289.3, 26.7 Hz, CF_2), 29.4 (m, $C_{3,4}$), 7.0 (s, $C_{1,2,5,6}$): IR (CCl_4) 3088 (w), 3012, 1401, 1342, 1331, 1256, 1168, 1138 (3), 1112, 1053 (s), 1016, 974 cm^{-1}; mass spectrum, m/z (relative intensity) 160 ($M^+ - 20$, 7.0), 145 (100), 127 (33), 116 (31), 115 (70), 111 (50), 109 (77), 101 (60), 90 (58), 77 (63), 75 (42), 64 (43), 51 (59) and 39 (80).

Acknowledgment. Support of this work in part by the National Science Foundation if gratefully acknowledged.

Registry No. **1**, 67884-63-3; **2**, 67884-64-4; **3**, 100207-83-8; **4**, 100207-84-9; **5**, 100296-07-9; **6**, 100207-85-0; **7**, 100296-08-0; **8**, 5471-63-6; **9**, 100207-86-1; **10**, 100207-87-2; **11**, 100207-88-3; **12**, 100207-89-4; **13**, 100207-90-7; **17**, 100207-92-9; **18**, 100207-93-0; $H_2C{=}C(Cl)CH_2Cl$, 428-59-1; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $F_2C{=}CCl_2$, 79-35-6; $ClCF_2CH_2C(Cl){=}CH_2$, 100207-91-8; hexafluoropropylene oxide, 428-59-1; cyclopentadiene, 542-92-7; furan, 110-00-9; cyclopentadiene dimer, 7313-32-8.

Synthesis of 1,5-Diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole (DABT) and Its Use as a 1,4-Benzadiyne Equivalent[1]

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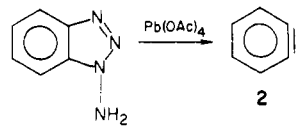
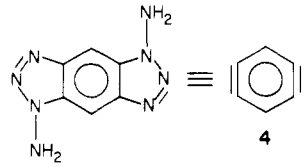
Amination of 1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole (**9**) gives the 1,5- and 1,7-diamino derivatives **3** and **10**, both useful as 1,4-benzadiyne equivalents, as well as the 1,6 isomer **11** and the recyclable monoamino derivatives **12** and **13**. Sixteen examples of the synthetic utility of DABT (**3**) with lead tetraacetate in bisannulations are described (Table I). The aryne-trapping dienes include ester, halogen, and carbonyl functionality; often the reactions are quite regio- and stereoselective as a consequence of the stepwise nature of the annulations.

Oxidation of 1-aminobenzotriazole (**1**) with lead tetraacetate has long been known as a useful way of generating benzyne (**2**) under mild conditions.[2,3] We will describe



1 2

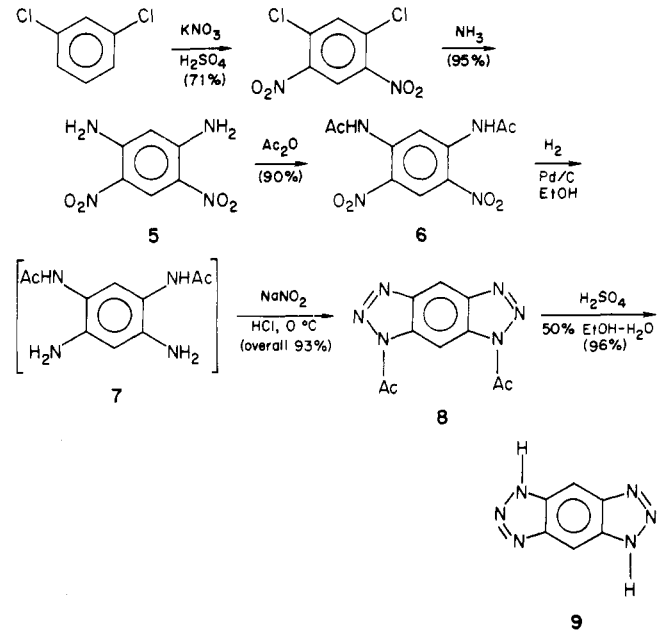
here the synthesis of **3** (1,5-diamino-1,5-dihydrobenzo-[1,2-*d*:4,5-*d*']bistriazole for which we use the acronym DABT) and its use via similar oxidations as the synthetic equivalent of 1,4-benzadiyne (**4**).



3 4

We have recently described the use of 1,2,4,5-tetrabromobenzene and analogous polyhaloarenes as synthetic equivalents of **4** as a consequence of metal–halogen exchange with butyllithium and subsequent aryne formation by lithium bromide elimination.[4,5] One limitation of this method when applied to biscycloadditions is that the diene cannot contain functionality that will react with butyllithium and, hence, prevent aryne formation. In practice, this means that the diene usually cannot contain certain carbonyl functions, halogens, and so on. It was thought that **3** would be useful as a benzadiyne equivalent in these instances and this notion has turned out to be correct.

Scheme I



5 6 7 8 9

(1) For a preliminary account, see: Hart, H.; Ok, D. *Tetrahedron Lett.* **1984**, *25*, 2073.

(2) Campbell, C. D.; Rees, C. W. *J. Chem. Soc. C* **1969**, 742, 748, 752.

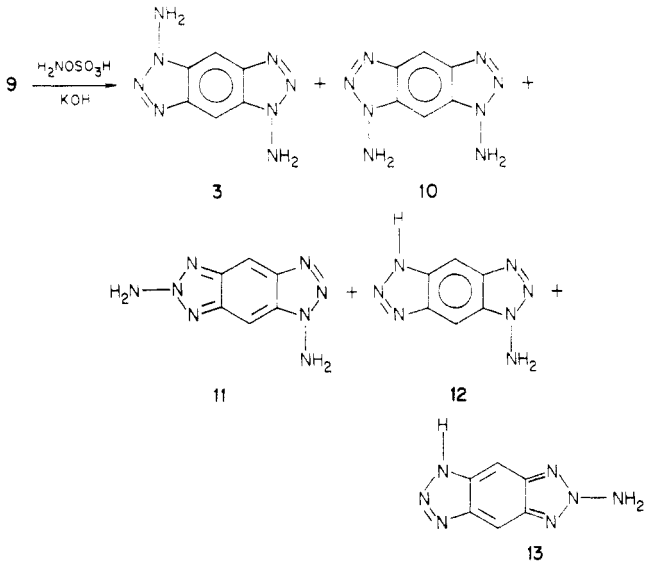
(3) Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes"; Academic Press; New York, 1967; p 81.

(4) Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7. Hart, H.; Lai, C.-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649. Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251. Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427. Hart, H.; Shamouilian, S. *J. Org. Chem.* **1981**, *46*, 4874. Hart, H.; Nwokogu, G. *Tetrahedron Lett.* **1983**, *24*, 5721. Hart, H.; Harada, K. *Tetrahedron Lett.* **1985**, *26*, 29. Hart, H.; Harada, K.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 3104. Harada, K.; Hart, H.; Du, C.-J. F. *J. Org. Chem.* **1985**, *50*, 5524. Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron*, in press.

(5) Other di-aryne equivalents which have seen limited use include (a) treatment of 1,4-dibromoarenes with strong base (Cadogan, J. I. G.; Harger, M. J. P.; Sharp, J. T. *J. Chem. Soc. B* **1971**, 602. Stringer, M. B.; Wege, D. *Tetrahedron Lett.* **1980**, *21*, 3831), (b) treatment of bis(*o*-bromotosylates) with strong base (LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 1682), and (c) thermal cycloadditions to bis(1,4-epoxyarenes) (Hart, H.; Raju, N.; Meador, M. A.; Ward, D. L. *J. Org. Chem.* **1983**, *48*, 4357).

0022-3263/86/1951-0979$01.50/0

Scheme II



Results

Preparation of DABT. The most direct route to **3** is via amination of the known[6,7] 1,5-dihydrobenzo[1,2-*d*:4,5-*d*']bistriazole (**8**), which is prepared from *m*-dichlorobenzene in five steps and 54% overall yield as shown in Scheme I. Compound **5** was prepared as described in ref 8 and acetylated to **6**.[7] The literature method for conversion of **6** to **8**[7] in our hands always gave very low yields (reported 60%, but we obtained <10%), and we describe in the Experimental Section an imporved procedure which consistently gives a 93% yield of **8** from **6**. The major changes were to use ethanol in place of acetic acid for the hydrogenation, to use more catalyst, and to use 0 °C instead of room temperature for the diazotization of **7** (not isolated). Conversion of **8** to **9** proceeded as described.[7]

Direct amination of **9** in aqueous base with hydroxylamine-*O*-sulfonic acid at 66–68 °C gave a mixture of five products, the three possible diamino derivatives **3**, **10**, and **11** and the two monoamino derivatives **12** and **13** (Scheme II). The combined yields of diamino and monoamino products were 45% and 48%, respectively; the latter could by recycled using the same reaction conditions, thus substantially increasing the yields of diamino derivatives. The ratio of **3**:**10**:**11** was determined by NMR integration to be 53:12:35 (the aromatic proton signals which were integrated appeared at δ 8.24 for **3**, δ 8.69 and 7.71 for **10**, and δ 8.59 and 7.96 for **11**).

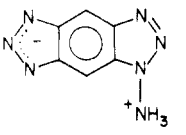
The three diamino derivatives were separated in excellent purity by fractional crystallization from ethanol. Isomer **11** is very soluble in hot ethanol and **3** is less soluble than **10**. The structures were assigned from spectral data.

Compound **3**, mp 292 °C dec, showed only two types of protons in the NMR, aromatic protons at δ 8.24 and NH protons at δ 7.18; the ^{13}C NMR spectrum showed only three signals, at δ 144.16, 131.40, and 97.43. These data are only consistent with the C_{2h} symmetry of **3**. The infrared spectrum of **3** showed strong primary amine absorption at 3386 and 3610 cm^{-1}.

The ^1H NMR spectrum of **10**, mp 263 °C, showed equal-area doublets for the mutually coupled aromatic protons (J = 1 Hz) at δ 8.69 (C4) and 7.71 (C8) and a sharp singlet for the amine protons at δ 7.09. The ^{13}C spectrum showed four peaks, at δ 142.93, 133.32, 108.42, and 87.43. These data are consistent with the C_{2v} symmetry of **10**.

The least symmetric isomer **11**, mp 271–273 °C, showed six peaks in its ^{13}C NMR spectrum as required, at δ 143.36, 139.98, 138.87, 132.72, 104.63, and 91.08. The ^1H NMR spectrum showed two doublets (J = 1 Hz) for the aromatic protons, at δ 8.59 (C4) and 7.96 (C8); the amine protons were not differentiated, however, and appeared as a singlet at δ 7.09.

The ratio of monoamines **12**/**13** was 4:1 as determined by integrating aromatic proton peaks at δ 8.10 and 7.65 (doublets, J = 1 Hz) for **12** and the aromatic proton singlet at δ 7.99 for **13**. The major product **12** was obtained pure by recrystallization from ethanol, but the minor product **13** was always contaminated with some **12**. The melting point of **12** was >400 °C, much higher than the melting points of the diamino products. This result indicates that the structure may be represented by the dipolar form **12a**.



12a

Although five amination products are obtained from this procedure, the situation is not as dire as one might first guess. As will be seen, both **3** and **10** serve as 1,4-benzadiyne equivalents; hence, they need not be separated if used for this purpose. Also, 80% of the monoamino product is the 1-amino derivative which can, on recycling, give additional **3** and **10**. Hence, it is possible to convert approximately 50% of the benzobistriazole **9** to diamino derivatives **3** and **10** for use as aryne precursors.

Use of DABT in Bisannulations. To convert 1-aminobenzotriazole to benzyne, Campbell and Rees[2] dissolved the aminotriazole in an anhydrous solvent (benzene, methylene chloride, toluene, acetic anhydride, or carbon tetrachloride) and added this solution at room temperature to a suspension of lead tetraacetate (LTA) in the same solvent. Due to its insolubility in these solvents, this method failed completely with DABT. Thus, although DABT is very slightly soluble in THF (ca. 3 mg per 100 mL), addition of a DABT–THF suspension to lead tetraacetate in THF at room temperature or at reflux gave no reaction. No nitrogen evolved, and the DABT was recovered quantitatively. Similar results were obtained in benzene, toluene, ether, and dimethyl sulfoxide.

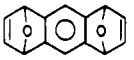
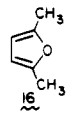
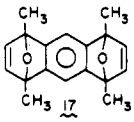
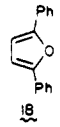
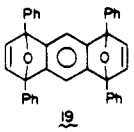
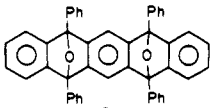
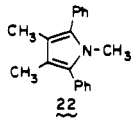
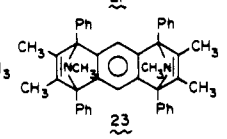
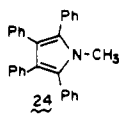
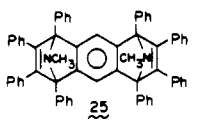
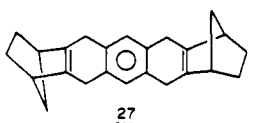
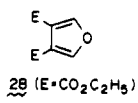
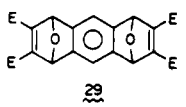
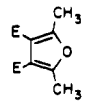
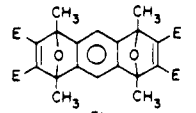
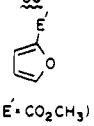
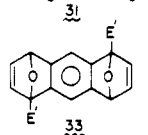
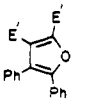
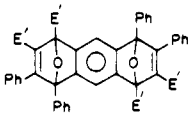
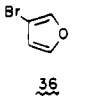
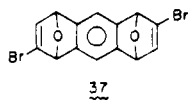
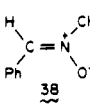
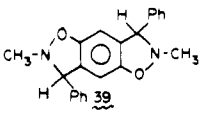
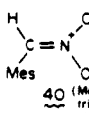
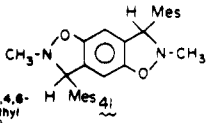
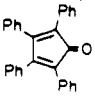
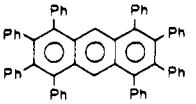
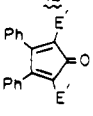
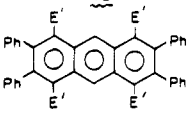
Inverse addition worked, however, presumably because the oxidation of an aminotriazole by LTA is exceedingly fast. Thus, when LTA suspended in THF was added to a stirred suspension of DABT in the same solvent at room temperature, nitrogen evolution was virtually instantaneous; in this way, bisannulations became possible.

The general procedure for using DABT in bisannulations involved adding in portions over 30 min at room temperature 2.2 mmol of LTA suspended in THF to a mixture containing 2 mmol of diene and 1 mmol of DABT in 100 mL of THF. After 10 min of additional stirring, the lead diacetate was filtered and the filtrate was worked up by extraction of the bisadduct with methylene chloride and purification by chromatography or crystallization. Table I lists examples.

Several aspects of these results warrant some comment. The first seven entries involve dienes containing no exceptional functionality, and similar reactions have been described using 1,2,4,5-tetrahaloarenes as 1,4-benzadiyne

(6) Muzik, F.; Allan, Z. J. *Coll. Czech. Chem. Commun.* **1959**, *24*, 474.
(7) Coburn, M. D.; Berlin, J. K. *Synthesis* **1974**, 869.
(8) Boyer, J. H.; Buriks, R. S. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 1067.
(9) Huang, N. Z.; Jia, J. H.; Wang, L. L. *Tetrahedron Lett.* **1982**, 4797. Carruthers, W.; Stewart, H. N. M.; Hansell, P. G.; Kelly, K. M. *J. Chem. Soc. C* **1967**, 2607.

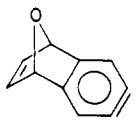
Table I. Bisannulations with DABT-LTA

entry	diene	bisadduct	yield, %
1	 14	 15	79 (anti:syn 77:23)
2	 16	 17	81 (anti:syn 81:19)
3	 18	 19	75
4	 20	 21	88
5	 22	 23	77
6	 24	 25	88
7	 26	 27	93 (anti:syn 91:9)
8	 28 (E=$CO_2C_2H_5$)	 29	40
9	 30	 31	67
10	 32 (E=CO_2CH_3)	 33	47
11	 34	 35	78[a]
12	 36	 37	69
13	 38	 39	91
14	 40 (Mes=2,4,6-tri-methyl phenyl)	 41	78
15	 42	 43	56[a]
16	 44	 45	93

[a] At reflux; no reaction (entry II) or low yields (entry 15) were obtained at room temperature.

equivalents[4] although, as will be seen when individual entries are discussed below, there are some differences in the two types of benzadiyne equivalents. Entries 8–16 involve dienes containing functionality that may react with the *n*-butyllithium used to generate arynes from tetrahaloarenes; hence, these dienes are uniquely suited to the DABT–LTA reagent.

Bis(furan) adduct **15** was obtained as a 77:23 anti/syn mixture from DABT–LTA in THF at room temperature. When synthesized from 1,2,4,5-tetrabromobenzene and butyllithium at −78 °C, the anti:syn ratio in **15** was 55:45.[4] In the most simplistic formulation, both reactions proceed in a stepwise manner, in which case, the same intermediate aryne **46** is involved. The difference in anti/syn selectivity



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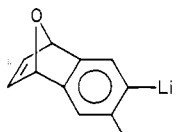

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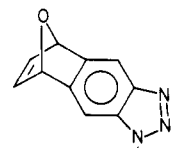

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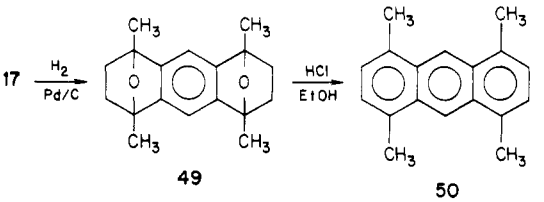
may be a consequence of the different reaction conditions under which **46** is generated or it may be that **46** is not entirely "free" under one or both sets of conditions. The immediate precursor of **46** when 1,2,4,5-tetrabromobenzene is used is presumably the bromolithio derivative **47**, whereas with DABT, it may be the nitrene **48**. Fragments derived from these different precursors could be present and influence the regioselectivity.

2,5-Dimethylfuran gave adduct **17**, whose structure was proved by catalytic hydrogenation to **49** followed by dehydration to the known 1,4,5,8-tetramethylanthracene (**50**). Cycloaddition to 2,5-dimethylfuran was selected to compare the reactivity of **3** and **10** with lead tetraacetate. Both 1,4-benzadiyne precursors gave adduct **17** in the same overall yield and with identical anti:syn ratios of 81:19. Hence, **10** functions as well as **3** as a 1,4-benzadiyne equivalent, and the two isomers need not be separated if they are to be used for this purpose.



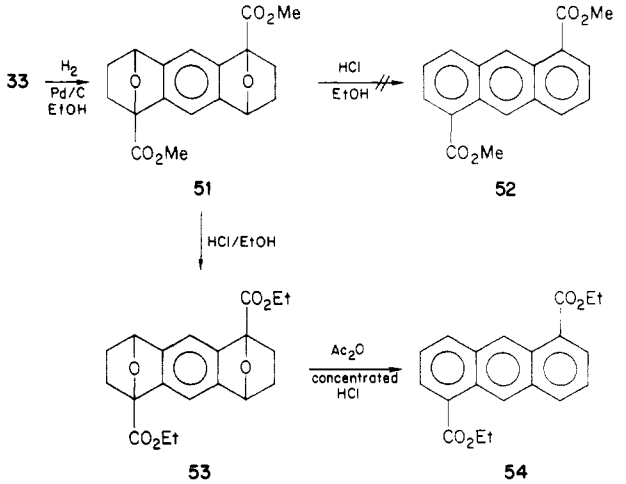
49 **50**

As the table indicates, in many reactions the product consisted mainly of a single stereo- or regioisomer. For example, the product in entry 3 had a sharp melting point

(264–265 °C) and showed only one singlet (δ 6.74) in the vinyl proton region of the ^1H NMR spectrum, suggesting that only one isomer (anti?) was isolated. Similarly, in entry 4, the product **21**, obtained in high yield, melted sharply at 306–308 °C and had a ^{13}C NMR with only 10 signals, consistent with formation of only one isomer. This entry is also notable for the high yield. Campbell and Rees reported[2] difficulty in a similar experiment with **1**, where the yield of adduct was only 43%; competing oxidation of the diene **20** gave *o*-dibenzoylbenzene. For some reason, that difficulty was not a problem in our work.

DABT apparently reacts with LTA faster than do pyrroles **22** and **24** since bisadducts **23** and **25** were easily obtained in good yield (entries 5, 6) without accompanying oxidation products derived from the pyrroles. Previous attempts to prepare adduct **25** by using 1,2,4,5-tetrabromobenzene–butyllithium as the 1,4-benzadiyne equivalent were unsuccessful.[10]

Entries 8–11 in Table I show that the DABT–LTA system can tolerate the ester functionality in the diene. The bisadducts appeared to be mainly single isomers. For example, **29** melted sharply (188–190 °C) and showed sharp singlets at δ 7.45 and 5.90 for the aromatic and bridgehead protons, respectively. Also, the ^{13}C NMR spectrum showed only the required seven peaks. Similar results were obtained with adducts **31**, **33** and **35**. The latter two examples are particularly striking since four products are, in principle, possible—two stereoisomers (syn and anti) of each of the two possible regioisomers. Nevertheless, **33** appeared to be only one compound. It melted sharply at 240–242 °C and had ^1H and ^{13}C NMR spectra consistent with a single isomer. The aromatic protons appeared as a sharp singlet at δ 7.35, suggesting that the ester functions were "trans", a conclusion that was confirmed chemically. Catalytic hydrogenation gave the saturated diester **51**. Attempts to dehydrate **51** to **52** with



HCl in refluxing ethanol led instead to the transesterification product **53**. This was dehydrated with acetic anhydride and concentrated hydrochloric acid to give the known[11] anthracene diester **54**. Thus, the ester functions in **33** are trans to one another; the geometry of the oxygen bridges is not known but is most likely "anti".

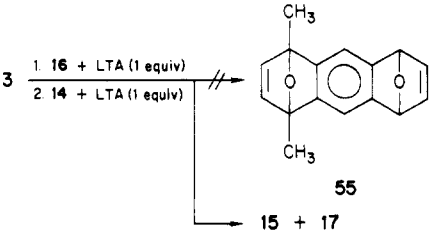
The product in entry 12, formed in 69% yield, also has the functionality trans. The aromatic protons in **37** (as in **33**) appeared as a singlet (δ 7.32). This example is also interesting because the bromofuran would probably react with butyllithium and hence be an unsuitable substrate if a tetrahaloarene were used as the 1,4-benzadiyne equivalent.

Entries 13 and 14 provide the first examples of 1,3-dipolar cycloadditions to a 1,4-benzadiyne equivalent. The cycloaddition of benzyne to nitrones was first described by Huisgen.[12] Remarkably, the reaction of DABT–LTA with nitrones **38** and **40** gave, in each case, a single crystalline bisadduct in high yield. Thus, **39**, mp 142–143 °C, was obtained in 91% yield. The aromatic protons in the central ring appeared as a sharp singlet (δ 6.42) as required by the 1,4-orientation of the oxygen substituents. The benzylic and *N*-methyl protons also appeared as singlets (δ 5.04 and 2.94, respectively). The ^{13}C NMR spectrum showed only nine peaks, as required. These spectra establish the orientation around the central aryl ring. The phenyl (and in **41**, mesityl) orientation is not established but is probably trans.

Campbell and Rees showed that 1-aminobenzotriazole (**1**) reacts with tetraphenylcyclone (**42**) and LTA to give 1,2,3,4-tetraphenylnaphthalene in excellent yield.[2] Entries 15 and 16 show that DABT–LTA can be used similarly. Thus, 1,2,3,4,5,6,7,8-octaphenylanthracene (**43**), mp 415–417 °C, was easily obtained in one step; carbon monoxide loss accompanies the cycloaddition. The lower yield of **43** compared with **45** may be a consequence of low solubilities. The structures of **43** and **45** rest on their method of synthesis, analyses, and spectra.

The results described in this section (Table I) show that DABT–LTA can be a useful reagent for fusing two new rings to an existing benzene ring. A variety of dienes (furans, pyrroles, cisoid dienes, cyclopentadienones) can be used, and they may contain functionality such as esters, ketone, or halogen that may not be compatible with the tetrahaloarene–butyllithium reagent described previously.[4] Thus, DABT–LTA is a useful supplement to this methodology.

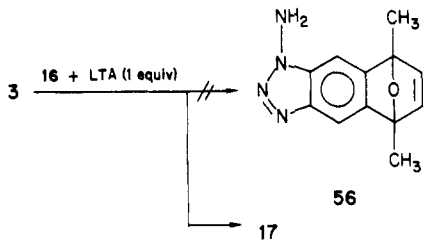
Miscellaneous Observations. It was thought that the utility of DABT–LTA could be extended if two different dienes could be trapped successively to give unsymmetric bisadducts. Thus, a mixture of DABT and 1 equiv of 2,5-dimethylfuran in THF was treated with 1 equiv of LTA. After a suitable time, 1 equiv of furan and a second equivalent of LTA were added, with the hope that the product would be unsymmetric bisadduct **55**. However,



the products isolated after the usual workup were only the two symmetric adducts **15** and **17**, each formed in good yield. The explanation presumably lies in the solubility difference between DABT and its monoadducts such as **56**. That is, **56** is apparently much more soluble in THF than is DABT so that as soon as some **56** is formed, it reacts further with LTA to give bisadduct. Indeed, in a separate experiment, treatment of **3** with 1 equiv each of 2,5-dimethylfuran and LTA gave none of the monoadduct **56**, only bisadduct **17** and recovered, unreacted DABT.

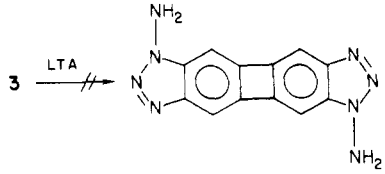
In an attempt to get around this roadblock, the monoamino bistriazole **12** and furan were treated with 1 equiv

(10) Lai, C.-Y. Ph.D. Thesis, Michigan State University, East Lansing, MI, 1981.
(11) Coulson, E. A. *J. Chem. Soc.* **1930**, 1931.
(12) Huisgen, R.; Knorr, R. *Naturwissenschaften* **1961**, *48*, 716. Seidl, H.; Huisgen, R.; Knorr, R. *Chem. Ber.* **1969**, *102*, 904.



of LTA with the thought that the monoadduct could then be aminated and used again. However, no reaction occurred at all, presumably due to the insolubility of **12** in THF (see structure **12a**).

1-Aminobenzotriazole (**1**) is known to give a good yield (83%) of biphenylene when oxidized with LTA in methylene chloride in the absence of any added benzyne-trapping agent.[2] However, similar treatment of DABT with LTA did not give **57** or an oligomer thereof; no identifiable



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product was isolated. Attempts at 2 + 2 cycloadditions using DABT and vinyl acetate[13] or 1,1-dimethoxyethylene[14] also met with failure.

Experimental Section

General Procedures. ^{1}H NMR spectra were measured at 60 MHz (Varian T-60) or at 250 MHz (Bruker WM-250) by using $(CH_3)_4Si$ as an internal standard; chemical shifts are recorded in δ units. ^{13}C NMR spectra were measured at 62.89 MHz (Bruker WM-250). The solvent for all NMR spectra was $CDCl_3$ unless otherwise noted. IR spectra were determined on a Perkin-Elmer Model 167 spectrometer. Mass spectra were measured 70 eV by using a Finnigan 4000 spectrometer with the INCOS system, operated by either Ernest Oliver or Richard Olsen. Melting points, measured on either a Fisher Scientific electrothermal melting point apparatus or a Thomas Hoover Unimelt apparatus, are uncorrected. Microanalyses were performed by either Spang Microanalytical Laboratory, Eagle Harbor, MI, or Guelph Chemical Laboratories, Ltd., Guelph, Ontario, Canada.

1,7-Diacetyl-1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]bistriazole (8). A suspension of 1,5-bis(acetylamino)-2,4-dinitrobenzene (**6**)[7] (12 g, 42.5 mmol) in absolute ethanol (150 mL) was hydrogenated at 60 psi (Parr apparatus) over 3 g of 10% Pd on charcoal. When the reaction was complete (3 h), the mixture was filtered. The filtrate was diluted with 400 mL of water and filtered again to remove all the catalyst.[15] The filtrate was treated with concentrated hydrochloric acid (20 mL) and a solution of sodium nitrite (8.89 g, 127.5 mmol) in water (40 mL) at 0 °C over 30 min. The product was collected by filtration, washed with water, and dried to give 9.6 g (93%) of pure **8**, mp 205 °C (recrystallized from ethyl acetate/hexane as yellow needles; lit.[7] 239 °C; we could not obtain a sample that matched the literature value); ^{1}H NMR δ 9.14 (d, J = 1 Hz, 1 H), 8.87 (d, J = 1 Hz, 1 H), 3.06 (s, 6 H); mass spectrum, m/e (relative intensity) 244 (16), 202 (38), 174 (8), 160 (56), 43 (100).

Amination of 1,5-Dihydrobenzo[1,2-*d*:4,5-*d'*]bistriazole (9) with Hydroxylamine-*O*-sulfonic Acid. Bistriazole **9**[7] (6 g, 37.5 mmol) was dissolved in a solution of KOH (19.8 g, 85% purity) in water (200 mL) at 60 °C. Solid hydroxylamine-*O*-sulfonic acid (16.95 g, 0.15 mol) was added in portions during 1 h, the temperature being maintained at 66–68 °C. The mixture was stirred for 1 h at 65 °C, cooled, and filtered. The alkaline solution was continuously extracted with ether for 72 h. Removal of the ether gave 3.2 g (45%) of a mixture of the 1,5-, 1,7- and 1,6-diamino derivatives **3**, **10**, and **11**. Recrystallization from ethanol gave 1.4 g of pure **3**. Additional product (0.58 g, mixture of **3** and **10**) was obtained from the mother liquor. Concentration of the mother liquor gave 1.2 g of nearly pure (>95%) 1,6-isomer **11**. Integration of peaks at δ 8.24 (**3**), 8.69 and 7.71 (**10**), and 8.59 and 7.96 (**11**) showed that in the crude product before purification the three isomers were present in the ratio 53:12:35.

3: mp 292 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 8.24 (s, Ar H's), 7.18 (s, NH_2 protons); ^{13}C NMR (Me_2SO-d_6) proton decoupled δ 144.16, 131.40, 97.43; proton coupled δ 144.38, 131.65, 99.13, 96.37; mass spectrum, m/e (relative intensity) 190 (16), 162 (14), 133 (27), 118 (19), 105 (100), 78 (52), 63 (45), 51 (66); IR (KBr) 3610, 3386, 3020, 1600, 1520, 1440, 1310, 1040, 923 cm^{-1}. Anal. Calcd for $C_6H_8N_8$: C, 37.90; H, 3.18; N, 58.92. Found: C, 37.96; H, 3.18; N, 58.81.

10: mp 263 °C; ^{1}H NMR (Me_2SO-d_6) δ 8.69 (d, J = 1 Hz, 1 H), 7.71 (d, J = 1 Hz, 1 H), 7.09 (s, 4 H, NH_2); ^{13}C NMR (Me_2SO-d_6) proton decoupled δ 142.93, 133.32, 108.42, 87.43; proton coupled 142.92, 133.26, 109.78, 107.07, 88.83, 86.04; mass spectrum, m/e (relative intensity) 190 (13), 162 (12), 147 (7), 133 (39), 105 (100), 78 (61), 63 (29), 51 (57); IR (KBr) 3320, 3275, 3160, 1635, 1375, 1310, 1278, 1262, 1160, 1090 cm^{-1}; high-resolution mass spectrum calcd for $C_6H_6N_8$ 190.071 54, found 190.071 57.

11: mp 271–273 °C (light tan solid from ethanol); ^{1}H NMR (Me_2SO-d_6) δ 8.59 (d, J = 1 Hz, 1 H), 7.96 (d, J = 1 Hz, 1 H), 7.09 (s, 4 H); ^{13}C NMR (Me_2SO-d_6) δ 143.36, 139.98, 138.87, 132.72, 104.63, 91.08; mass spectrum, m/e (relative intensity) 190 (2), 184 (6), 175 (17), 160 (74), 147 (30), 132 (35), 118 (26), 105 (20), 90 (39), 85 (33), 77 (58), 52 (100); IR (KBr) 3280, 3170, 1600, 1260, 970, 840 cm^{-1}; high-resolution mass spectrum calcd for $C_6H_6N_8$ 190.071 54, found 190.071 94.

The basic aqueous solution recovered from the continuous ether extraction was neutralized with 10% aqueous hydrochloric acid, to precipitate a mixture of monoaminated products **12** and **13** (3.2 g, 48%). Recrystallization from ethanol gave pure **12**, mp >400 °C, as a light tan solid. **12**: ^{1}H NMR (Me_2SO-d_6) δ 8.10 (d, J = 1 Hz, 1 H), 7.65 (d, J = 1 Hz, 1 H), 6.83 (s, 2 H); ^{13}C NMR (Me_2SO-d_6) 146.19, 144.96, 142.18, 130.54, 101.60, 90.66; IR (KBr) 3250, 1620, 1313, 1282, 1180, 1120, 875, 847, 805 cm^{-1}. The crude mixture of **12** and **13** contained a singlet at δ 7.99 considered to be due to the aromatic protons of **13**. Integration of the peaks at δ 8.10 and 7.65 (**12**) against that at δ 7.99 (**13**) gave the ratio of the two monoamines as 79:21.

Amination of 9 with *O*-(2,4-Dinitrophenyl)hydroxylamine. To a solution of **9** (6 g, 37.5 mmol) in dimethylformamide (DMF, 160 mL) under argon was added 3.3 g (2.2 equiv) of 60% sodium hydride (freed of mineral oil by washing with hexane). After 5 min, the mixture was heated with stirring at 90–100 °C for 1 h. After the mixture was cooled to room temperature, 14.93 g (75 mmol) of *O*-(2,4-dinitrophenyl)hydroxylamine[16] in 120 mL of dry DMF was added over 30 min and the mixture was stirred for 1 h and then poured into ether (700 mL). The yellow precipitate (2,4-dinitrophenol) was filtered, and the filtrate was concentrated (vacuo) to give 8.3 g of aminated products contaminated with DMF. An aqueous potassium hydroxide solution (12.6 g in 100 mL of H_2O) was added, and the mixture was stirred at 70 °C for 1 h. The cooled mixture was continuously extracted with ether (72 h) to give a mixture of **3**, **10**, and **11** in the ratio 54:9:37. Several runs on this scale gave yields varying from 1.86 to 4.6 g (26–65%). After extraction, the remaining alkaline solution was neutralized with 10% aqueous hydrochloric acid to recover the monoaminated products for recycling.

Typical Bisannulation Procedure. Preparation of 15. To a mixture of **3** (0.2 g, 1.05 mmol) and furan (0.716 g, 10.5 mmol) in dry THF (50 mL) at room temperature was added in portions 1.03 g (2.32 mmol) of lead tetraacetate (LTA) in 30 mL of THF over 30 min. After 10 min of additional stirring, the lead diacetate was removed by filtration, and the filtrate was diluted with water and extracted with methylene chloride. Combined extracts were

(13) Wasserman, H. H.; Solodar, J. *J. Am. Chem. Soc.* **1965**, *87*, 4002.
(14) Stevens, R. V.; Bisacchi, G. S. *J. Org. Chem.* **1982**, *47*, 2393.
(15) The catalyst was recycled after washing with 20% aqueous potassium hydroxide and then water.
(16) Tamura, Y.; Minamikawa, J.; Sumoto, K.; Fuji, S.; Imeda, M. *J. Org. Chem.* **1973**, *38*, 1239.

washed with saturated $NaHCO_3$ solution and saturated NaCl solution and dried ($MgSO_4$). Removal of the solvent and flash chromatography over silica gel, eluting with $CHCl_3$, gave 0.147 g (80%) of **15** as a mixture of syn/anti isomers (23:77 by NMR integration[5c]), mp 196–203 °C (lit.[5c] syn, mp 191–193 °C; anti, mp 245 °C).

In this experiment, when only 2.1 mmol of furan was used, the yield of bisadduct was essentially unaffected (79%). The reaction was also repeated with inverse addition. To a stirred suspension of 2.57 g (5.79 mmol) of LTA and 1.8 g (26.47 mmol) of furan in 100 mL of dry THF at room temperature under argon was added 0.5 g (2.63 mmol) of **3** suspended in 50 mL of the same solvent over 30 min (no N_2 evolved during the addition). After additional stirring (1 h), 5 mL of ethylene glycol and 500 mL of water were added and the reaction was worked up as usual. Unreacted **3** was recovered quantitatively (0.5 g).

1,4,5,8-Tetramethyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (17). From 0.13 g (0.684 mmol) of DABT, 0.657 g (6.84 mmol) of 2,5-dimethylfuran, and 0.667 g (1.5 mmol) of LTA, there was obtained, following the general procedure, 0.147 g (81%) of **17** as a mixture of two isomers in the ratio of 19:81 as determined by NMR integration (δ 6.78 vs. 6.76): mp 229 °C dec; ^1H NMR δ 6.96 (s, Ar H), 6.78 (s, minor isomer, vinyl), 6.76 (s, major isomer, vinyl), 1.87 (s, major, methyl), 1.86 (s, minor, methyl); ^{13}C NMR δ 151.14, 147.26 (major), 147.43 (minor), 110.62 (major), 110.32 (minor), 88.74, 15.33; mass spectrum, *m/e* (relative intensity) 266 (5), 240 (9), 214 (7), 197 (33), 181 (18), 165 (13), 43 (100); IR (KBr) 3065, 2980, 2935, 1440, 1385, 1305, 1290, 1240, 1135 cm^{-1}.

Conversion of 17 to 1,4,5,8-Tetramethylanthracene (50). A solution of **17** (0.7 g, 2.63 mmol) in absolute ethanol (70 mL) containing 0.03 g of 10% Pd on charcoal was hydrogenated at 60 psi and room temperature over 2 h. To the filtered mixture was added 10 mL of concentrated hydrochloric acid, and the resulting solution was heated at reflux for 1 h, cooled, poured into 200 mL of water, and extracted with methylene chloride (2 × 50 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (2 × 50 mL) and dried ($MgSO_4$). Removal of the solvent (vacuo) gave crude product that was recrystallized from ethyl acetate to give 0.5 g (83%) of **50**: mp 220 °C (lit.[9] 221–222 °C); ^1H NMR δ 8.53 (s, 2 H), 7.15 (s, 4 H), 2.73 (s, 12 H); mass spectrum, *m/e* (relative intensity) 234 (100), 219 (35), 202 (13), 178 (3), 117 (1), 40 (18).

1,4,5,8-Tetraphenyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (19). From DABT (0.293 g, 1.54 mmol), 2,5-diphenylfuran (0.678 g, 3.08 mmol), and LTA (1.50 g, 3.38 mmol) in 100 mL of THF, there was obtained with the general procedure 0.59 g (75%) of **19** as a pale yellow solid (from preparative TLC using 4:1 benzene/hexane as eluent): mp 264–265 °C; ^1H NMR δ 7.67–7.25 (m, 22 H), 6.74 (s, 4 H); ^{13}C NMR δ 151.02, 146.24, 144.49, 135.61, 128.70, 126.93, 113.42, 93.53; mass spectrum, *m/e* (relative intensity) 514 (100), 498 (18), 105 (18); IR (KBr) 3035, 1605, 1495, 1450, 1425, 1350, 1105, 985 cm^{-1}. Anal. Calcd for $C_{38}H_{26}O_2$: C, 88.69; H, 5.09. Found: C, 88.58; H, 5.08.

5,7,12,14-Tetraphenyl-5,7,12,14-tetrahydropentacene 5,14:7,12-Diendoxide (21). From DABT (0.097 g, 0.51 mmol), 1,3-diphenylisobenzofuran (0.276 g, 1.02 mmol), and LTA (0.5 g, 1.12 mmol) in 40 mL of THF, there was obtained, after recrystallization from ethyl acetate/hexane, 0.28 g (88%) of **21** as white crystals: mp 306–308 °C; ^1H NMR δ 8.2–6.85 (m); ^{13}C NMR δ 149.22, 134.85, 128.80, 128.43, 126.61, 125.68, 120.36, 113.49, 113.29, 90.50; mass spectrum, *m/e* (relative intensity) 614 (41), 493 (19), 404 (45), 105 (100), 77 (15); IR (KBr) 3065, 3040, 1600, 1495, 1450, 1425, 1340, 1312 cm^{-1}. Anal. Calcd for $C_{46}H_{30}O_2$: C, 89.88; H, 4.92. Found: C, 89.76; H, 4.85.

***N,N'*-Dimethyl-2,3,6,7-tetramethyl-1,4,5,8-tetraphenyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-Bisimine (23).** From DABT (0.267 g, 1.4 mmol), 2,5-diphenyl-1,3,4-trimethylpyrrole[10] (0.73 g, 2.8 mmol), and LTA (1.37 g, 3.08 mmol) in THF (60 mL), there was obtained after chromatography over silica gel using 2:3 chloroform/benzene as eluent 0.64 g (77%) of pure **23**: mp 273–275 °C from ethyl acetate/hexane; ^1H NMR δ 7.6–7.2 (m, 22 H), 1.8 (s, 12 H), 1.6 (s, 6 H); ^{13}C NMR δ 130.52, 130.06, 130.02, 129.04, 128.35, 128.02, 127.72, 31.47, 29.66, 12.70; mass spectrum, *m/e* (relative intensity) 596 (2), 542 (1), 424 (2), 118 (100), 56 (33); IR (KBr) 3065, 3035, 2940, 2860, 1600, 1495, 1450, 1295, 1155 cm^{-1}. Anal. Calcd for $C_{44}H_{40}N_2$: C, 88.55; H, 6.76; N, 4.69. Found: C, 88.23; H, 6.63; N, 4.58.

***N,N'*-Dimethyl-1,2,3,4,5,6,7,8-octaphenyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-Bisimine (25).** From DABT (0.308 g, 1.62 mmol), *N*-methyl-2,3,4,5-tetraphenylpyrrole[17] (1.25 g, 3.24 mmol), and LTA (1.58 g, 3.56 mmol) in 100 mL THF, there was obtained, after recrystallization from benzene, 1.2 g (88%) of **25** as a white solid: mp 205–207 °C; ^1H NMR δ 7.8–6.6 (m), 2.12 (br s); ^{13}C NMR δ 134.58, 131.37, 130.98, 128.46, 128.07, 127.66, 127.31, 127.03, 126.96, 126.85, 126.62, 77.14, 31.46; mass spectrum, *m/e* (relative intensity) 844 (M^+, not observed), 399 (3), 385 (8), 178 (100); IR (KBr) 3060, 3030, 2950, 1605, 1485, 1443, 1325, 1290, 1155 cm^{-1}. Anal. Calcd for $C_{64}H_{48}N_2$: C, 90.96; H, 5.72; N, 3.31. Found: C, 90.85; H, 5.70; N, 3.25.

1,4:8,11-Dimethano-1,2,3,4,5,7,8,9,10,11,12,14-dodecahydropentacene (27). From DABT (0.28 g, 1.47 mmol), 2,3-bis(methylene)bicyclo[2.2.1]heptane[17] (0.39 g, 3.25 mmol), and LTA (1.5 g, 3.38 mmol) in 100 mL THF, there was obtained after recrystallization from ethyl acetate/hexane 0.43 g (93%) of **27** as a mixture of syn and anti isomers, white solid: mp 245–250 °C; ^1H NMR δ 7.56 (s, minor), 7.43 (s, minor), 6.96 (s, major), 3.35 (s, 8 H), 2.70 (m, 4 H), 1.80–0.90 (m, 12 H); mass spectrum, *m/e* (relative intensity) 314 (31), 286 (13), 253 (10), 245 (6), 229 (6), 217 (19), 179 (13), 129 (12), 115 (23); IR (KBr) 2942, 2855, 2810, 1428, 1277, 1100 cm^{-1}; high-resolution mass spectrum calcd for $C_{24}H_{26}$ 314.203 44, found 314.203 68. Integration of the singlets at δ 7.56 and 7.43 vs. the singlet at δ 6.96 gave a syn/anti ratio of 9:91.

2,3,6,7-Tetrakis(ethoxycarbonyl)-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (29). DABT (0.68 g, 3.57 mmol), diethyl 3,4-furandicarboxylate[18] (1.52 g, 7.14 mmol), and LTA (3.4 g, 7.67 mmol) in 200 mL THF gave a yellow solid which was chromatographed on silica gel with 1:1 ethyl acetate/petroleum ether as eluent to give 0.71 g (40%) of **29**: mp 188–190 °C recrystallized from ethyl acetate; ^1H NMR δ 7.45 (s, 2 H), 5.90 (s, 4 H), 4.30 (q, J = 7 Hz, 8 H), 1.35 (t, J = 7 Hz, 12 H); ^{13}C NMR δ 162.50, 151.31, 146.52, 115.76, 85.18, 61.54, 14.07; mass spectrum, *m/e* (relative intensity) 498 (20), 425 (7), 381 (51), 350 (91), 328 (30), 254 (100), 226 (45), 158 (27), 139 (27); IR (KBr) 2983, 1695, 1628, 1465, 1442, 1395, 1290, 1215, 1125 cm^{-1}; high-resolution mass spectrum calcd for $C_{26}H_{26}O_{10}$ 498.152 58, found 498.152 82.

2,3,6,7-Tetrakis(ethoxycarbonyl)-1,4,5,8-tetramethyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (31). DABT (0.65 g, 3.42 mmol), diethyl 2,5-dimethylfuran-3,4-dicarboxylate[19] (1.642 g, 6.84 mmol), and LTA (3.34 g, 7.52 mmol) in 100 mL of THF gave crude **31** which was flash chromatographed over silica gel with 1:1 chloroform/hexane as eluent to give 1.26 g (67%) of one isomer of **31**, colorless needles from ethyl acetate: mp 233–236 °C; ^1H NMR δ 7.19 (s, 2 H), 4.18 (q, J = 7 Hz, 8 H), 1.95 (s, 12 H), 1.29 (t, J = 7 Hz, 12 H); ^{13}C NMR δ 163.00, 153.14, 149.81, 112.91, 112.32, 61.36, 61.24, 14.02; mass spectrum, *m/e* (relative intensity) 554 (10), 512 (9), 466 (8), 378 (41), 310 (5), 296 (28), 267 (9), 214 (16), 43 (100); IR (KBr) 2990, 2940, 1700, 1628, 1445, 1385, 1370, 1310, 1260, 1145 cm^{-1}. Anal. Calcd for $C_{30}H_{34}O_{10}$: C, 64.97; H, 6.18. Found: C, 64.86; H, 6.15.

1,5-Bis(methoxycarbonyl)-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (33). DABT (1.0 g, 5.26 mmol), methyl 2-furoate[18] (1.46 g, 11.6 mmol), and LTA (5.13 g, 11.6 mmol) in 100 mL THF gave crude **33** which was triturated with pentane (10 mL) and then ether (20 mL). Chromatography over silica gel with 1:3 ethyl acetate/hexane as eluent gave 0.8 g (47%) of pure **33**, white crystals from ethyl acetate: mp 240–242 °C; ^1H NMR δ 7.35 (s, 2 H, Ar), 7.10 (s, 2 H, vinyl), 7.08 (s, 2 H, vinyl), 5.74 (s, 2 H, bridgehead), 4.07 (s, 6 H, methyl); ^{13}C NMR δ 168.05, 147.07, 144.05, 142.84, 113.96, 96.11, 82.47, 66.05, 52.82; mass spectrum, *m/e* (relative intensity) 326 (29), 300 (25), 274 (15), 239 (25), 213 (100), 179 (34), 152 (43), 126 (15); IR (KBr) 3130, 3095, 3040, 2960, 1760, 1445, 1350, 1200, 1150 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_6$: C, 66.26; H, 4.32. Found: C, 66.23; H, 4.40.

Aromatization of 33. Bisadduct **33** (0.21 g, 0.648 mmol) in

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(18) Aldrich Chemical Co.
(19) Gardner, J. A.; Rydon, H. N. *J. Chem. Soc.* **1938**, *45*. Knorr, L. *Chem. Ber.* **1884**, *17*, 2863.

ethanol (50 mL) was hydrogenated with 20 mg of 10% Pd on charcoal for 2 h at room temperature and 60 psi of hydrogen. The catalyst was removed by filtration, and the filtrate was refluxed with 3 mL of concentrated hydrochloric acid for 12 h. The cooled mixture was poured into water (500 mL) and extracted with methylene chloride (3 × 50 mL), and the combined extracts were washed with saturated aqueous $NaHCO_3$ (3 × 100 mL), dried ($MgSO_4$), and concentrated in vacuo to give 0.22 g (96%) of saturated diethyl ester **53**. This ester (0.22 g, 0.614 mmol) was refluxed with 3 mL of concentrated hydrochloric acid and 30 mL of acetic anhydride for 2 h to afford 0.17 g (81%) of diethyl anthracene-1,5-dicarboxylate (**54**): mp 185 °C (lit.[11] 185 °C); ^1H NMR δ 9.67 (s, 2 H), 8.31 (m, 2 H), 7.50 (m, 4 H), 4.53 (q, J = 7 Hz, 4 H), 1.51 (t, J = 7 Hz, 6 H).

1,2,5,6-Tetrakis(methoxycarbonyl)-3,4,7,8-tetraphenyl-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (35). The general procedure was followed, but the reaction was carried out at reflux temperature. DABT (0.4 g, 2.1 mmol), dimethyl 4,5-diphenylfuran-2,3-dicarboxylate[20] (1.41 g, 4.2 mmol), and LTA (2.05 g, 4.62 mmol) in 100 mL THF gave a crude product which was recrystallized from chloroform to give 1.22 g (78%) of one isomer of **35**, colorless needles: mp 283–287 °C; ^1H NMR δ 8.11 (s, 2 H), 7.45–7.10 (m, 20 H), 3.97 (s, 6 H), 3.61 (s, 6 H); mass spectrum, m/e (relative intensity) 746 (trace), 586 (5), 426 (28), 129 (29), 105 (100); IR (KBr) 3060, 2960, 1775, 1725, 1445, 1343, 1205, 1165, 1029 cm^{-1}. Anal. Calcd for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4.59. Found: C, 73.79; H, 4.70.

When this reaction was carried out at room temperature, no **35** was formed and diene **34** was recovered quantitatively.

2,6-Dibromo-1,4,5,8-tetrahydroanthracene 1,4:5,8-Diendoxide (37). From DABT (0.92 g, 4.842 mmol), 3-bromofuran[18] (1.565 g, 10.6 mmol), and LTA (5.15 g, 11.6 mmol) in 100 mL of THF, there was obtained crude **37** which was recrystallized from chloroform to give 1.23 g (69%) of a single isomer of **37** as white crystals: mp 115 °C dec; ^1H NMR δ 7.32 (s, 2 H), 6.96 (d, J = 2 Hz, 2 H), 5.69 (br s, 2 H), 5.38 (d, J = 2 Hz, 2 H); mass spectrum, m/e (relative intensity) 368 (20), 289 (7), 287 (6), 262 (14), 180 (37), 152 (100), 126 (16); IR (KBr) 3090, 3020, 1573, 1335, 1237, 1210, 1122, 1028, 985 cm^{-1}. Anal. Calcd for $C_{14}H_8Br_2O_2$: C, 45.69; H, 2.19. Found: C, 45.55; H, 2.27.

2,6-Dimethyl-3,7-diphenyl-2,3,6,7-tetrahydrobenzo[1,2-*d*:4,5-*d'*]diisoxazole (39). DABT (0.504 g, 2.653 mmol), *N*-methyl-α-phenylnitrone[21] (0.717 g, 5.31 mmol), and LTA (2.6 g, 5.86 mmol) in 100 mL of THF gave a yellow solid which was flash chromatographed on silica gel with 3:1 ethyl acetate/hexane as eluent to give 0.83 g (91%) of **39**, white crystals, mp 142–143 °C; ^1H NMR δ 7.38–7.33 (m, 10 H, phenyl), 6.42 (s, 2 H, central Arom ring), 5.04 (s, 2 H, benzylic), 2.94 (s, 6 H, *N*-methyl); ^{13}C NMR δ 151.05, 129.88 (2 overlapped signals), 128.62, 128.26, 127.82, 103.53, 77.00, 45.94; mass spectrum, m/e (relative intensity) 344 (100), 329 (31), 314 (83), 286 (24), 267 (49), 115 (63); IR (KBr) 3095, 3040, 2965, 2880, 2830, 1460, 1340, 1165, 1145 cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.79; H, 5.85; N, 8.10.

***N*-Methyl-α-(2,4,6-trimethylphenyl)nitrone (40).** Freshly distilled mesitaldehyde (10 g, 67.56 mmol) was added to a mixture of *N*-methylhydroxylamine hydrochloride (7.05 g, 8.44 mmol) in 150 mL of methylene chloride. Sodium bicarbonate (20 g, 238 mmol) was added and the mixture was heated at reflux for 12 h. The cooled mixture was filtered to remove the sodium bicarbonate (which was washed with methylene chloride) and the combined organic layers were evaporated at reduced pressure to give 11 g (92%) of crude **40**. The product was recrystallized from ethyl acetate: mp 172–173 °C; ^1H NMR δ 7.50 (s, 1 H, vinyl), 6.84 (s, 2 H, Ar), 3.82 (s, 3 H, *N*-CH_3), 2.24 (s, 3 H, CH_3), 2.26 (s, 6 H, CH_3); ^{13}C NMR δ 138.82, 136.99, 135.08, 127.93, 125.46, 52.77, 20.71, 19.36; mass spectrum, m/e (relative intensity) 177 (9), 162 (100), 145 (24), 115 (10); IR (KBr) 3080, 2910, 1570, 1440, 1410, 1395, 1370, 1180, 1038 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.41; H, 8.78; N, 7.81.

2,6-Dimethyl-3,7-bis(2,4,6-trimethylphenyl)-2,3,6,7-tetrahydrobenzo[1,2-*d*:4,5-*d'*]diisoxazole (41). DABT (0.227 g, 1.194 mmol), nitrone **40** (0.42 g, 2.39 mmol), and LTA (1.16 g, 2.62 mmol) in 50 mL THF gave a crude product which was flash chromatographed on silica gel using 3:2 ether/chloroform as eluent to give 0.40 g (78%) of **41** as a white solid: mp 239–241 °C; ^1H NMR δ 6.85 (s, 4 H, mesityl Ar), 6.14 (s, 2 H, central ring Ar), 5.66 (s, 2 H, benzylic), 2.96 (s, 6 H, *N*-CH_3), 2.30 (br s, 12 H), 2.27 (s, 6 H); ^{13}C NMR δ 151.22, 141.70, 139.05, 138.05, 130.12, 130.09, 129.17, 101.38, 72.59, 46.45, 20.83; mass spectrum, m/e (relative intensity) 428 (100), 413 (10), 384 (84), 309 (19), 160 (3), 133 (21); IR (KBr) 3010, 2960, 2920, 2860, 1610, 1475, 1440, 1315, 1160 cm^{-1}; high-resolution mass spectrum calcd for $C_{28}H_{32}N_2O_2$ 428.246 36, found 428.239 01.

1,2,3,4,5,6,7,8-Octaphenylanthracene (43). From DABT (0.018 g, 0.0945 mmol), 1,2,3,4-tetraphenylcyclopentadienone (0.0728 g, 0.190 mmol), and LTA (0.093 g, 0.21 mmol) in 300 mL of THF at reflux, there was obtained, after recrystallization from benzene, 0.041 g (56%) of **43** as a yellow solid: mp 415–417 °C; ^1H NMR (Me_2SO-d_6, 110 °C) δ 7.33 (s, 2 H), 7.1–6.7 (m, 40 H); mass spectrum, m/e (relative intensity) 786 (71), 105 (9), 44 (100); IR (KBr) 3080, 3055, 3030, 1595, 1490, 1443, 1032 cm^{-1}; high-resolution mass spectrum calcd for $C_{62}H_{42}$ 786.3284, found 786.3313.

1,4,5,8-Tetrakis(methoxycarbonyl)-2,3,6,7-tetraphenylanthracene (45). DABT (0.20 g, 1.052 mmol), 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone[22] (0.732 g, 2.10 mmol), and LTA (1.026 g, 2.31 mmol) in 50 mL of THF gave a crude grey product that was flash chromatographed over silica gel eluting with 2:1 chloroform/hexane to give 0.70 g (93%) of **45** as yellow crystals from ethyl acetate: mp 375–376 °C; ^1H NMR δ 8.55 (s, 2 H), 7.25–7.07 (m, 20 H), 3.65 (s, 12 H); ^{13}C NMR δ 168.75, 138.37, 138.13, 133.37, 130.40, 129.99, 128.34, 126.66, 52.11; mass spectrum, m/e (relative intensity) 714 (100), 683 (1), 619 (3), 504 (5), 476 (8), 325 (48), 237 (38); IR (KBr) 3060, 3025, 2950, 1721, 1434, 1360, 1226, 1092, 1041 cm^{-1}. Anal. Calcd for $C_{46}H_{34}O_8$: C, 77.30; H, 4.79. Found: C, 77.33; H, 4.88.

1,7-Diamino-1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]bistriazole (10) as a 1,4-Benzadiyne Equivalent. 1,7-Diaminobistriazole **10** (0.31 g, 1.63 mmol), 2,5-dimethylfuran (0.35 g, 3.64 mmol), and LTA (1.59 g, 3.58 mmol) in 100 mL of THF, using the same general procedure as with **3**, gave crude bisadduct **17** that was chromatographed over silica gel by using 1:1 chloroform/ether as eluent to give 0.35 g (80%) of pure **17**, mp 229 °C. The physical properties and syn:anti ratio were identical with those obtained by using **3** as the 1,4-benzadiyne equivalent.

Attempted Stepwise Annulation. To a stirred mixture of DABT (0.29 g, 1.5 mmol) and 2,5-dimethylfuran (0.145 g, 1.5 mmol) in 75 mL of dry THF was added over 30 min at room temperature in portions LTA (0.665 g, 1.5 mmol) suspended in 30 mL of THF. After LTA addition was complete, furan (0.102 g, 1.5 mmol) was added followed by another 0.665 g (1.5 mmol) of LTA in 30 mL of THF (30 min). The mixture was stirred an additional 10 min. The lead diacetate was removed by filtration, and the reaction was worked up as usual. Chromatography on silica gel using 2:1 chloroform/hexane as eluent gave first 0.12 g of **17** followed by 0.11 g of **15**. No cross-addition product was observed.

Reaction of 3 with 1 Equiv Each of 16 and LTA. To a stirred mixture of **3** (0.37 g, 1.947 mmol) and 2,5-dimethylfuran (0.187 g, 1.947 mmol) in 100 mL of THF at room temperature was added in portions over 30 min LTA (0.86 g, 1.947 mmol) suspended in 20 mL of THF. After the usual workup, the crude product was chromatographed on silica gel using 1:1 chloroform/ether as eluent to give 0.18 g (70%) of **17** with properties as described above.

Attempted Reaction of 12 with 16 and LTA. To a stirred mixture of the 1-aminobis(triazole) (**12**) (0.3 g, 1.71 mmol) and 2,5-dimethylfuran (0.8 g, 8.32 mmol) in 150 mL of dry THF at reflux under argon was added LTA (1.67 g, 1.71 mmol) in portions over 30 min. The usual workup gave a tan residue shown by NMR to be recovered **12**.

Reaction of 3 with LTA in the Absence of a Trapping Diene. LTA (0.7 g, 1.58 mmol) in 30 mL of THF was added in portions over 20 min to a stirred suspension of **3** (0.3 g, 1.58 mmol)

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(21) Dicken, C. M.; DeShong, P. *J. Org. Chem.* **1982**, *47*, 2047.
(22) White, D. M. *J. Org. Chem.* **1974**, *39*, 1951.

in 50 mL of THF under argon at room temperature. The usual workup gave a brown polymeric powder from which no pure product could be isolated.

Attempted 2 + 2 Cycloadditions of DABT. LTA (3.1 g, 6.95 mmol) in 50 mL of dry THF was added in portions over 30 min to a stirred suspension of DABT (0.6 g, 3.16 mmol) and 1,1-dimethoxyethene[23] (0.62 g, 6.95 mmol) in 100 mL of THF (argon, room temperature). Lead diacetate was removed by filtration. Workup led to recovery of the unreacted 1,1-dimethoxyethene (0.57 g, 95%). Similar results were obtained with vinyl acetate.

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Registry No. **3**, 91477-70-2; **6**, 42783-40-4; **8**, 54807-06-6; **9**, 7221-63-8; **10**, 100367-17-7; **11**, 100367-18-8; **12**, 100367-19-9; **13**, 100367-20-2; **14**, 110-00-9; *anti*-**15**, 87207-46-3; *syn*-**15**, 87248-22-4; **16**, 625-86-5; *anti*-**17**, 100367-21-3; *syn*-**17**, 100483-34-9; **18**, 955-83-9; **19**, 100430-68-0; **20**, 5471-63-6; **21**, 100367-22-4; **22**, 24956-46-5; **23**, 100367-23-5; **24**, 2406-01-1; **25**, 100367-24-6; **26**, 36439-78-8; *anti*-**27**, 100367-25-7; *syn*-**27**, 100483-35-0; **28**, 30614-77-8; **29**, 100367-26-8; **30**, 19434-69-6; **31**, 100430-69-1; **32**, 611-13-2; **33**, 91477-72-4; **34**, 1048-83-5; **35**, 91477-73-5; **36**, 22037-28-1; **37**, 91477-75-7; **38**, 3376-23-6; **39**, 91477-76-8; **40**, 41106-03-0; **41**, 100367-27-9; **42**, 479-33-4; **43**, 100367-30-4; **44**, 16691-79-5; **45**, 91477-71-3; **50**, 2960-97-6; **53**, 100367-28-0; **54**, 100367-29-1; mesitaldehyde, 487-68-3.

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Trapping Reactive Intermediate Carbanions Generated by Lithium Tetramethylpiperidide Treatment of 7-Oxabicyclo[2.2.1]heptenes in the Presence of Trimethylsilyl Chloride

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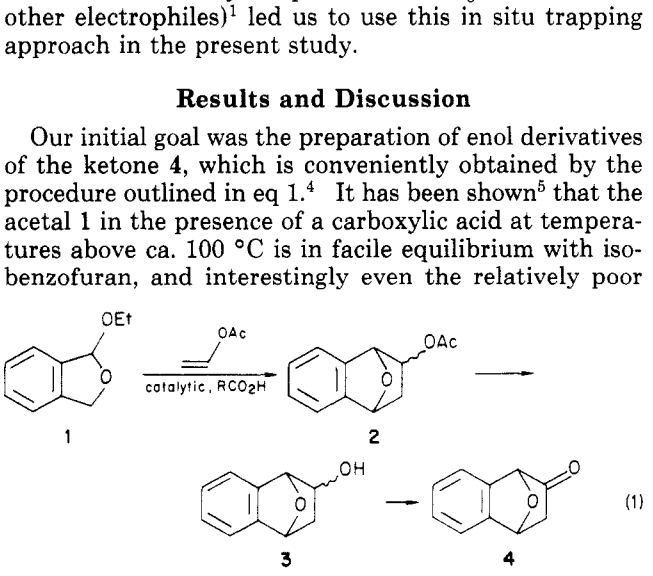
Standard strong base induced methods for preparing enol ether derivatives fail with oxabicyclic ketone **4**, giving instead an aldol product. The trimethylsilyl enol ether **5** can be prepared by addition of lithium tetramethylpiperidide (LTMP) to a mixture of **4** and trimethylsilyl chloride (Me_3SiCl) in THF solvent. Further reactions of **5** are observed under these conditions, leading to proximal bridgehead and vinyl trimethylsilylated products. These reactions appear to be general for benzannulated 7-oxabicyclo[2.2.1]heptenes; i.e., the enol ether function, while exerting a directing influence, is not needed for the reaction. Bridgeheads are somewhat more reactive than vinyl sites. Silylation of 9,10-dihydro-9,10-epoxyanthracene (**15**), which has $pK_a \geq 40$, occurs readily, demonstrating the utility of this in situ LTMP/Me_3SiCl approach for the trapping of very small equilibrium amounts of carbanions (reactive intermediates.) The benz[*a*]anthracene analogue **18** is similarly mono- and bis(trimethylsilylated), with a modest level of regioselection for the 7-position.

Some unusual reactions of substituted 7-oxabicyclo-[2.2.1]heptenes have been discovered by treatment of these substrates, *in the presence of trimethylsilyl chloride* (*Me_3SiCl*), with lithium tetramethylpiperidide (LTMP). The recent finding by Martin and co-workers that LTMP is at least moderately compatible with Me_3SiCl (and a few other electrophiles)[1] led us to use this in situ trapping approach in the present study.

Results and Discussion

Our initial goal was the preparation of enol derivatives of the ketone **4**, which is conveniently obtained by the procedure outlined in eq 1.[4] It has been shown[5] that the acetal **1** in the presence of a carboxylic acid at temperatures above ca. 100 °C is in facile equilibrium with isobenzofuran, and interestingly even the relatively poor dienophile vinyl acetate is efficiently trapped under these conditions (twofold exess of dienophile, PhCl solvent, sealed tube, 130 °C for 56 h) to afford **2** (85% endo, 15%



(1)

† Formerly known as Bagher Mir-Mohamad-Sadeghy.

(1) Krizan, T. D.; Martin, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 6155. Taylor, S. L.; Lee, D. Y.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. These authors noted NMR evidence for the rapid formation of a complex (−78 °C) of LTMP and Me_3SiCl, which was nonetheless suitable for the deprotonations described. The extent of compatibility of LTMP/Me_3SiCl (i.e., stability vs. self-destructive reactions) is not completely understood. One might expect deprotonation of Me_3SiCl to occur, based on a study of the course of the reaction of this material with *tert*-butyllithium.[2] The Martin group studies suggest somewhat more efficient utilization of the reagents when mixed at low temperature, but successful ambient temperature applications are also reported. Very recently, Eaton and Castaldi[3] have described the in situ use of $HgCl_2$ to trap LTMP-generated carbanionic species in a cubane derivative.

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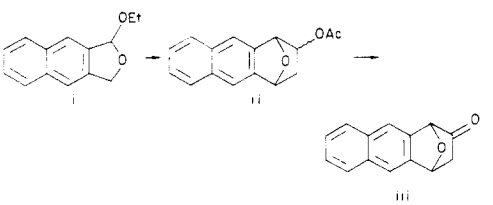
(4) This approach is also useful for preparing the benzo[*f*]isobenzofuran analogue, viz;



Cycloadduct ii (endo, exo mixture) was isolated in 79% yield, with subsequent methanolysis and Jones oxidation giving iii (74%); unpublished work of S. Mirsadeghi.

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