22), 328 (15), 296 (58), 285 (100). *Anal.* Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.51; H, 7.87.

For 18: ^{1}H NMR (one isomer): δ 1.966 (s, 6 H), 2.015 (s, 6 H), 2.399 (s, 3 H), 6.769-6.824 (AB q, 4 H); mass spectrum, *m/e* (rel. intensity) 314 (M$^+$, 7), 271 (22), 245 (90), 229 (96), 43 (100); High resolution mass spectrum: Calcd for $C_{19}H_{19}ClO_2$: 314.1062. Found: 314.1074.

For 20: ^{1}H NMR (one isomer): δ 5.57 (s, 4 H), 6.93 (s, 4 H); mass spectrum, *m/e* (rel. intensity) 278 (M$^+$, 30), 252 (18), 223 (70), 189 (100), 152 (63). *Anal.* Calcd for $C_{14}H_8Cl_2O_2$: C, 60.24; H, 2.89. Found: C, 60.13; H, 2.90.

For 22 (one isomer): ^{1}H NMR: δ 1.40 (s, 6 H)[20], 6.73-7.83 (m, 28 H); ^{13}C NMR: δ 17.43, 91.67, 122.01, 124.65, 126.46, 128.59, 128.80, 129.01, 129.63, 134.95, 150.31, 150.53, 150.92; mass spectrum, *m/e* (rel. intensity) 642 (M$^+$, 11), 537 (21), 432 (82), 340 (15), 105 (100). High resolution mass spectrum: Calcd. for $C_{48}H_{34}O_2$: 642.2617. Found: 642.2607.

For 23 (one isomer): ^{1}H NMR: δ 2.66 (s, 6 H)[20], 6.9-8.0 (m, 28 H); ^{13}C NMR: δ 60.93, 91.37, 121.64, 125.64, 128.05, 128.38, 128.61, 129.14, 129.39, 134.34, 144.22, 145.41, 150.91; mass spectrum (CI) 675 (M$^+$+1). High resolution mass spectrum: Calcd for $C_{41}H_{29}O_3$ (M$^+$-C_7H_5O): 569.2117. Found: 569.2055.

For 25 (one isomer): ^{1}H NMR: δ 1.03 (s, 6 H)[20], 7.16 (s, 4 H), 7.17-7.66 (m, 20 H); ^{13}C NMR: δ 14.67, 94.29, 124.10, 127.96, 128.29, 128.53, 137.13, 144.47, 150.66; mass spectrum, *m/e* (rel. intensity) 542 (M$^+$, trace), 527 (trace), 437 (2), 105 (100), 77 (12). High resolution mass spectrum: Calcd for $C_{40}H_{30}O_2$: 542.2245. Found: 542.2247.

For 26 (one isomer): ^{1}H NMR: δ 1.96 (s, 6 H)[20], 7.0-7.6 (m, 24 H); mass spectrum, *m/e* (rel. intensity) 574 (M$^+$, trace), 469 (42), 443 (14), 364 (8), 105 (100). High resolution mass spectrum: Calcd for $C_{33}H_{25}O_3$ (M$^+$-C_7H_5O): 469.1804. Found: 469.1784.

For 28 (one isomer): ^{1}H NMR: δ 2.13 (s, 12 H), 6.9-7.8 (m, 28 H); ^{13}C NMR: δ 22.97, 92.29, 121.63, 125.98, 127.67, 127.95, 128.74, 129.01, 129.69, 135.21, 149.43, 149.66; mass spectrum, *m/e* (rel. intensity) 720 (M$^+$, 3), 615 (8), 600 (2), 510 (5), 105 (100), 77 (23). High resolution mass spectrum: Calcd for $C_{54}H_{40}O_2$: 720.3028. Found: 720.3008.

5,7,12,14-Tetraphenyl-6,13-bis-methylene-6,13-dihydropentacene (29).

A suspension of 22 (200 mg) and zinc dust (4 g) in glacial acetic acid (100 mL) was heated at reflux for 6 h. After cooling and solvent removal (rotavap), the organic product was dissolved in chloroform (100 mL), washed with water and dried ($MgSO_4$). Concentration of the solution deposited 190 mg (100%) of 29 (starts to sublime at 240°C, melts on rapid heating at 270-272°C). ^{1}H NMR: δ 4.86 (s, 4 H), 7.0-7.40 (m, 28 H); mass spectrum, *m/e* (rel. intensity) 608 (M$^+$, 80), 571 (15), 265 (57), 257 (52), 226 (58), 91 (37), 43 (100). High resolution mass spectrum: Calcd for $C_{48}H_{32}$: 608.2504. Found: 608.2478.

Reaction of 23 with Zn-HOAc.

A suspension of 23 (100 mg) and zinc dust (2 g) in glacial acetic acid (80 mL) was heated at reflux under argon in the dark for 2 h. After cooling, 50 mL of oxygen-free water was added. The greenish-blue solid was filtered under argon, washed with oxygen-free water and dried to give 80 mg (84%) of crude 6,13-dimethoxy-5,7,12,14-tetraphenylpentacene, mp 285-290°C (rapid heating). ^{1}H NMR: δ 3.61 (s, 6 H), 6.90-7.30 (m, 28 H); mass spectrum, *m/e* (rel. intensity) 642 (M$^+$, 3), 584 (30), 303 (16), 291 (37), 253 (100), 214 (31). High resolution mass spectrum: Calcd for $C_{48}H_{34}O_2$: 642.2559. Found: 642.2549.

6,7-Dibromo-8-methoxy-1,4,5-trimethyl-1,4-dihydronaphthalene-1,4-endoxide (30).

To a solution of 10 (4.5 g, 10.5 mmol) and 2,5-dimethylfuran (5.2 g, 54 mmol) in THF (100 mL) cooled to -78°C under argon was added BuLi (5 mL of 2.2M in hexane, diluted with 30 mL of additional hexane) over 2 h, and the mixture slowly warmed to 25°C (6 h). Methanol (5 mL) was added, the solvent was removed (rotavap), and the residue was dissolved in CH_2Cl_2 (100 mL), washed with water and dried (Na_2SO_4). Solvent removal (rotavap) and chromatography on alumina, eluted with 10% CH_2Cl_2 in hexane, gave 1.1 g of recovered 19 and 0.9 g (42%) of 2,3,6-tribromo-4-methoxytoluene 31, mp 123-124°C (lit[21] 115°C). ^1H NMR: δ 2.57 (s, 3 H), 3.83 (s, 3 H), 6.97 (s, 1 H). Further elution with CH_2Cl_2 gave 0.9 g (42%) of 30, mp 149-151°C (recrystallised from CH_2Cl_2-CH_3OH). ^1H NMR: δ 1.97 (s, 6 H), 2.43 (s, 3 H), 3.70 (s, 3 H), 6.63 (br s, 2 H); mass spectrum *m/e* (rel intensity) 374 (M^+, 2), 331 (62), 293 (34), 252 (13), 125 (17), 43 (100). *Anal.* Calcd for $C_{14}H_{14}Br_2O_2$: C, 44.96; H, 3.77; Br, 42.72. Found: C, 44.97; H, 3.62; Br, 42.61.

6,7-Dibromo-5,8-dimethoxy-1,2,3,4-tetramethyl-1,4-dihydronaphthalene-1,4-endoxide (32).

In a procedure and workup analogous to that described for 30, from 2.24 g (4.9 mmol) of 13, 3 g (24 mmol) of 8, 300 mL of THF and BuLi (3 mL of 1.9M in hexane, further diluted with 20 mL of hexane), there was obtained 0.6 g (35%) of 2,3,6-tribromo-1,4-dimethoxybenzene 33, mp 98-99°C (lit[22] 101-102°C). ^1H NMR (CCl_4): δ 3.73 (s, 3 H), 3.78 (s, 3 H), 6.87 (s, 1 H). Further elution with CH_2Cl_2 gave 0.8 g (51%) of 32, mp 94-96°C (methanol). ^1H NMR: δ 1.63 (s, 6 H), 1.77 (s, 6 H), 3.71 (s, 6 H); mass spectrum, *m/e* (rel. intensity) 418 (M^+, 4), 375 (35), 339 (42), 124 (24), 43 (100). *Anal.* Calcd for $C_{16}H_{18}Br_2O_3$: C, 45.96; H, 4.33; Br, 38.22. Found: C, 46.03; H, 4.36; Br, 38.28.

Typical Procedure for Mono-Cycloaddition of Furans (Table 2). 6,7-Dibromo-1,4,5,8-tetramethyl-1,4-dihydronaphthalene-1,4-endoxide (36).

To a suspension of 4 (4.22 g, 10 mmol) and 6 (5 g) in toluene (100 mL) at -78°C under argon was added dropwise (2 h) 10 mmol of BuLi in 50 mL of hexane. After 2 h (stirring), the mixture was allowed to warm slowly to rt and was quenched with methanol (1 mL). The toluene solution was washed with water, dried ($MgSO_4$) and concentrated to give 3.56 g (98%) of 36, mp 146-147°C (CH_3OH). ^1H NMR: δ 1.984 (s, 6 H), 2.482 (s, 6 H), 6.772 (s, 2 H); ^{13}C NMR: δ 18.61, 20.21, 89.64, 128.11, 129.69, 146.66, 150.53; mass spectrum, *m/e* (rel. intensity) 361 (0.4), 360 (2), 359 (0.8), 358 (4), 155 (91), 153 (86), 152 (85), 139 (61), 129 (46), 128 (100), 127 (48), 115 (57), 77 (40), 76 (40). *Anal.* Calcd for $C_{14}H_{14}OBr_2$: C, 46.96; H, 3.94; Br, 44.63. Found: C, 47.05; H, 3.95; Br, 44.62.

Spectroscopic Properties of Furan Mono-Adducts (Table 2).

For 35: ^1H NMR: δ 2.37 (s, 6 H), 5.65 (s, 2 H), 6.88 (s, 2 H); mass spectrum, *m/e* (rel. intensity) 330 (M^+, 28), 304 (32), 223 (100), 141 (44), 115 (27). *Anal.* Calcd for $C_{12}H_{10}Br_2O$: C, 43.67; H, 3.05; Br, 48.42. Found: C, 43.75; H, 3.05; Br, 48.32.

For 37: ^1H NMR: δ 1.97 (s, 6 H), 3.73 (s, 6 H), 6.67 (s, 2 H); mass spectrum, *m/e* (rel. intensity) 390 (M^+, 6), 347 (64), 311 (42), 43 (100). *Anal.* Calcd for $C_{14}H_{14}Br_2O_3$: C, 43.11; H, 3.62; Br, 40.97. Found: C, 43.00; H, 3.48; Br, 40.98.

Pyrroles (Table 3).

Pyrroles 38,[23] 40 (R = CH_3,[23] *n*-Bu,[24] *i*-Pr,[24] Bn,[24] Ph[24]), 42,[25] 44[23] and 46 (R = CH_3)[25] were prepared by standard literature procedures.

For 40 (R = NMe_2), a mixture of 23.6 g (0.16 mol) of 3,4-dimethyl-2,5-hexanedione (from the oxidation of 2-butanone with lead dioxide) and 1,1-dimethylhydrazine (10 g, 0.16 mol) in benzene (300 mL) was heated at reflux with a Dean-Stark trap until no additional water formed (10 h). The mixture was concentrated, and the residue distilled under reduced pressure to give 24.7 g (90%) of 40 (R = NMe_2) as a yellow oil, bp 88-92°C at 4 torr. ^1H NMR (CCl_4): δ 1.73 (s, 6 H), 2.03 (s, 6 H), 2.76 (s, 6 H); IR (neat): 1460 (s), 1380 (m), 1360 (s), 1250 (w), 1075 (m), 925 (m) cm^{-1}; mass spectrum, *m/e* (rel. intensity) 166 (100), 151 (73), 136 (12), 125 (24), 122 (90), 110 (96), 106 (15).

For 46 (R = NMe_2), 2,2'biscyclohexanone[26] (20 g, 0.1 mol) and 1,1-dimethylhydrazine (15 mL) in benzene (300 mL) was heated at reflux overnight, then concentrated and distilled to give 18.4 g (82%) of 46 (R = NMe_2), bp 126-130°C at 0.4 torr. ^1H NMR: δ 1.66 (m, 8 H), 2.16 (m, 4 H), 2.53 (m, 4 H), 2.76 (s, 6 H); IR (neat): 1460 (m), 1375 (m) cm^{-1}; mass spectrum, *m/e* (rel. intensity) 218 (100), 203 (58), 189 (24), 174 (48), 161 (10), 148 (65); high resolution mass spectrum: Calcd for $C_{14}H_{22}N_2$: 218.1783. Found: 218.1786.

For 50 (R = NMe_2), *N*-dimethylamino-2,5-dimethylpyrrole[23] (3.36 g, 25 mmol), 2,5 hexanedione (4 g, 35 mmol) and aq. acetic acid (80 V/V, 125 mL) were heated at reflux under argon for 20 h. The cooled mixture was basified (50% aq. NaOH) and the precipitated solid was washed with water and vacuum dried to give 2.7 g (43%) of crude 50 (R = NMe_2). ^1H NMR: δ 2.55 (s, 6 H), 2.65 (s, 6 H), 2.89 (s, 6 H), 6.28 (s, 2 H). This unstable substance, which rapidly turns black in air, was used without further purification.

Typical Procedure for Bis-Cycloadditions of Pyrroles (Table 3). Bis(*N*-methyl)-1,2,3,4,5,6,7,8,9,10-decamethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-bis-imine (41, R = CH_3).

A solution of 4 (4.22 g, 10 mmol) and 2.74 g (20 mmol) of 40 (R = CH_3) in anhydrous toluene (200 mL) was cooled to -78°C under argon (most of the 4 precipitates from solution). To this suspension was added dropwise over 2 h with stirring BuLi (22 mmol in 30 mL of hexane). After 3 h stirring at -78°C, the mixture was allowed to warm slowly to rt and maintained there for 1 h. Water (20 mL) was added and the organic product extracted with CH_2Cl_2, dried ($MgSO_4$) and evaporated (rotavap). The residue was recrystallized from $CHCl_3$-hexane to give 2.97 g (79%) of **41**, R = CH_3 (syn/anti mixture). One isomer was obtained pure by washing with ether to give 1.72 g (46%), mp 256-258°C. ^1H NMR: δ 1.63 (s, 12 H), 1.68 (s, 12 H), 1.93 (s, 6 H), 2.23 (s, 6 H); mass spectrum, m/e (rel. intensity) 376 (8), 361 (1), 322 (6), 268 (27), 134 (7); high resolution mass spectrum: Calcd for $C_{26}H_{36}N_2$: 376.2879. Found: 376.2901.[26]

Spectroscopic Properties of Pyrrole Bis-Adducts (Table 3).

For 39 (one isomer): ^1H NMR: δ 1.71 (s, 12 H), 1.98 (s, 6 H), 2.25 (s, 6 H), 6.53 (s, 4 H); mass spectrum, m/e (rel. intensity) 320 (40), 305 (22), 279 (25), 265 (100), 250 (46), 238 (99), 222 (22); high resolution mass spectrum: Calcd for $C_{22}H_{28}N_2$: 320.2253. Found: 320.2271. Anti/syn ratio 73:27 by integrating peaks at δ 1.71 and 1.98.[26]

For 41 (R = n-Bu) (one isomer): Recrystallization solvent, acetonitrile. ^1H NMR: δ 0.91 (m, 6 H), 1.33 (m, 8 H), 1.61 (s, 12 H), 1.65 (s, 12 H), 2.06 (m, 4 H), 2.25 (s, 6 H); ^{13}C NMR: δ 11.56, 14.10, 14.79, 17.16, 21.33, 34.59, 45.79, 77.66, 125.16, 145.58, 148.43; mass spectrum, m/e (rel. intensity) 460 (0.6), 406 (0.6), 363 (2), 352 (1), 308 (5), 264 (0.3), 250 (0.4), 228 (0.4), 98 (100). *Anal.* Calcd for $C_{32}H_{48}N_2$: C, 83.42; H, 10.50. Found: C, 83.47; H, 10.41. Anti/syn ratio 80:20 by integrating peaks at δ 1.61 (anti) and 1.55 (syn).[26]

For 41 (R = i-Pr) (one isomer): Recrystallization solvent, methanol-water. ^1H NMR: δ 1.05 (d, 12 H, J=7 Hz), 1.78 (s, 12 H), 1.91 (s, 12 H), 2.38 (s, 6 H), 2.91 (q, 2 H, J=7 Hz); ^{13}C NMR: δ 11.84, 15.78, 18.08, 23.97, 47.90, 76.03, 122.93, 147.17, 150.03; mass spectrum, m/e (rel. intensity) 432 (30), 417 (7), 378 (16), 349 (65), 294 (68), 276 (15), 263 (12), 149 (18), 84 (100). *Anal.* Calcd for $C_{30}H_{44}N_2$: C, 83.27; H, 10.24; N, 6.47. Found: C, 83.40; H, 10.40; N, 6.57. Anti/syn ratio 75:25 by integration at δ 1.01 (syn) and 1.05 (anti).[26]

For 41 (R = Benzyl) (one isomer): Recrystallization solvent, hexane-chloroform. ^1H NMR: δ 1.55 (s, 12 H), 1.66 (s, 12 H), 2.23 (s, 6 H), 3.31 (s, 4 H), 7.10 (m, 10 H); mass spectrum, m/e (rel. intensity) 528 (0.4), 474 (0.8), 420 (1), 397 (2), 342 (10), 329 (1), 264 (8), 91 (100). *Anal.* Calcd for $C_{38}H_{44}N_2$: C, 86.31; H, 8.38; N, 5.29. Found: C, 86.40; H, 8.46; N, 5.25. Anti/syn ratio 75:25 by integrating at δ 1.53 (syn) and 1.55 (anti).[26]

For 41 (R = Ph) (one isomer): Recrystallization solvent, methanol. ^1H NMR: δ 1.68 (s, 12 H), 1.76 (s, 12 H), 2.20 (s, 6 H), 6.86 (m, 10 H); mass spectrum, m/e (rel. intensity) 500 (3), 446 (3), 383 (8), 328 (42), 291 (11), 193 (8), 118 (100). *Anal.* Calcd for $C_{36}H_{40}N_2$: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.40; H, 8.11; N, 5.61.[26]

For 41 (R = NMe$_2$): The syn/anti product mixture, obtained as white crystals, was chromatographed over alumina with hexane as eluent to give one isomer (mp 203-206°C): ^1H NMR: δ 1.61 (s, 12 H), 1.75 (s, 12 H), 2.23 (s, 6 H), 2.35 (s, 12 H); IR (CCl_4) 1455 (m), 1440 (s), 1375 (m), 1245 (w), 1090 (w), 1050 (w) cm^{-1}; mass spectrum, m/e (rel. intensity) no M^+, 318 (100), 303 (16), 273 (5), 85 (16), 58 (9). Further elution gave the second isomer (mp 190-191°C): ^1H NMR: δ 1.61 (s, 24 H), 2.20 (s, 6 H), 2.28 (s, 12 H); mass spectrum, m/e (rel. intensity) no M^+, 318 (100), 303 (23), 288 (6), 273 (8), 85 (21).

For 43 (one isomer): Yield of pure isomer, 39%. ^1H NMR: δ 1.70 (s, 12 H), 2.21 (s, 6 H), 2.25 (s, 6 H), 6.91 (m, 20 H); mass spectrum (CI) m/e (rel. intensity) 625 (M^++1, 76), 447 (20), 268 (50), 179 (100), 149 (14).[26]

For 45 (one isomer): Yield of pure isomer, 37%, recrystallized from methanol-$CHCl_3$. ^1H NMR: δ 1.46[20] (s, 6 H), 1.60[20] (s, 6 H), 1.86 (s, 12 H), 7.23 (m, 20 H); mass spectrum, m/e (rel. intensity) 624 (0.9), 569 (1), 516 (2), 452 (10), 258 (6), 118 (100); high resolution mass spectrum: Calcd for $C_{46}H_{44}N_2$: 624.3505. Found: 624.3502.[26]

For 47 (R = CH$_3$) (one isomer): Yield of pure isomer, 48%, recrystallized from methanol-CH_2Cl_2. ^1H NMR: δ 1.60-2.03 (m, 16 H), 2.20 (s, 6 H), 2.23 (m, 16 H), 2.43 (s, 6 H); ^{13}C NMR: δ 15.00, 22.84, 23.80, 24.89, 26.02, 29.78, 76.32, 127.58, 142.48, 144.81; mass spectrum, m/e (rel. intensity) 480 (33), 465 (7), 291 (8), 188 (100); high resolution mass spectrum: Calcd for $C_{34}H_{44}N_2$: 480.3505. Found: 480.3520.[26]

For 47 (R = NMe$_2$) (one isomer): ^1H NMR: δ 1.26 (m, 24 H), 2.33 (s, 12 H), 2.45 (s, 6 H), 2.13-2.76 (m, 8 H); mass spectrum, m/e (rel. intensity) no M^+, 422 (3), 407 (2), 320 (2), 264 (9), 218 (28), 203 (17), 116 (100). *Anal.* Calcd for $C_{36}H_{50}N_4$: C, 80.25; H, 9.35; N, 10.40. Found: C, 80.13; H, 9.38; N, 10.39.[26]

For 48 (R = NMe$_2$) (one isomer): A mixture of two isomers was obtained by recrystallization from methanol-ether; ratio 55/45 from integration at δ 3.60 (major) and 3.63 (minor). Chromatography over alumina, hexane-ether eluent, gave first a mixture, then the pure major isomer (38%); ^1H NMR: δ 1.40 (s, 24 H), 2.41 (s, 12 H), 3.60 (s, 6 H); ^{13}C NMR: δ 11.05, 14.32, 45.02, 63.56, 76.59, 144.42, 146.14, 147.30; IR (CCl_4): 1460 (s), 1420 (s), 1380 (m), 1270 (m), 1220 (m), 1080 (m), 1030 (s) cm^{-1}; mass spectrum, m/e (rel. intensity) no M^+, 350 (43), 335 (100), 290 (7), 175 (12), 117 (6), 85 (16).[26]

For 49 (R = NMe$_2$) (one isomer): A mixture of two isomers was obtained by triturating the crude product with hexane, ratio 55:45 from integrating at δ 1.73 (major) and 1.88 (minor). Chromatography (alumina, ether) gave pure major isomer (27%): ^{1}H NMR: δ 1.63 (s, 12 H), 1.73 (s, 12 H), 2.33 (s, 12 H), 2.63 (s, 12 H); mass spectrum, m/e (rel. intensity) no M$^+$, 484 (1), 396 (88), 381 (22), 366 (10), 361 (10), 183 (5), 160 (6), 43 (100).[26]

For 51 (R = NMe$_2$) (one isomer): Chromatography (alumina, ether) gave a single product (56%). ^{1}H NMR: δ 2.14 (s, 12 H), 2.34 (s, 12 H), 2.56 (s, 6 H), 6.53 (s, 4 H); ^{13}C NMR: δ 15.25, 19.00, 19.48, 76.17, 122.06, 127.73, 128.47, 148.98, 150.75;[27] mass spectrum, m/e (rel. intensity) 534 (M$^+$, 1), 490 (3), 476 (7), 432 (7), 418 (15), 391 (6), 85 (100). *Anal.* Calcd for $C_{36}H_{46}N_4$: C, 80.86; H, 8.66; N. 10.47. Found: C, 80.49; H, 8.56; N, 10.31.

Decamethylanthracene from 41 (R = NMe$_2$).

Bis-adduct 41 (R = NMe$_2$) (500 mg, 1.15 mmol) was heated at 165°C under reduced pressure for 50 min. Chromatography of the residue (alumina, 1:1 benzene–hexane) gave 165 mg (46%) of 52 and 132 mg (36%) of 53, each of which had ^{1}H NMR and mass spectra identical with an authentic sample.[10] Pyrolysis under similar conditions, but for 20 min, allowed the isolation of 1,2,3,4,5,6,7,8,9,10-decamethyl-1,4-*N*-dimethylaminoimino-1,4-dihydroanthracene, mp 192-194°C; ^{1}H NMR: δ 1.66 (s, 6 H), 1.86 (s, 6 H), 2.25 (s, 6 H), 2.33 (s, 6 H), 2.43 (s, 6 H), 2.50 (s, 6 H); mass spectrum, m/e (rel. intensity) no M$^+$, 332 (trace), 318 (53), 303 (22), 273 (7), 43 (100). Further pyrolysis of this intermediate decomposition product afforded 52 and 53 in the same ratio as above.

To a mixture of *m*-CPBA (517 mg, Aldrich tech grade, 85%, 2.5 mmol) and sodium carbonate (340 mg, 3.2 mmol) in acetonitrile (50 mL) was added dropwise a solution of 41 (R = NMe$_2$) (500 mg, 1.15 mmol) in methylene chloride (20 mL). The mixture was stirred (5 min), then heated under reflux (2 h). The solvent was removed (rotavap) and the residue dissolved in CH_2Cl_2, washed with water (3x), dried ($MgSO_4$), concentrated and chromatographed (alumina, 1:1 benzene–hexane) to give 260 mg (72%) of 52 and 45 mg (12%) of 53.

9,10-Dimethoxy-1,2,3,4,5,6,7,8-octamethylanthracene (54).

Bis-adduct 42 (R = NMe$_2$) (466 mg, 1 mmol) was heated at 180°C and 20 torr for 30 min. The residue was recrystallized from methanol-ether (1:1) to give 347 mg (99%) of 54 as yellow crystals, mp 118-120°C. ^{1}H NMR: δ 2.38 (s, 12 H), 2.76 (s, 12 H), 3.33 (s, 6 H); IR (CCl_4) 1675 (s), 1460 (s), 1380 (m), 1360 (s), 1325 (s), 1210 (m), 1080 (s), 1045 (s), 920 (s) cm^{-1}; UV (cyclohexane) λ_{max} 418 nm (log ε 4.06), 399 (4.14), 378 (4.07), 280 (5.27); mass spectrum, m/e (rel. intensity) 350 (25), 335 (100), 175 (45), 160 (33), 138 (15), 130 (16), 115 (12), 84 (12). *Anal.* Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.11; H, 8.64.

Dodecamethylnaphthacene (55).

Finely powdered 49 (R = NMe$_2$) (512 mg, 1 mmol) was heated at 185°C and 25 torr for 30 min. The red residue was recrystallized from chloroform–methanol to give 387 mg (98%) of 55 as shiny crystals, mp 265-267°C (lit[1a] 265-266°C), ^{1}H NMR identical with that reported.[1a]

1,2,3,4,5,8,9,10-Octamethyl-1,4-*N*-methylimino-5,8-epoxy-1,4,5,8-tetrahydroanthracene (57).

To a suspension of 38 (1.79 g, 5 mmol) and 40 (R = CH$_3$) (0.68 g, 5 mmol) in dry toluene (100 mL) at -78°C under argon was added BuLi (12 mmol, 2 M in hexane diluted with 100 mL hexane) over 2 h. After an additional 2 h, the mixture was allowed to warm slowly to rt and quenched with methanol (1 mL). Workup gave a crude product which was chromatographed (alumina, CH_2Cl_2) to give 0.69 g (42%) of 57 as a 60:40 mixture of two isomers. ^{1}H NMR (major): δ 1.65 (s, 6 H), 1.66 (s, 6 H), 1.95 (s, 6 H), 2.03 (s, 3 H), 2.25 (s, 6 H), 6.79 (s, 2 H); ^{1}H NMR (minor): δ 1.61 (s, 6 H), 1.65 (s, 6 H), 1.96 (s, 6 H), 2.03 (s, 3 H), 2.31 (s, 6 H), 6.78 (s, 2 H); mass spectrum, m/e (rel. intensity) 355 (2), 238 (11), 255 (3), 281 (3), 56 (100); high resolution mass spectrum: Calcd for $C_{23}H_{29}NO$: 335.2249. Found: 335.2251.

6,7-Dibromo-1,2,3,4,5,8-hexamethyl-1,4-*N*-methylimino-1,4-dihydronaphthalene (56).

A solution of 4 (4.22 g, 10 mmol) and 40 (R = CH$_3$) (1.37 g, 10 mmol) in toluene (100 mL) under argon was cooled to -78°C (most of the 4 precipitated). To this suspension was added dropwise (2 h) BuLi (12 mmol in 50 mL of hexane). After warming slowly to rt, the reaction was quenched with methanol (1 mL). Toluene was removed (rotavap) and the residue was dissolved in ether, washed with water, dried ($MgSO_4$) and concentrated to give 3.95 g of crude product. Chromatography (alumina, hexane) gave 3.5 g (88%) of 56, mp 118-120°C. ^{1}H NMR: δ 1.66 (br s, 12 H), 1.93 (s, 3 H), 2.42 (s, 6 H); ^{13}C NMR: δ 11.13, 15.74, 20.83, 30.60, 77.04, 126.06, 132.17, 145.47, 149.60; mass spectrum, m/e (rel. intensity) 402 (3), 398 (8), 355 (22), 320 (10), 277 (45), 197 (14), 128 (16), 115 (50), 70 (44), 56 (100); high resolution mass spectrum: Calcd for $C_{17}H_{21}Br_2N$: 397.0042. Found: 397.0053.

57 from 56.

In a procedure similar to the preparation of 57 from 38, treatment of 56 (1.67 g, 5 mmol) with 2.5 g of 6 in 100 mL of toluene at -78°C with 5.5 mmol of BuLi in hexane gave 1.66 g of crude product. Chromatography (alumina, CH_2Cl_2) gave 1.43 g (88%) of 57 as a anti/syn 71:29 mixture.

1,2,3,4,5,8,9,10-Octamethyl-1,4:5,8-bis(*N*-methylimino)-1,4,5,8-tetrahydroanthracene (58).

In a procedure analogous to the preparation of 56, treatment of 56 (2.97 g, 7.5 mmol) and 38 (0.817 g, 7.5 mmol) in 100 mL of toluene at -78°C with 12 mmol of BuLi in hexane gave, after chromatography (alumina, 3:1 hexane-chloroform) 0.42 g (24%) of 58 as a mixture of two isomers. ^{1}H NMR (mixture): δ 1.63, 1.66, 1.76 (s, 1,2,3,4,5,6-CH_3's, 18 H), 1.86, 1.90, 1.96, 2.00 (s, N-CH_3's, 6 H), 2.18, 2.23 (s, 9,10-CH_3's, 6 H), 6.60 (br s, vinyl H's); mass spectrum, *m/e* (rel. intensity) 348 (5), 293 (15), 278 (12), 268 (29), 238 (23), 220 (9), 205 (27), 56 (100); high resolution mass spectrum: Calcd for $C_{24}H_{32}N_2$: 348.2566. Found: 348.2584.

N-Methyl-bis(tetrahydrobenzo[1,2;3,4])-6,7-dibromo-5,8-dimethyl-1,4-dihydronaphthalene-1,4-imine (59).

A suspension of 4 (4.2 g, 10 mmol) and 46 (R = CH_3) (1.89 g, 10 mmol) in 200 mL of anhydrous toluene was cooled to -78°C and BuLi (11 mmole, commercial 2.4 M diluted 5x with hexane) was added under argon (2 h). After 3 h at -78°C (stirring), the mixture was warmed to rt and after 1 h quenched (H_2O, 20 mL). The organic product was extracted with CH_2Cl_2, dried ($MgSO_4$), concentrated and the crude product recrystallized from methanol-chloroform to give 3.24 g (72%) of 59, mp 168-169°C; ^{1}H NMR: δ 1.52 (m, 12 H), 1.85 (s, 3 H), 2.20-2.65 (m, 4 H), 2.50 (s, 6 H); mass spectrum, *m/e* (rel. intensity) 435 (45), 451 (76), 449 (40), 436 (13), 423 (25), 408 (32), 394 (13), 370 (5), 290 (5), 188 (100).

Bis(*N*-methyl)-bis(tetrahydrobenzo[1,2;3,4])-5,6,7,8,9,10-hexamethyl-1,4,5,8-tetrahydroanthracene-1,4;5,8-bis-imine (60).

To a solution of 59 (2.25 g, 5 mmol) and 40 (R = CH_3) (1.5 g, 11 mmol) in anhydrous THF (200 mL) at -78°C (most of the 59 precipitated) under argon was added dropwise (2 h) with stirring BuLi (8 mmol in 30 mL of hexane). After 3 h, the mixture was warmed slowly to rt, stirred 1 h and quenched with water (20 mL) and CH_2Cl_2 (50 mL). The organic layer was dried ($MgSO_4$), concentrated, and the residue triturated with acetone to give 1.71 g (80%) of 60 (two isomers). Chromatography (alumina, hexane-ether) gave first 0.12 g of the mixture, then 1.59 g (75%) of pure major isomer, mp 265-266°C; ^{1}H NMR: δ 1.60-2.01 (m, 12 H), 1.63 (s, 6 H), 1.66 (s, 6 H), 1.86 (s, 3 H), 1.96 (s, 3 H), 2.20-2.56 (m, 4 H), 2.30 (s, 6 H); mass spectrum, *m/e* (rel. intensity) 428 (29), 413 (3), 400 (2), 374 (27), 359 (6), 188 (8), 56 (100); high resolution mass spectrum: Calcd for $C_{30}H_{40}N_2$: 428.3192. Found: 428.3224.

N-Dimethylamino-6,7-dibromo-1,2,3,4,5,8-hexamethyl-1,4-dihydronaphthalene-1,4-imine (61, R = NMe$_2$).

Using a procedure analogous to that for 59, 4 (13.9 g, 33 mmol), 40 (R = NMe$_2$) (5.5 g, 33 mmol) and BuLi (36 mmol) in toluene gave a crude product that was triturated with 95% ethanol to give 8.68 g (62%) of 61 that was recrystallized from chloroform-methanol, mp 140-142°C; ^{1}H NMR: δ 1.61 (s, 6 H), 1.73 (s, 6 H), 2.33 (s, 6 H), 2.46 (s, 6 H); mass spectrum, *m/e* (rel. intensity) no M^+, 372 (5), 370 (10), 368 (6), 210 (5), 195 (9), 179 (9), 165 (9).

2,3-Dibromo-1,4,5,6,7,8-hexamethylnaphthalene (62).

Crystalline imine 61 (1 g, 2.3 mmol) was heated in an oil bath at 155°C for 5 h. The residue was recrystallized from methanol-chloroform to give 858 mg (99%) of 62, mp 176-178°C (lit[10] 177-178°C); ^{1}H NMR: δ 2.28 (s, 6 H), 2.45 (s, 6 H), 2.65 (s, 6 H).

N-Dimethylamino-bis(tetrahydrobenzo[1,2;3,4])-5,6,7,8,9,10-hexamethyl-1,4-dihydroanthracene-1,4-imine (63).

Using a procedure analogous to that for 60, 62 (1.41 g, 3.8 mmol), 46 (R = NMe$_2$) (1 g, 4.5 mmol) and BuLi (5 mmol) in anhydrous THF gave crude product that was recrystallized from chlorofrom-methanol to give 1.49 g (91%) of 63 as white crystals, mp 192-194°C; ^{1}H NMR: δ 1.40-2.05 (m, 8 H), 2.26 (s, 6 h), 2.31 (s, 6 H), 2.43 (s, 6 H), 2.56 (s, 6 H), 2.05-2.80 (m, 8 H); mass spectrum, *m/e* (rel. intensity) 428 (trace), 383 (2), 370 (76), 355 (31), 340 (10), 310 (3), 185 (11).

Pyrolysis of 63.

Crystalline 63 (500 mg, 1.1 mmol) was heated at 190°C and 25 torr for 30 min. The yellow powder (434 mg), presumably 64, gradually rearranged to 65 during recrystallization. Hence, no warmed to rt, was quenched with methanol (1 mL), washed with water and dried ($MgSO_4$). After solvent removal (rotavap), the residue was chromatographed (alumina, hexane) to give 2.27 g (97%) of 71, mp 105-107°C; ^{1}H NMR: δ 2.13 (m, 4 H), 2.20 (s, 6 H), 3.80 (t, 4 H), 6.60 (t, 4 h); ^{13}C NMR: δ 14.73, 48.19, 70.02, 122.76, 143.31, 146.58; mass spectrum, *m/e* (rel. intensity) 234 (69), 219 (100), 203 (24), 193 (51), 178 (36), 165 (26), 152 (17), 102 (19), 89 (18). *Anal.* Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.84.

Spectroscopic Properties of Adducts in Table 4.

For 72 (major isomer, yield 54%): ^{1}H NMR: δ 1.45 (s, 12 H), 2.26 (s, 6 H), 4.33-4.43 (t, 4 H), 6.66-6.76 (t, 4 H); ^{13}C NMR: δ 14.74, 18.91, 48.62, 99.89, 121.38, 143.28, 145.44, 161.38;

mass spectrum, m/e (rel. intensity) 314 (100), 299 (25), 288 (16), 269 (14), 247 (45), 232 (15), 215 (21); high resolution mass spectrum: Calcd for $C_{24}H_{26}$: 314.2036. Found: 314.2033.

For 73 (one isomer): Too insoluble for NMR; mass spectrum, m/e (rel. intensity) 562 (77), 371 (56), 227 (39), 178 (55), 165 (40), 152 (18), 191 (100); high resolution mass spectrum: Calcd for $C_{44}H_{34}$: 562.2661. Found: 562.2670.

For 74 (major isomer, yield 68%): ^{1}H NMR: δ 0.50 (m, 8 H), 2.16 (s, 6 H), 3.13-3.23 (t, 4 H), 6.60-6.76 (t, 4 H); ^{13}C NMR: δ 8.96, 10.01, 14.75, 53.84, 65.13, 121.43, 142.72, 145.98; mass spectrum, m/e (rel. intensity) 286 (100), 271 (27), 258 (76), 241 (30), 227 (43), 215 (53), 202 (44), 114 (47), 108 (37). *Anal.* Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.77.

For 76 (major isomer): ^{1}H NMR: δ 1.00-1.73 (m, 16 H), 2.10 (s, 6 H), 3.33-3.43 (t, 4 H), 6.50-6.60 (t, 4 H); ^{13}C NMR: δ 14.76, 25.89 (2), 33.75, 33.85, 56.98, 90.67, 123.04, 142.79, 146.24; mass spectrum, m/e (rel. intensity) 342 (100), 327 (30), 259 (14), 215 (16). *Anal.* Calcd for $C_{26}H_{30}$: C, 91.17; H, 8.83. Found: C, 91.07; H, 8.80.

For 77: ^{1}H NMR: δ 2.06 (s, 6 H), 2.13 (m, 2 H), 2.20 (s, 6 H), 3.96 (t, 2 H), 6.63 (t, 2 H); ^{13}C NMR: δ 15.96, 16.22, 48.83, 68.23, 127.39, 130.52, 142.97, 167.87; mass spectrum, m/e (rel. intensity) 198 (40), 183 (100), 172 (10), 168 (10), 165 (12), 157 (21), 153 (13), 141 (17), 128 (11), 115 (14), 91 (10). *Anal.* Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.98; H, 9.05.

For 78: ^{1}H NMR: δ 1.50 (s, 6 H), 2.10 (s, 6 H), 2.23 (s, 6 H), 4.33-4.46 (t, 2H), 6.20-6.60 (t, 2 H); ^{13}C NMR: δ 16.01, 16.20, 18.99, 49.20, 101.21, 126.56, 130.90, 142.86, 145.79, 160.39; mass spectrum, m/e (rel. intensity) 238 (100), 223 (27), 208 (13), 193 (11), 171 (17). High resolution mass spectrum: Calcd for $C_{18}H_{22}$: 238.1722. Found: 238.1725.

For 79: ^{1}H NMR: δ 2.13 (s, 6 H), 2.20 (s, 6 H), 4.40-4.50 (t, 2 H), 6.76-6.86 (t, 2 H), 6.86-7.16 (m, 10 H); mass spectrum, m/e (rel. intensity) 362 (45), 191 (75), 171 (100), 165 (60), 158 (88). *Anal.* Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.22. Found: C, 92.73; H, 7.21.

For 80: ^{1}H NMR: δ 0.53 (m, 4 H), 2.10 (s, 6 H), 2.16 (s, 6 H), 3.30-3.40 (t, 2 H), 6.66-6.76 (t, 2 H); ^{13}C NMR: δ 15.93, 16.16, 54.26, 63.25, 126.88, 130.28, 142.31, 146.55; mass spectrum, m/e (rel. intensity) 224 (94), 209 (74), 196 (100), 181 (56), 165 (45), 149 (27). *Anal.* Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.80; H, 9.08.

For 81: ^{1}H NMR: δ 1.10-1.70 (m, 8 H), 2.06 (s, 6 H), 2.16 (s, 6 H), 3.43-3.60 (t, 2 H), 6.43-6.60 (t, 2 H); ^{13}C NMR: δ 16.00, 16.23, 25.60 (2), 33.54, 33.80, 57.79, 88.37, 127.54, 130.11, 142.70, 164.99; mass spectrum, m/e (rel. intensity) 252 (100), 237 (49), 223 (8), 208 (10). *Anal.* Calcd for $C_{19}H_{24}$: C, 90.41; H, 9.59. Found: C, 90.28; H, 9.48.

Reaction of 4 with Li Cyclopentadienide and BuLi.

To a solution of freshly distilled cyclopentadiene (1.32 g, 10 mmol) in 100 mL of anhydrous ether at 0°C under argon was added 20 mmol of BuLi (the lithium cyclopentadienide precipitated). To this suspension, 4 (4.22 g, 10 mmol) was added, and the mixture was cooled to -78°C. BuLi (20 mmol in 50 mL of hexane) was added dropwise (2 h). Warming to room temperature and workup as for 71 gave only cyclopentadiene dimer and some polymeric products. No trace of 71 was observed.

N-Dimethylamino-bis(tetrahydrobenzo[1,2;3,4])-5,6,7,8-tetramethyl-1,4-dihydronaphthalene-1,4-imine 82 (R = CH_3).

Using a procedure analogous to that for 59, 76[28] (2.92 g, 10 mmol) and 46 (R = NMe_2) (2.18 g, 10 mmol) and BuLi (15 mmol) in THF gave a residue which was first triturated with hexane-acetone to give crude 82 as a white powder (2.42 g). Recrystallization from chloroform-hexane gave pure 82 (R = CH_3), 2.17 g (62%), mp 166-167°C; ^{1}H NMR: δ 1.75-1.78 (m, 8 H), 2.01-2.55 (m, 4 H), 2.06 (s, 6 H), 2.23 (s, 6 H), 2.26 (s, 6 H), 2.46 (m, 4 H); ^{13}C NMR: 16.03, 16.41, 23.54, 23.89, 24.50, 29.46, 46.20, 75.22, 127.01, 132.41, 144.07, 146.71; mass spectrum, m/e (rel. intensity) no M^+, 304 (2), 292 (100), 277 (19), 262 (5), 249 (12), 235 (5), 219 (8).

9,10,11,12-Tetramethyl-1,2,3,4,5,6,7,8-octahydrotriphenylene (83, R = CH_3).

Imine 82 (R = CH_3, R' = NMe_2) (350 mg, 1 mmol) was heated at 250°C and 25 torr for 1 h. The residue, washed with methanol, was essentially pure 83 (R = CH_3), 286 mg (98%), mp 172-174°C. ^{1}H NMR: δ 1.5-2.05 (m, 8 H), 2.13 (s, 6 H), 2.33 (s, 6 H), 2.50 (m, 4 H), 2.83 (m, 4 H); ^{13}C NMR: δ 16.98, 21.72, 23.57 (2), 26.90, 32.66, 128.75, 131.04, 131.96, 132.66, 134.58; mass spectrum, m/e (rel. intensity) 292 (100), 277 (19), 264 (8), 249 (12), 234 (6), 219 (8).

1,2,3,4-Tetramethyltriphenylene (84, R = CH_3).

A mixture of 83 (R = CH_3) (100 mg, 0.34 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (300 mg, 1.32 mmol) in 15 mL of anhydrous benzene was heated at reflux for 5 h. Chromatography over alumina (benzene) gave 67 mg (68%) of 84 (R = CH_3), mp 175-177°C. ^{1}H NMR: δ 2.43 (s, 6 H), 2.78 (s, 6 H), 7.3 (m, 4 H), 8.03 (m, 2 H), 8.30 (m, 2 H); UV (heptane): λ max 302 nm (sh, log ε 3.86), 273 (4.72), 264 (4.60); mass spectrum, m/e (rel. intensity) 284 (100), 269 (36), 254 (29), 239 (6), 142 (22), 127 (43). *Anal.* Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.89; H, 7.14.

N-Dimethylamino-bis(tetrahydrobenzo[1,2;3,4])-6,7-dibromo-5,8-dimethyl-1,4-dihydronaphthalene-1,4-imine 82 (R = Br).

Using a procedure analogous to that for 59, 4 (4.2 g , 10 mmol), 46 (R = NMe$_2$) (2.18 g, 10 mmol) and BuLi (15 mmol in toluene) gave a crude product which was triturated with ethanol to give pure 82 (R = Br, R' = NMe$_2$), 4.24 g (88%), mp 189-191°C. ^{1}H NMR: δ 1.44-2.20 (m, 12 H), 2.33 (s, 6 H), 2.56 (s, 6 H), 2.20-2.61 (m, 4 H); mass spectrum, *m/e* (rel. intensity) no M$^+$, 434 (trace), 424 (61), 422 (100), 420 (46), 344 (9), 342 (12), 262 (18), 247 (16), 234 (20), 209 (28), 203 (32), 191 (23).

10,11-Dibromo-9,12-dimethyl-1,2,3,4,5,6,7,8-octahydrotriphenylene (83, R = Br).

Crystalline 82 (R = Br, R' = NMe$_2$) (478 mg, 1 mmol) was heated in an oil bath at 190-200°C for 25 min. The residue was recrystallized from methanol-chloroform to give 407 mg (97%) of 83 (R = Br) as white crystals, mp 217-219°C. ^{1}H NMR: δ 1.5-2.15 (m, 8 H), 2.15-2.85 (m, 8 H), 2.60 (s, 6 H); mass spectrum, *m/e* (rel. intensity) 424 (26), 422 (54), 420 (29), 262 (10), 247 (10), 232 (5), 219 (6), 203 (24). *Anal.* Calcd for $C_{20}H_{22}Br_2$: C, 56.89; H, 5.25; Br, 37.85. Found: C. 56.73; H, 5.22; Br, 37.80.

2,3-Dibromo-1,4-dimethyltriphenylene (84, R = Br).

A mixture of 83 (R = Br) (500 mg, 1.2 mmol) and DDQ (1.7 g, 7.5 mmol) in 50 mL of benzene was heated at reflux under argon (4 h). The solution was passed through basic alumina with benzene as eluent and concentrated to give 316 mg (65%) of 84 (R = Br), mp 212-214°C. ^{1}H NMR: δ 2.93 (s, 6 H), 7.05 (m, 4 H), 7.93 (m, 2 H), 8.23 (m, 2 H); UV (heptane): λ_{max} 299 nm (log ε 4.13), 277 (4.79), 267 (4.63); mass spectrum, *m/e* (rel. intensity) 416 (20), 414 (31), 412 (14), 399 (1), 254 (31), 252 (52), 239 (76), 126 (100). *Anal.* Calcd for $C_{20}H_{14}Br_2$: C, 58.00; H, 3.40. Found: C, 57.85; H, 3.39.

N-Dimethylamino-1,2,3,4,5,6,7,8-octamethyl-1,4-dihydronaphthalene-1,4-imine (85).

Using a procedure analogous to that for 59, a mixture of 76[28] (5.2 g, 18 mmol) and 46 (R = NMe$_2$) (3.4 g, 20 mmol) was treated with 27 mmol of BuLi in toluene. Crude product was chromatographed (alumina, 1:1 CH_2Cl_2-hexane) and recrystallized from $CHCl_3$-methanol to give 4.35 g (82%) of 85, mp 127-129°C. ^{1}H NMR: δ 1.60 (s, 6 H), 1.93 (s, 6 H), 2.08 (s, 6 H), 2.21 (s, 6 H), 2.30 (s, 6 H); ^{13}C NMR; δ 11.13, 15.82, 16.26, 17.09, 45.31, 76.88, 126.65, 131.96, 147.16; IR (CCl_4): 1450 (s), 1380 (s), 1260 (w), 1150 (w), 1075 (m) cm^{-1}; mass spectrum, *m/e* (rel. intensity) 298 (M$^+$, trace), 254 (trace), 240 (100), 225 (30), 195 (5), 179 (4). *Anal.* Calcd for $C_{20}H_{30}N_2$: C, 80.48; H, 10.13; N, 9.38. Found: C, 80.62; H, 10.19; N, 9.45.

Octamethylnaphthalene (86).[11,29]

Powdered 85 (300 mg, 1 mmol) was heated at 200°C under argon until bubbling ceased (10 min). The residue was triturated with methanol, then recrystallized from methanol-hexane to give 242 mg (100%) of 86, mp 184-185°C (lit[29] 181-181.5°C); ^{1}H NMR: δ 2.30 (s, 12 H), 2.46 (s, 12 H).

1,4,5,6,7,10,11,12-Octamethyl-1,4,7,10-tetrahydrobinaphthylene-1,4;7,10-bis-endoxide (87).

To a solution of 38 (1.79 g, 5 mmol) in anhydrous ether (50 mL) at -78°C under argon was added dropwise (1 h) BuLi (5 mmol in 25 mL of hexane). After 6 h at -78°C, the reaction was quenched with 1 mL of methanol. The ether solution was washed with water, dried ($MgSO_4$), concentrated and the residue chromatographed (alumina, 3:1 hexane-chloroform) to give 198 mg (10%) of 87 as a mixture (syn/anti). The major isomer was purified by successive washing with ether, mp 315-317°C. ^{1}H NMR: δ 1.90 (s, 12 H), 2.13 (s, 12 H), 6.63 (s, 4 H); mass spectrum, *m/e* (rel. intensity) 396 (47), 370 (40), 353 (23), 344 (55), 327 (100), 310 (41), 43 (98); high resolution mass spectrum: Calcd for $C_{28}H_{28}O_2$: 396.2089. Found: 396.2163.

X-ray Data for Anti-7.

Crystals of anti-7, $C_{20}H_{22}O_2$, are monoclinic; space group $P2_1/n$; a = 9.697 (5), b = 7.582 (4), c = 11.186 (6)Å, β = 111.17 (4)°; Z = 2; M = 294.39; ρ_c = 1.275 g cm^{-3}. Lattice dimensions were determined using a Picker FACS-I diffractometer and MoKα (λ = 0.70926Å) radiation.

Intensity data were measured using MoKα radiation ($2\theta_{max}$ = 65°) yielding 2772 total unique data and, based on $I > 2\sigma(I)$, 2297 observed data. The data were reduced;[30] the structure was solved by direct methods;[31] the refinement was by full-matrix, least-squares techniques.[32] The final R value was 0.048.[33]

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4. The published[2b] experimental description of this reaction unfortunately omitted part of the text. We give here a correct and scaled up procedure for the preparation of pure syn- and anti-3 (we are indebted to Dr. Jihmei Luo for this procedure).

   To a stirred solution of 1 (39.4 g, 0.1 mol) and furan (120 mL, freshly distilled) in dry toluene (1400 mL) at -23°C under argon was slowly added (5 h) BuLi (0.22 mol in 150 mL hexane). After addition, the mixture was allowed to warm to rt and stirred overnight. Water (20 mL) was added and the mixture was stirred vigorously for 20 min. The organic layer was washed with water (150 mL x 2), dried ($MgSO_4$) and the solvent removed (rotavap). The resulting gummy yellow solid was pumped to dryness. Methanol (70 mL) was added and the off-white crystals were collected and washed with a small amount of methanol. Recrystallization from acetone gave white plates of anti-3 (7.81 g, 37%), mp 245°C (dec). The methanol solution was evaporated to dryness. The residue was either recrystallized from methanol (3-4x) or chromatographed (silica gel, 1:2 ethyl acetate-hexane) to give 5.85 g (28%) of syn-3, mp 191-193°C.

5. It is noteworthy that only 31, and not its regioisomer, is formed. The formation of nearly equal amounts of 30 and 31 suggests that lithiation of 8 by BuLi may be nearly regiorandom, but that elimination of LiBr (and capture of the resulting aryne to give 30) may be favored when the Li is adjacent to the methyl (rather than the methoxyl) substituent. This question bears further investigation.

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20. Note the substancial shielding of the methyl or methoxyl protons by the adjacent phenyl substituents.

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