extracted with ether. The ether layer was analyzed by GC on a 5% Carbowax 1540 on Chromosorb W AW DMCS column: yield, 91%.

Homologation of 2-(1-Hexyl)-1,3-dioxaborinane Using CH_2Cl_2 and *sec*-BuLi. A solution of 2-(1-hexyl)-1,3-dioxaborinane (0.85 g, 5 mmol) and CH_2Cl_2 (0.45 mL, 7 mmol) in THF (5 mL) was cooled to −78 °C (dry ice–acetone bath). To this was added chilled *sec*-BuLi (5 mL, 7 mmol, 1.4 M solution in cyclohexane) dropwise from a syringe (bringing the tip of the syringe needle very close to the surface of the cold solution), and the reaction mixture was stirred at −78 °C for 0.5 h. It was then rapidly brought to room temperature and refluxed at 65 °C for 1.5 h. The ^{11}B NMR spectrum of the reaction mixture revealed the formation of 2-(1-chloro-1-heptyl)-1,3-dioxaborinane (δ +27). The intermediate α-chloroboronic ester was reduced without isolating with KIPBH (7 mL, 7 mmol, 1 M solution in THF) at 25 °C for 0.5 h, as indicated by the ^{11}B NMR analysis (δ +30). This was then oxidized with alkaline H_2O_2, and the oxidation product was analyzed by GC: yield; 86%.

Characterization of the Homologated Products by Oxidation. The other boronic esters homologated (Table II) were not isolated, but characterized by oxidation with alkaline hydrogen peroxide. The alcohols produced were characterized by GC examination and the yield established by analysis of the alcohols (Table II).

Acknowledgment. Financial support from the National Science Foundation (Grant CHE 8414171) is gratefully acknowledged.

Registry No. $LiCHCl_2$, 2146-67-0; CH_2Cl_2, 75-09-2; $BrCH_2Cl$, 74-97-5; ICH_2Cl, 593-71-5; 2-(1-heptyl)-1,3-dioxaboronane, 101031-41-8; 2-(benzyl)-1,3-dioxaboronane, 62930-28-3; 2-(3-hexyl)-1,3-dioxaboronane, 86290-28-0; 2-(2,3-dimethyl-1-butyl)-1,3-dioxaboronane, 98303-39-0; 2-(cyclopentylmethyl)-1,3-dioxaboronane, 101031-43-0; 2-(cyclohexylmethyl)-1,3-dioxaboronane, 102746-89-4; 2-((2-bicyclo[2.2.1]heptyl)methyl)-1,3-dioxaboronane, 102746-90-7; 2-((*trans*-2-methylcyclopentyl)-methyl)-1,3-dioxaboronane, 98303-41-4; 2-((*trans*-2-methylcyclohexyl)methyl)-1,3-dioxaboronane, 98303-42-5; 2-(2,2,3-trimethyl-1-butyl)-1,3-dioxaboronane, 101031-44-1; 2-[((1α,2α,3β,5α)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl)methyl]-1,3-dioxaboronane, 102849-29-6; 2-(1-hexyl)-1,3-dioxaboronane, 86290-24-6; 2-(phenyl)-1,3-dioxaboronane, 4406-77-3; 2-(3-methyl-2-butyl)-1,3-dioxaboronane, 98303-38-9; 2-(cyclopentyl)-1,3-dioxaboronane, 30169-74-5; 2-(2-bicylco[2.2.1]-heptyl)-1,3-dioxaboronane, 102746-91-8; 2-(cyclohexyl)-1,3-dioxaboronane, 30169-75-6; 2-(*trans*-2-methylcyclopentyl)-1,3-dioxaboronane, 86290-31-5; 2-(*trans*-2-methylcyclohexyl)-1,3-dioxaboronane, 98392-60-0; 2-(2,3-dimethyl-2-butyl)-1,3-dioxaboronane, 63689-74-7; 2-((1α,2α,3β,5α)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl)-1,3-dioxaboronane, 102849-30-9; 2-(1-chloro-1-heptyl)-1,3-dioxaboronane, 102746-92-9; 2-(α-chlorobenzyl)-1,3-dioxaboronane, 102746-93-0.

Cycloadducts of Arynes with 1,3-Bis(trimethylsilyl)naphtho[1,2-*c*]furan: Formation of Novel Polycyclic Aromatic Derivatives and Related Reactions

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A recently developed procedure for the preparation of trimethylsilylated isobenzofurans and the use of these materials in cycloaddition reactions has been extended to an isonaphthofuran analogue. The 1,3-bis(trimethylsilyl)naphtho[1,2-c]furan (7) has been isolated; its reaction with maleic anhydride at room temperature is rapid and readily reversible as shown by endo to exo cycloadduct interconversion. The failure of 7 to give cycloadduct with 2-butenolide indicates that it is less reactive than the parent naphtho[1,2-c]furan. In situ generation and cycloaddition reactions with various arynes (benzyne, 4-methylbenzyne, 3,4-pyridyne, 9,10-phenanthrolyne, 1,2-naphthalyne, and 2,3-naphthalyne) are described. The three unsymmetrical arynes all give mixtures of cycloadducts indicative of negligible regioselectivity in Diels–Alder reactions with 7; thus, in spite of possible steric hindrance the reaction with 1,2-naphthalyne gives a 1:1 mixture of dibenz[a,h]- and dibenz[a,j]anthracene derivatives. In contrast, the reaction of 1-ethoxy-3-(trimethylsilyl)naphtho[1,2-c]furan (21) with 1,2-naphthalyne exhibits modest regioselectivity, favoring the formation of the dibenz[a,j]anthracene derivative. Various reactions of the cycloadducts are described.

A recently developed procedure[1] allows the one-flask conversion of 1,3-dihydro-1-ethoxyisobenzofuran to 1,3-bis(trimethylsilyl)isobenzofuran, and subsequent cycloaddition with in situ generated arynes, to afford novel polycyclic materials. This paper describes the extension of this methodology to the naphtho[1,2-c]furan (benzo[e]isobenzofuran) system, which has been shown[2] to be accessible through lithium dialkylamide induced 1,4-elimination reactions. We were interested in the feasibility of forming the bis(trimethylsilyl) derivative, its relative reactivity, whether cycloaddition reactions with arynes would occur, and whether these would exhibit regioselectivity.

Results and Discussion

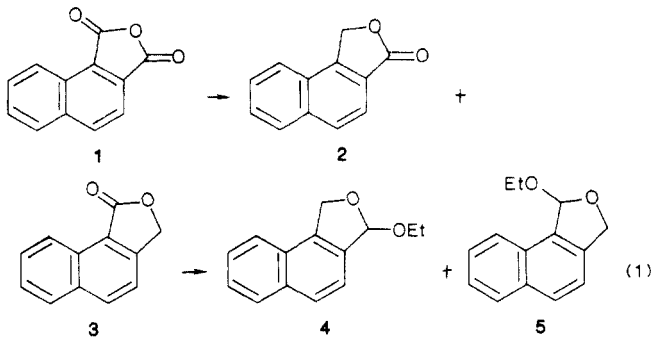
The 1,2-naphthalic anhydride (1) used in this study was prepared by the method of Newman and co-workers.[3] Sodium borohydride reduction of 1 gave a mixture (75%) of the lactones 2 and 3 in nearly equal amounts. This mixture was O-ethylated and then reduced as described previously for the individual lactone isomers[2] to provide a mixture of the acetals 4 and 5 (63%) as outlined in eq 1. Since both 4 and 5 serve as precursors to naphtho[1,2-c]furan (6), this mixture of isomers was used without separation in further applications. Thus, treatment with

(1) (a) Crump, S. L.; Netka, J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 2746. (b) Netka, J.; Crump, S. L.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1189. (c) Camenzind, R.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1914.

(2) Cornejo, J. J.; Ghodsi, S.; Johnson, R. D.; Woodling, R.; Rickborn, B. *J. Org. Chem.* **1983**, *48*, 3869.

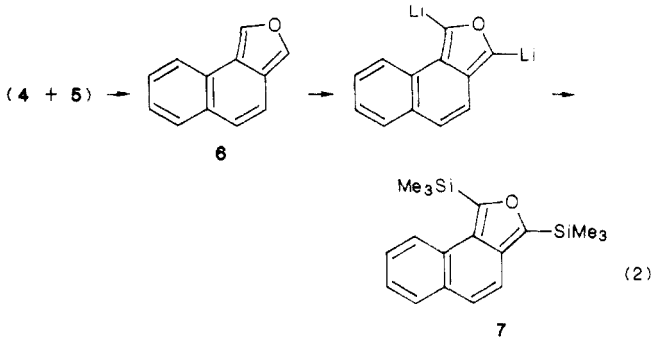
(3) Newman, M. S.; Dhawan, B.; Hashem, M. M.; Khanna, V. K.; Springer, J. M. *J. Org. Chem.* **1976**, *41*, 3925.

0022-3263/86/1951-3155$01.50/0



(1)

3 equiv of *n*-butyllithium and a catalytic amount[4] of lithium dialkylamide, followed by trimethylsilyl chloride, caused the conversion of (4 + 5) to 1,3-bis(trimethylsilyl)naphtho[1,2-*c*]furan, **7**, as shown in eq 2. This pro-

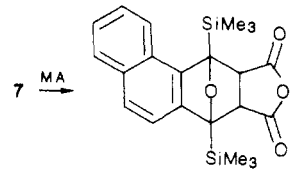


(2)

cedure is efficient, indicating that all of the individual reaction steps including the introduction of the trimethylsilyl group into the "bay" position occur without difficulty. As expected on the basis of the properties of **6**, **7** could be isolated by column chromatography and was obtained as a waxy solid, mp 38–42 °C. Solid **7** has been stored under N_2 at −10 °C for several months without evidence of decomposition or polymerization; however, material exposed to the atmosphere at ambient temperature began to yellow after several hours.

The reactivity of **7** as a diene in cycloaddition reactions was addressed by treatment with maleic anhydride (MA) in $CDCl_3$ at room temperature. The reaction was complete within the few minutes required to obtain an NMR spectrum, giving cycloadduct **8** as a mixture of endo and exo isomers. Stereochemical assignments for these isomers (not isolated) were made by attributing the more downfield aliphatic absorption to the exo ring fusion protons of the endo anhydride, based on comparison with the bridgehead protonated analogues generated from **6** and MA.[2] The latter species undergoes slow (days) endo to exo interconversion at 61 °C; although the equilibrium position was not established at this temperature, at 131 °C the exo isomer is strongly favored.[2] Cycloadduct **8** exhibits several interesting differences in behavior; the Me_3Si groups cause a greater kinetic preference for endo.cycloadduct formation, and the interconversion of the isomers occurs even at room temperature at an appreciable rate (see data in eq 3). No further change was observed after 3.5 h, indicating that equilibrium is attained at the endo/exo ratio of 32/68 for this system at 25 °C. Both the greater endo kinetic preference and diminished equilibrium exo preference of the silylated material may be due to steric interactions of the Me_3Si groups and the dienophile.

The poorer dienophile 2-butenolide failed to react with **7** when examined over a period of 10 days at room temperature ($CDCl_3$ solvent; decomposition of **7** was noted



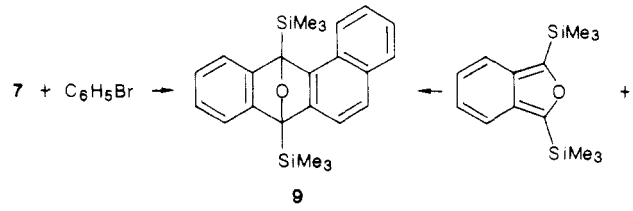
(3)

time	% endo	% exo
init	90	10
0.3 h	69	31
3.5 h	32	68

after several days). Since **6** gives a substantial yield of cycloadduct under similar conditions (100 h at room temperature is required[2]), it is clear that **7** is less reactive than **6** in this cycloaddition, and presumably this feature extends to other dienophiles.

Our primary interest in **7** was its potential for reactions with arynes. As noted in the earlier study of this methodology, use of the bis(trimethylsilyl) derivative allows the formation of arynes by lithium tetramethylpiperidide (LTMP) induced dehydrohalogenation of aryl halides, thereby greatly increasing the generality of the sequence. This approach does not give cycloadduct when the unprotected isobenzofuran is used, and this failure is associated with rapid deprotonation (lithiation) of the 1- and 3-positions by the strong base. Although this point was not specifically addressed in the present work, it is assumed that the same feature would prevent the use of the LTMP method for cycloadduct formation from **6**.

When **7** was formed as described above (without isolation) and treated with bromobenzene and LTMP, the benz[*a*]anthracene derivative **9** was formed and isolated in 67% yield; this product is identical with that formed from 1,3-bis(trimethylsilyl)isobenzofuran and 1,2-naphthalyne as described previously[1a] (eq 4). The protio-



1-$BrC_{10}H_7$ (4)

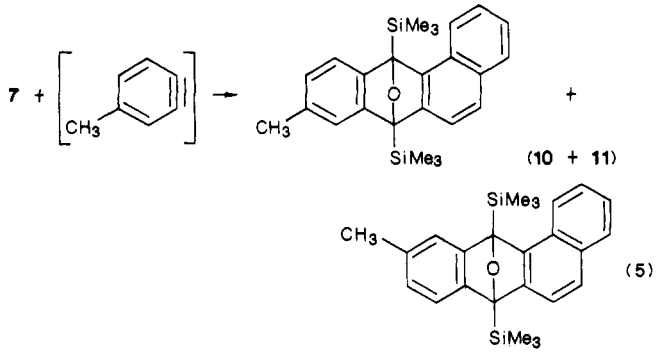
desilylation of **9** and subsequent conversion to benz[*a*]anthracene have also been demonstrated.[1a] More recently it has been shown[1b] that **9** will undergo a regiospecific acid-induced conversion to benz[*a*]anthracen-(7,12*H*)-one, which opens the 7-position to further substitution. These two independent routes to **9** (eq 4) should allow greater latitude in the construction of specifically substituted benz[*a*]anthracene derivatives, subject to the usual limitations of the strongly basic conditions employed.

With this example establishing the ability of **7** to trap benzyne, our next goal was to explore possible regioselectivity due to the dissymmetry of **7**, in reactions with unsymmetrical arynes. The previous work with **6** and the dienophiles 2-butenolide and α-acetoxyacrylonitrile indicated that these reactions (reversible at higher temperatures) are devoid of both kinetic and thermodynamic regioselectivity.[2] Although considered unlikely, it was not known if the trimethylsilyl groups present in **7** would alter this outcome, and three arynes were used to examine this feature. As detailed below, these experiments show that, within measurement error, **7** also behaves *as though it were a symmetrical diene.*

The reaction of *p*-chlorotoluene with LTMP was used to generate 4-methylbenzyne in the presence of **7**, resulting

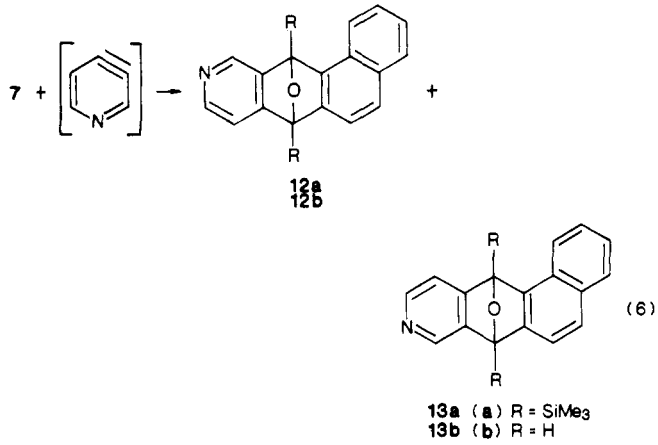
(4) Crump, S. L.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 304.

in the formation of the two isomeric cycloadducts **10** and **11** (eq 5). The presence of two equal area methyl group



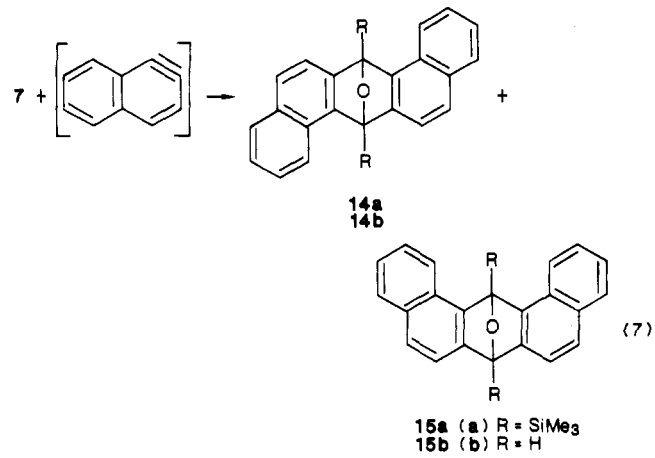
absorptions and other corroborating features in the NMR spectrum of the crude product indicated that **10** and **11** were formed as a 50/50 (± 5%) mixture. Although there were no sufficiently distinctive signals to allow isomer assignment (i.e., which is **10** and which is **11**), partial fractional crystallization did permit the individual NMR designations given in the Experimental Section. The combined yield of recrystallized material was 73%, showing that the trapping is reasonably efficient, although devoid of regioselectivity. Treatment of a mixture of **10** + **11** with KOH/Me_2SO gave product which exhibited four distinct bridgehead proton absorptions, further supporting the gross structures shown.

The reaction of 3-bromopyridine with LTMP occurs rapidly (complete within a few minutes at room temperature) to generate 3,4-pyridyne. When done in the presence of **7**, the isomeric adducts **12a** and **13a** were isolated in 46% yield by chromatography (1:1 ratio as judged by equal area downfield singlets) (eq 6). When the crude



product was subjected to KOH/Me_2SO protiodesilylation,[1] the overall yields of **12b** + **13b** based on acetal (**4** + **5**) in two experiments were 35% and 40%; in both instances the ratio of **12**/**13** was 50/50 (± 3%), with analysis done by NMR integration of the four distinguishable bridgehead proton singlets. Separation of **12b**/**13b** was not feasible by column chromatography (single spot by TLC), but a nearly pure sample of **12b** was obtained by fractional crystallization, and this allowed (partial) designation of the NMR signals for both isomers. The specific structural assignments are based on the assumption that **12** will exhibit the most deshielded absorption, a singlet for the "bay" side proton on the carbon adjacent to nitrogen. This assignment is consistent with the spectral features of the related benz[*g*]isoquinoline derivative reported earlier.[1a]

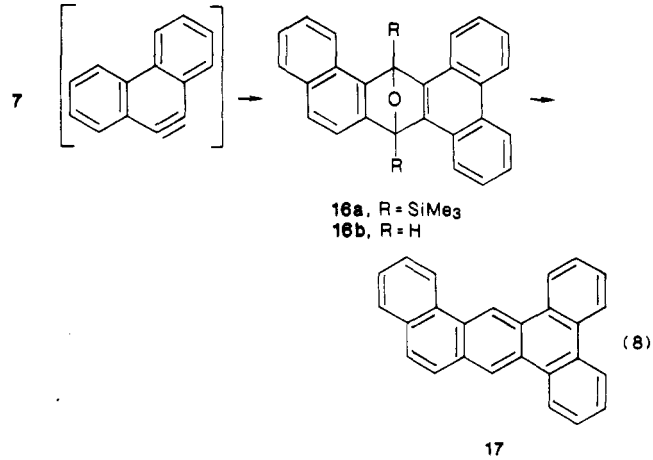
A more interesting test of potential regioselectivity is provided by the reaction of **7** with 1,2-naphthalyne (generated by LTMP treatment of 1-bromonaphthalene), since in addition to dissymmetric electronic features, steric factors not present in the preceding examples might alter the outcome. However, the reaction (eq 7) again gave an



equal mixture of the isomeric cycloadducts, dibenz[*a*,*h*]- and -[*a*,*j*]anthracene derivatives **14a** and **15a**. The NMR of the crude product exhibited a Me_3Si group singlet attributed to **14a**, partially overlapping one of a pair of singlets for **15a**, with integration showing a **14a**/**15a** ratio of 50/50 (± 5%). The best yield obtained was 63%, isolated by silica gel chromatography with no indication of separation of the isomers. Fractional crystallization, however, gave a sample of **15a**, which allowed additional ^1H NMR signal associations to be made. The formation of **15a** and more significantly the absence of regioselectivity in this reaction are somewhat surprising since the "bay region" of this material appears to be sterically congested. Although the exact geometry is not known, a model shows that the bay peri protons and the bay Me_3Si group in this folded structure point to an approximately common apex.

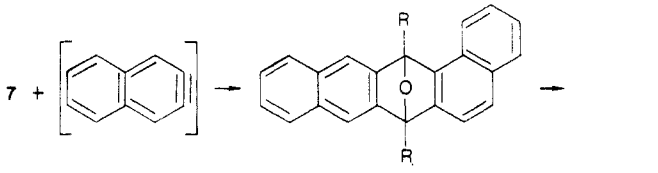
Protio-desilylation of a mixture of **14a**, **15a** occurred upon treatment with KOH/Me_2SO, giving **14b** + **15b** in 91% yield. The bridgehead protons of **14b** appear as the expected singlet, at 6.74 ppm, while the two bridgehead proton singlets of **15b** are found at 6.39 and 7.15 ppm (bay region). These data reinforce the structural assignments, and integration of these peaks confirmed the conclusion that this cycloaddition reaction is essentially devoid of regioselectivity.

The generation of 9,10-phenanthryne from 9-bromophenanthrene appeared to be rather sluggish, and excess base was used to effect this step; cycloaddition to **7** afforded the naphtho[1,2-*b*]triphenylene derivative **16a** in low (8–15%) yield (eq 8). The ^1H NMR spectrum of this material exhibited features anticipated by comparison with

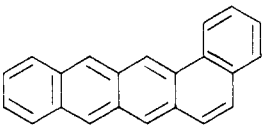


14a/15a, including two singlet Me_3Si absorptions at 0.55 and 0.56 ppm. Protio-desilylation gave **16b**, with bridgehead protons appearing at 6.86 and 7.29 ppm. The method described previously[5] (heating with $Fe_2(CO)_9$) was used to deoxygenate **16b** to provide a sample of the known[6] polycyclic aromatic hydrocarbon naphtho[1,2-*b*]triphenylene (**17**).

Certain arynes are not accessible by dehydrohalogenation. One such is 2,3-naphthalyne (both 1- and 2-halonaphthalenes undergo elimination to form 1,2-naphthalyne[7]), and to generate this species we utilized the alkyllithium dehalogenation of 2,3-dibromonaphthalene.[1b,8] This very rapid reaction allows cycloaddition to both isobenzofuran[1a] and its 1,3-bis(trimethylsilyl) derivative,[1b] i.e., neither deprotonation nor lithium/silane exchange processes interfere significantly in the simpler system. This approach is also successful with **7**, as shown by the reaction illustrated in eq 9, which afforded the benza[*a*]-



18a, R = $SiMe_3$
18b, R = H

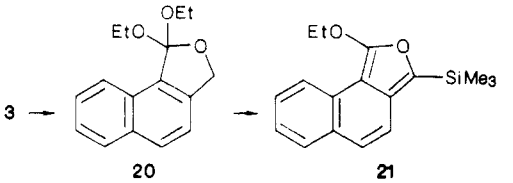


19 (9)

naphthacene derivative **18a** in 30% yield. Protiodesilylation gave **18b**, which was used for further characterization. An alternative method[1b] was employed for the conversion of **18a** to the aromatic hydrocarbon; treatment with trifluoroacetic acid gave the anthrone, which was reduced by $LiAlH_4$ and dehydrated to give bright yellow **19**.[9]

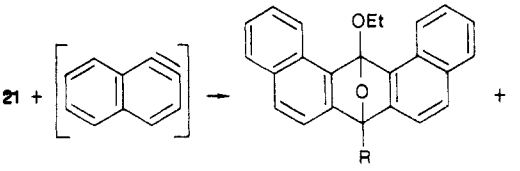
These last two examples illustrate the utility of this approach for the straightforward construction of moderately complex aromatics.

Recent unpublished work in this laboratory[10] has shown that it is possible to carry out some related reactions with 3-trimethylsilylated-1-alkoxyisobenzofurans. Previous applications of the hydrolytically very unstable 1-alkoxyisobenzofurans have largely been restricted to acid-catalyzed reactions of orthoester precursors in the presence of reative dienophiles,[11] and only recently have we been able to obtain "stable" solutions of these materials.[12] The alkoxy substituent exerts very high "ortho" regiochemical control in the acid-catalyzed cycloaddition reactions of the orthoester **20** with the unsymmetrical dienophiles 2-butenolide and α-acetoxyacrylonitrile.[2] In contrast, a recent examination of the reaction of 1-(trimethylsilyl)isobenzofuran with α-acetoxyacrylonitrile indicates that the Me_3Si group exerts only a modest "ortho" directing influence.[13] It was therefore of interest to see if the complete lack of regioselectivity exhibited by **7** in reactions with arynes could be altered by the introduction of a suitably placed alkoxy substituent. To this end, the orthoester **20** was converted to 1-ethoxy-3-(trimethylsilyl)naphtho[1,2-*c*]-furan (**21**) (eq 10), by the same general procedure as used

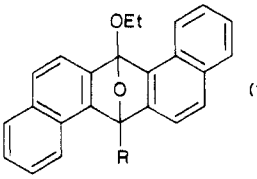


20 **21** (10)

for the formation of **7**. No effort was made to isolate **21**, which was used directly for subsequent reaction with in situ generated 1,2-naphthalyne. This gave the ketals **22a** and **23a** as outlined in eq 11, in overall 66% yield. The



22a
22b

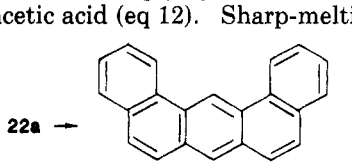


(11)

23a (**a**) R = $SiMe_3$
23b (**b**) R = H

ratio of **22a/23a** was 66/34. Although this is a modest level of regioselectivity, it is interesting to note that the favored product is the dibenz[*a*,*j*]anthracene derivative. The net selectivity observed in this instance is a composite due to the competing directive influences of the ethoxy and Me_3Si groups, unknown steric factors, and electronic factors associated with the dissymmetry of 1,2-naphthalyne.

The protiodesilylation reaction (KOH/Me_2SO) cleanly gave a mixture of **22b** + **23b**, with the ketal function intact; these materials were used for further characterization of the cycloadducts. Finally, it was found that the adduct **22a**, which was easily isolated by recrystallization of the initially formed mixture, could be converted into the relatively rare polycyclic aromatic hydrocarbon dibenz[*a*,*j*]anthracene[14] (**24**) simply by treatment with Zn dust in refluxing acetic acid (eq 12). Sharp-melting colorless



24 (12)

24 was obtained in 55% yield after column chromatography. This procedure, which was recently developed for

(5) Best, W. M.; Collins, P. A.; McCulloch, R. K.; Wege, D. *Aust. J. Chem.* **1982**, *35*, 843. Application of this procedure to isobenzofuran–aryne cycloadducts is described in ref 1a.

(6) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vol. 1, p 341 and references therein. There is an apparent error in the mp (225–282 °C) reported here; the original literature cited gives mp 225–228 °C. It should also be noted that prior to 1984, *Chem. Abstr.* listed this hydrocarbon under the name tribenz[*a*,*c*,*h*]anthracene.

(7) *Dehydrobenzene and Cycloalkynes*, Hoffmann, R. W., Ed.; Academic Press: New York, 1967; p 25.

(8) LeHouillier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 2364. These workers used phenyllithium to generate the aryne and obtained cycloadducts with furan and isoindoles.

(9) Reference 6, p 404.

(10) Unpublished work with D. Tobia and S. Mirsadeghi.

(11) Makhlouf, M. A.; Rickborn, B. *J. Org. Chem.* **1981**, *46*, 2734 and references therein.

(12) Mir-Mohamad-Sadeghy, B.; Rickborn, B. *J. Org. Chem.* **1984**, *49*, 1477.

(13) Mirsadeghi, S.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 986.

(14) Reference 6, p 337 and references therein. A recent improved (4–5% yield) procedure is given by Studt, P. *Amts-Mitteilungsbl.-Bundesanst-Materialpruef. Berlin* **1978**, *8*(14), 176; see *Chem. Abstr.* **1979**, *91*, 193043b.

similar conversion of a bis(trimethylsilyl) 1,4-epoxide to obtain pentaphene,[1c] thus may have wide utility for the preparation of polycyclic aromatic hydrocarbons.

Although the reactions described here exhibit nil or relatively small regioselectivity, in several instances they nonetheless provide useful alternatives to literature methods for the preparation of polycyclic aromatics. One avenue which deserves further attention is the use of orthoester derivatives, as illustrated by eq 10, to introduce or enhance selectivity in cycloaddition sequences.

Experimental Section

The general experimental conditions and analytical methods employed were identical with those described earlier.[1] ^{1}H NMR data were recorded at 300 MHz in $CDCl_3$, unless otherwise stated. Combustion analyses were performed by MicAnal, Tucson, AZ. The 1,2-naphthalic anhydride was prepared by a literature procedure[3] and had mp 172–173.5 °C (lit.[3] mp 165–167 °C). Commercial aryl halides were used as received; 2,3-dibromonaphthalene was prepared as described by Danish et al.[15] Solutions were dried with K_2CO_3 unless otherwise stated, and all reactions involving air-sensitive materials were carried out under an atmosphere of dry N_2.

Reduction of 1. Formation of 2 + 3. A stirred, ice bath cooled solution of 10.0 g (0.051 mol) of **1** in 200 mL of anhydrous THF was treated with 1.15 g (0.030 mol) of $NaBH_4$.[16] After 1 h, most of the solvent was removed by rotary evaporation, and the residual oil was taken up in 0.5 L of water. Concentrated HCl was added to bring the pH below 1. Filtration gave 9.3 g of tacky solid, which by NMR analysis was mainy **2/3** in a ratio of 43/57. Similar reactions gave, after charcoal filtration and recrystallization from a limited amount of methanol, mixtures of **2 + 3** in ca. 75% yield which were used in the preparation of acetals **4 + 5** as described below. In this stance, the crude material was taken up in ca. 200 mL of methanol, treated with charcoal, hot filtered, and evaporated to give 100 mL of solution. On standing overnight, 3.33 g of essentially pure **3** was deposited, mp 153–158 °C (lit.[2] mp 154.5–156 °C). Further evaporation to 45 mL gave a second crop (1.69 g) which was enriched in the other isomer (**2/3** = 90/10). This process was repeated twice more to give a total yield of 75% of the lactones. The **3** isolated as the first crop was retained for subsequent orthoester formation,[17] with the remaining fractions combined for conversion to acetals.

Acetals 4 + 5. A 35/65 mixture of **2/3** (7.00 g, 38 mmol) was added at 0 °C to a solution (40 mL) of diethoxycarbenium tetrafluoroborate (prepared as described previously[2] from 6.75 g (45.6 mmol) of triethyl orthoformate and 8.16 g (7.46 mL, 60.7 mmol) of BF_3·Et_2O). After 6 h of stirring at room temperature, the slurry was cannulated into an ice bath cooled solution of $NaBH_4$ (3.45 g, 91 mmol) in anhydrous DMF. This mixture was stirred for 1.5 h (25 °C), poured into 300 mL of water, and extracted with Skelly-solv (4 × 100 mL). The combined organic phase was washed with water, dried over K_2CO_3, and vacuum evaporated to give a semisolid residue. This was triturated with hexane (2 × 30 mL), leaving an insoluble solid (1.12 g) which by NMR was unreacted **2/3**, in essentially the same ratio as the starting material. The hexane soluble portion was evaporated to give an oil which was chromatographed on 100 g of activity grade III neutral alumina (10% ether/Skelly-solv) to give 5.15 g (63%) of **4/5** in a ratio of ca. 25/75.

1,3-Bis(trimethylsilyl)naphtho[1,2-c]furan (7). A sample of mixed **4 + 5** (175 mg, 0.817 mmol), in 6 mL of ether, was treated with excess (6.53 mmol) of LTMP in ether (2 mL)/hexane (4 mL). The mixture was stirred for 6.5 h, and then 0.829 mL (6.53 mmol) of Me_3SiCl was added, with stirring continued 4 more h. It was then taken up in water, extracted with CH_2Cl_2, dried, and evaporated to give 302 mg (118%) of a dark oil, which by NMR consisted of **7** contaminated by a small amount of aliphatic material. Chromatography on silica gel caused extensive decomposition, mostly to protio-desilylated **6** and intermediate mono-trimethylsilylated materials. However, chromatography on neutral activity III alumina (of a different sample) gave pure **7**: mp 38–42 °C; ^{1}H NMR δ 0.51 (s, 9 H), 0.61 (s, 9 H), 7.20 (d, 1 H, J = 9 Hz), 7.5 (m, 3 H), 7.72 (d, 1 H, J = 7.5 Hz), and 8.19 (d, 1 H, J = 7.5 Hz); IR (CCl_4) 3060, 3040, 2960, 2910, 1445, 1250, 1110, 965 cm^{-1}; MS calcd for $C_{18}H_{24}OSi_2$ 312.1365, found 312.1343; MS, m/z (rel intensity) 315 (2.2), 314 (11.0), 313 (30.3), 312 (100), 299 (5.5), 298 (14.9), 297 (51.4), 225 (2.3), 195 (6.4), 165 (5.2), 155 (3.0), 73 (34.8).

Reaction of 7 with Maleic Anhydride (Exo + Endo 8). A solution of 30 mg of **7** (0.096 mmol) in 0.5 mL of $CDCl_3$ was treated with 9.4 mg (0.096 mmol) of maleic anhydride. Examination of the NMR spectrum within 5 min of mixing indicated that **7** had been consumed, while a trace of maleic anhydride remained. The ^{1}H NMR spectrum exhibited a complex pattern in the aromatic region (7.4–8.2 ppm), four slightly separated Me_3Si group absorptions (0.4–0.6 ppm), and two AB quartets centered at 3.18 and 3.90 ppm, attributed to exo and endo cycloadducts, respectively, based on similarity of chemical shift with the unsilylated analogues.[2] The ratio of these AB quartets changed with time as shown in the text (eq 3).

7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxybenz[a]anthracene (9). The general procedure given here was used for all reactions involving **7**.

A stirred solution of 240 mg (1.12 mmol) of **4 + 5** and 16 μL of diisopropylamine in 5 mL of ether at 0 °C was treated with 2.45 mL of 1.6 M *n*-butyllithium in hexane (3.92 mmol). After 2 h the dark mixture was cooled in an ice bath, and 0.50 mL (3.92 mmol) of Me_3SiCl was added. To this solution of **7** was added 0.14 mL (1.34 mmol) of bromobenzene, followed by 2.69 mmol of LTMP (prepared in a separate flask by addition of *n*-butyllithium to tetramethylpiperidine in 5 mL of ether). The mixture was stirred at room temperature for 24 h and then taken up in water and ether, and the ether phase was collected. After drying, the solvent was vacuum evaporated to give an oil which was chromatographed on 30 g of neutral activity grade III alumina (hexanes) to afford 291 mg (67%) of essentially pure **9** as a colorless solid; the ^{1}H NMR spectrum of this material was identical with that reported earlier.[1a] Recrystallization of 270 mg from aqueous methanol gave 230 mg of **9** with mp 117–121 °C.

Reaction of 7 with 4-Methylbenzyne. Formation of 10 + 11. The general procedure was used; 345 mg (1.61 mmol) of **4 + 5** was treated with 27 μL (0.16 mmol) of tetramethylpiperidine and 5.62 mmol of *n*-butylllithium. After 1.7 h at 0 °C, Me_3SiCl (0.71 mL, 5.62 mmol) was added. The resulting orange solution with suspended solid was stirred for 2 h before addition of 0.23 mL (1.93 mmol) of *p*-chlorotoluene and 3.86 mmol of LTMP, with stirring continued for 18 h. Workup as described above was modified by washing the organic phase with 5% HCl to remove the amine. Vacuum evaporation gave 740 mg of a dark oil. The ^{1}H NMR of this crude product, analyzed by comparison with purified mixtures described below, indicated that it contained **10/11** in a ratio of 50/50 (± 5%).

This oil was chromatographed (silica gel, hexanes) to obtain a solid which was recrystallized from aqueous methanol. The first crop (263 mg) was a 1:1 ratio of **10/11**. Concentration of the mother liquor gave a second crop (130 mg) of similar constitution. Further evaporation of the mother liquor gave an oil which was rechromatographed (10% CH_2Cl_2/hexanes) to give a solid (79 mg) mixture of **10/11** in a ratio of 1:3.5. Recrystallization of the first crop from methanol gave a 75 mg sample which had a **10/11** ratio of 5:1.

The overall yield of **10 + 11** was 73%: MS calcd for $C_{25}H_{30}OSi_2$ 402.1835, found for 1:3.5 ratio mixture 402.1840, found for 5:1 ratio mixture 402.1855. Anal. Calcd: C, 74.57; H, 7.51. Found: C, 74.61; H, 7.50. The enriched mixtures were used to make the following NMR assignments (note that these data do not establish which isomer is the 9-methyl- and which the 10-methylbenz[a]anthracene derivative).

10: ^{1}H NMR δ 0.39 (s, 9 H), 0.46 (s, 9 H), 2.19 (s, 3 H), 6.63 (d, 1 H, J = 7 Hz), 7.10 (d, 1 H, J = 7 Hz), 7.13 (s, 1 H), 7.30 (t,

(15) Danish, A. A.; Silverman, M.; Tajima, Y. A. *J. Am. Chem. Soc.* **1954**, *76*, 6144. We thank Russell White for carrying out this preparation.

(16) The use of a larger excess of $NaBH_4$ should be avoided, as this leads to sizeable amounts of apparent overreduced product and difficulties in isolation of the lactones.

(17) The individual lactones **2** and **3** have been prepared separately by more elaborate routes.[2] The isolation, in poor yield, of **3** (and **2**) by fractional crystallization of the mixture obtained by Zn/HOAc reduction of **1** has been reported earlier.[18]

(18) Brewster, J. H.; Fusco, A. M. *J. Org. Chem.* **1963**, *28*, 501.

1 H, J = 7 Hz), 7.42 (t, 1 H, J = 7 Hz), 7.48 and 7.49 (2 H, AB q, apparent two s), 7.76 (d, 1 H, J = 8 Hz), and 7.98 (d, 1 H, J = 8 Hz).

11: ^{1}H NMR δ 0.41 (s, 9 H), 0.45 (s, 9 H), 2.20 (s, 3 H), 6.61 (d, 1 H, J = 7 Hz), 7.05 (s, 1 H), 7.19 (d, 1 H, J = 7 Hz), 7.28 (t, 1 H, J = 7 Hz), 7.40 (t, 1 H, J = 7 Hz), 7.49 (s, 2 H), 7.75 (d, 1 H, J = 8 Hz), and 7.97 (d, 1 H, J = 8 Hz).

A sample of **10/11** (ca. 1:1), 130 mg (0.323 mmol), was stirred for 18 h in 5 mL of dimethyl sulfoxide (Me_2SO) containing 150 mg of crushed solid KOH, then taken up in water, extracted with ether, dried, and evaporated to give a residue (87 mg) which on chromatography (silica gel, 20% CH_2Cl_2/hexanes) afforded 76 mg (91%) of the bridgehead protio-desilylated derivatives of **10/11** in a ca. 1:1 ratio. The ^{1}H NMR of this mixture exhibited distinct singlets for the methyl groups at 2.21 and 2.23 ppm, and bridgehead proton singlets at 6.18, 6.20, 6.52 and 6.53 ppm, in proper ratio to the aromatic region (6.70–7.88 ppm).

7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxynaphth[2,1-*g*]isoquinoline (12a) and 7,12-Bis(trimethylsilyl)-7,12-dihydro-7,12-epoxynaphth[1,2-*g*]isoquinoline (13a). The isonaphthofuran **7** was prepared as above from 1.71 mmol of **4** + **5**. To this was added 0.496 mL (5.15 mmol) of 3-bromopyridine followed by 8.21 mmol of LTMP. The resulting dark solution was stirred at ambient temperature for 3 h, then taken up in water and extracted with ether, CH_2Cl_2, and chloroform (in an effort to dissolve a dark precipitate). The combined organic phase was washed with brine, 5% HCl, and again with brine, dried, and rotary evaporated to give a dark oil, which by NMR contained **12a** and **13a** in a 1:1 ratio (singlets at 8.36 and 8.43 ppm, and four equal area Me_3Si peaks as indicated below). Chromatography (silica gel, 1:1 ether/hexanes) gave 297 mg (46%) of these products. Slight fractionation occurred which enabled the following NMR assignments to be made.

12a: ^{1}H NMR δ 0.40 (s, 9 H), 0.47 (s, 9 H), 7.17 (d, 1 H, J = 5 Hz), 7.35 (m, 1 H), 7.47 (m, 1 H), 7.49 (d, 1 H, J = 8 Hz), 7.55 (d, 1 H, J = 8 Hz), 7.79 (d, 1 H, J = 8 Hz), 7.97 (d, 1 H, J = 7 Hz), 8.10 (d, 1 H, J = 5 Hz), and 8.43 (s, 1 H).

13a: ^{1}H NMR δ 0.42 (s, 9 H), 0.46 (s, 9 H), 7.25 (d, 1 H, J = 4 Hz), 7.35 (m, 1 H), 7.47 (m, 1 H), 7.50 (d, 1 H, J = 8 Hz), 7.56 (d, 1 H, J = 8 Hz), 7.79 (d, 1 H, J = 8 Hz), 7.95 (d, 1 H, J = 8 Hz), 8.08 (d, 1 H, J = 5 Hz), and 8.36 (s, 1 H).

7,12-Dihydro-7,12-epoxynaphth[2,1-*g*]isoquinoline (12b) and 7,12-Dihydro-7,12-epoxynaphth[1,2-*g*]isoquinoline (13b). A solution of **7** was prepared in the usual way from 350 mg (1.64 mmol) of **4** + **5** and then cooled in an ice/salt bath (−10 °C). Excess 3-bromopyridine (0.63 mL, 6.55 mmol) and 8.21 mmol of LTMP were added. TLC indicated rapid consumption of **7**, and after 20 min the dark solution was taken up in water and extracted with chloroform. The usual drying and evaporation gave a dark oil which was flash chromatographed (15 g of silica gel, 1:1 ether/hexanes) to give 640 mg of crude **12a/13a**, contaminated with tetramethylpiperidine. This crude product was taken up in 10 mL of Me_2SO, and 275 mg of crushed KOH was added. After 1 h of stirring at room temperature, the mixture was taken up in water and extracted with ether. The organic phase was washed with brine, dried over K_2CO_3, and evaporated, and the residue was chromatographed (silica gel, 4% methanol/ether) to give 161 mg (40%) of yellow oil, a 50:50 (± 3%) mixture of **12b/13b**. This product partially solidified on standing; after removal of the oily liquid by pipette, the solid was recrystallized from CH_2Cl_2/hexane to give a small amount of nearly pure **12b**: mp 189–190 °C; ^{1}H NMR δ 6.26 (s, 1 H), 6.67 (s, 1 H), 7.30 (d, 1 H, J = 4.5 Hz), 7.44 (m, 1 H), 7.54 (m, 1 H), 7.57 (d, 1 H, J = 8 Hz), 7.64 (d, 1 H, J = 8 Hz), 7.84 (d, 1 H, J = 8 Hz), 7.91 (d, 1 H, J = 9 Hz), 8.29 (d, 1 H, J = 4.5 Hz), and 8.60 (s, 1 H); MS calcd for $C_{17}H_{11}NO$ 245.0840, found 245.0824. Three separately isolated samples submitted for combustion analysis gave inconsistent but low carbon values, perhaps indicative of partial oxidation of the samples.

The ^{1}H NMR of **13b** was obtained by subtraction of **12b** signals from the spectrum of the oil described above: δ 6.34 (s, 1 H), 6.58 (s, 1 H), 7.34 (d, 1 H, J = 4.5 Hz), 7.44 (m, 1 H), 7.54 (m, 1 H), 7.59 (d, 1 H, J = 8 Hz), 7.65 (d, 1 H, J = 8 Hz), 7.84 (d, 1 H, J = 8 Hz), 7.88 (d, 1 H, J = 9 Hz), 8.27 (d, 1 H, J = 4.5 Hz), and 8.56 (s, 1 H).

The assignment of structures **12b** and **13b** is based on the chemical shifts of bridgehead protons and the furthest downfield singlets, which exhibit differences due to proximity to nitrogen and the deshielding influence of the benz[*a*] ring.

7,14-Bis(trimethylsilyl)-7,14-dihydro-7,14-epoxydibenz[*a*,*h*]anthracene (14a) and 7,14-Bis(trimethylsilyl)-7,14-dihydro-7,14-epoxydibenz[*a*,*j*]anthracene (15a). The isonaphthofuran **7** prepared from 352 mg (1.64 mmol) of **4** + **5** was treated with 0.57 mL (4.1 mmol) of 1-bromonaphthalene and 8.2 mmol of LTMP, with stirring for 24 h. The usual workup gave crude product which by NMR (trimethylsilyl group features as detailed below) contained **14a/15a** in a ratio of 50/50 (± 5%). Chromatography on silica gel with hexanes (1% Et_3N) gave 457 mg (63%) of product (ratio 46/54) as a light yellow oil. An NMR sample ($CDCl_3$) on partial evaporation gave a small amount of crystalline material (mp 254–256 °C) which proved to be essentially pure **15a**. NMR features for both isomers were determined by appropriate subtractions.

14a: ^{1}H NMR δ 0.49 (s, 18 H), 7.2 (m, 2 H), 7.4 (m, 4 H), 7.58 (d, 2 H, J = 8 Hz), 7.71 (d, 2 H, J = 8 Hz), and 8.0 (d, 2 H, J = 8 Hz).

15a: ^{1}H NMR δ 0.45 (s, 9 H), 0.50 (s, 9 H), 7.24 (m, 2 H), 7.38 (m, 2 H), 7.41 (d, 2 H, J = 8 Hz), 7.48 (d, 2 H, J = 8 Hz), 7.70 (d, 2 H, J = 8 Hz), and 8.15 (d, 2 H, J = 9 Hz); MS calcd for $C_{28}H_{30}OSi_2$ 438.1815, found 438.1825. Anal. Calcd: C, 76.66; H, 6.89. Found: C, 76.39; H, 6.86.

7,14-Dihydro-7,14-epoxydibenz[*a*,*h*]anthracene (14b) and 7,14-Dihydro-7,14-epoxydibenz[*a*,*j*]anthracene (15b). A portion (84 mg, 0.191 mmol) of a ca. 1:1 mixture of **14a/15a** and 33 mg of KOH in 20 mL of Me_2SO was stirred for 1 h and worked up in the usual manner. Chromatography gave 51 mg (91%) of products **14b/15b** (ca. 1:1); the ^{1}H NMR spectrum of this mixture exhibited a singlet at 6.74 ppm (2 H, bridgehead protons of **14b**) and singlets at 6.39 and 7.15 ppm (1 H each, bridgehead protons of **15b**) in addition to the anticipated complex aromatic absorptions between 7.3–8.0 ppm; MS calcd for $C_{22}H_{14}O$ 294.1044, found (for the mixture) 294.1024.

9,16-Bis(trimethylsilyl)-9,16-dihydro-9,16-naphtho[1,2-*b*]triphenylene (16a). A solution of **7** prepared from 700 mg (3.29 mmol) of **4** + **5** was treated with 1.014 g (3.94 mmol) of 9-bromophenanthrene and 13.1 mmol of LTMP, with stirring for 6 days. The mixture was then added to water and extracted with CH_2Cl_2. The organic phase was washed with 5% HCl and brine, dried over K_2CO_3, and evaporated to give 2 g of a dark oil. Chromatography on 40 g of basic activity grade III alumina (5% CH_2Cl_2/hexanes) gave impure product, which was recrystallized from CH_2Cl_2/hexane to afford 112 mg (8%) of **16a**: mp 272.5–275 °C; ^{1}H NMR δ 0.555 and 0.559 (2 s, 18 H total); remainder of spectrum at 500 MHz: 7.23 (m, approximate t, 1 H, J = 6 Hz), 7.38 (m, 1 H), overlapping 7.39 (d, 1 H, J = 7 Hz), 7.49–7.61 (m, 4 H), 7.62 (d, 1 H, J = 8 Hz), 7.69 (d, 1 H, J = 8 Hz), 8.17 (d, 1 H, J = 9 Hz), 8.21 (d, 1 H, J = 8 Hz), 8.36 (d, 1 H, J = 8 Hz), and 8.63 (t, 2 H, J = 8 Hz; this absorption is an identical t at 300 MHz, showing that it is not an overlapping dd); MS calcd for $C_{32}H_{32}OSi_2$ 488.1992, found 488.1972. Anal. Calcd: C, 78.64; H, 6.60. Found: C, 78.73; H, 6.65.

9,16-Dihydro-9,16-epoxynaphtho[1,2-*b*]triphenylene (16b). The experiment described above was repeated to the point prior to chromatography, again giving 2 g of dark oil which was added directly to 40 mL of Me_2SO containing 1.5 g of crushed KOH. Workup after 22 h gave 1.84 g of a dark oil which was chromatographed (silica gel, 40% CH_2Cl_2/hexanes) to afford 200 mg (18%) of solid **16b** (pure by NMR); recrystallization from CH_2Cl_2/hexane gave **16b** with mp 237.5–239.5 °C: ^{1}H NMR δ 6.86 (s, 1 H), 7.29 (s, 1 H), 7.30 (m, 1 H), 7.47 (m, 1 H), 7.49 (d, 1 H, J = 8 Hz), 7.54–7.68 (m, 5 H), 7.73 (d, 1 H, J = 8 Hz), 8.07 (m, 2 H), 8.17 (d, 1 H, J = 8 Hz), and 8.63 (m, apparent dd, 2 H); MS calcd for $C_{26}H_{16}O$ 328.1252, found 328.1230.

A sample of purified **16a** from the preceding experiment was subjected to similar KOH/Me_2SO treatment and gave **16b** in essentially quantitative yield.

Naphtho[1,2-*b*]triphenylene (17). A sample (113 mg, 0.328 mmol) of **16b** was taken up in 5 mL of benzene, 298 mg (0.820 mmol) of $Fe_2(CO)_9$ (*HOOD!*) was added, and the mixture was refluxed for 7 h. Volatiles were evaporated (*HOOD!*) under a stream of N_2 by heating on a steam bath. The residue was taken

up in CH_2Cl_2 and filtered through Celite. After evaporation, the residue was chromatographed (silica gel, 20% CH_2Cl_2/hexanes) to give 50 mg (46%). Recrystallization from acetic acid gave 36 mg of yellow solid 17: mp 227–228.5 °C (lit.[6] mp 225–228 °C); ^1H NMR δ 7.6–7.8 (m, 7 H), 7.92 (d, 2 H, J = 9 Hz), 8.62–8.65 (m, 2 H), 8.78–8.82 (m, 1 H), 8.95 (t, 2 H, J = 8 Hz), 9.06 (s, 1 H), and 9.93 (s, 1 H); MS, m/z (rel intensity) 329 (31.4), 328 (100), 327 (4.8), 326 (13.3), 279 (19.7), 278 (82.6), 277 (3.6), 276 (12.1), 274 (4.1), 164.5 (6.0), 164 (18.9), 163.5 (3.2), 163 (9.7), 162.5 (2.6), 162 (6.8), 139 (16.0).

7,14-Bis(trimethylsilyl)-7,14-dihydro-7,14-epoxybenzo[*a*]naphthacene (18a). To a solution of 7 prepared from 0.85 mmol of 4 + 5 was added 267 mg (0.93 mmol) of 2,3-dibromonaphthalene, followed by 0.80 mL (1.27 mmol) of 1.6 M *n*-butyllithium in hexane. After 1.5 h the deep red solution was taken up in water and extracted with ether. The organic phase was dried and evaporated to give a dark oil which was chromatographed (silica gel, 10% CH_2Cl_2/hexanes) to give 111 mg (30%) of essentially pure **18a**. Recrystallization of 73 mg from aqueous methanol gave 66 mg of **18a**: mp 189.5–195 °C; ^1H NMR δ 0.46 (s, 9 H), 0.52 (s, 9 H), 7.30–7.34 (m, 3 H), 7.44 (t, 1 H, J = 8 Hz), 7.52 (s, 2 H), 7.54 (s, 1 H), 7.59–7.62 (m, 2 H), 7.64 (s, 1 H), 7.76 (d, 1 H, J = 8 Hz), and 8.05 (d, 1 H, J = 9 Hz); MS calcd for $C_{28}H_{30}OSi_2$ 438.1835, found 438.1823.

7,14-Dihydro-7,14-epoxybenzo[*a*]naphthacene (18b). A separate reaction to form **18a** was carried out starting with 344 mg (1.64 mmol) of 4 + 5, 507 mg (1.77 mmol) of 2,3-dibromonaphthalene, and 2.42 mmol of *n*-butyllithium. Workup as before gave crude product which was treated directly with KOH (1.0 g) in 25 mL of Me_2SO (14 h). The mixture was taken up in water, acidified to pH 1, and extracted with ether. The usual drying and evaporation gave 470 mg of a dark semisolid which was chromatographed on 10 g of silica gel, with product eluted by 30–40% CH_2Cl_2/hexanes (257 mg, 54%). Recrystallization of a portion (160 mg) of this material from CH_2Cl_2/hexane gave 100 mg of pure **18b**: mp 200.5–202 °C; ^1H NMR (500 MHz) δ 6.35 (s, 1 H), 6.68 (s, 1 H), 7.36–7.42 (m, 3 H), 7.52 (symmetrical m, 1 H), 7.58 (d, 1 H, J = 8 Hz), 7.62 (d, 1 H, J = 8 Hz), 7.65–7.69 (m, 2 H), 7.68 (s, 1 H), 7.73 (s, 1 H), 7.80 (d, 1 H, J = 8 Hz), and 7.97 (d, 1 H, J = 8 Hz); MS calcd for $C_{22}H_{14}O$ 294.1045, found 294.1052. Anal. Calcd: C, 89.77; H, 4.79. Found: C, 89.38; H, 4.54.

In a separate experiment, 15 mg of purified **18a** was subjected to the KOH/Me_2SO treatment to afford 10 mg (100%) of **18b**, pure by NMR, showing that the cycloaddition step is yield limiting.

Benzo[*a*]naphthacene (19). Under N_2, a solution of 62 mg (0.14 mmol) of **18a** in 2.4 mL of CH_2Cl_2 was treated with 0.424 mmol of trifluoroacetic acid in 0.6 mL of the same solvent. After 1.5 h the volatiles were removed by rotary evaporation to give 46 mg of yellow solid. This material was taken up in 10 mL of THF and added dropwise to 84 mg (2.2 mmol) of $LiAlH_4$ in a like volume of the same solvent. After 0.5 h, concentrated HCl was added (carefully at first to quench excess hydride) with stirring at room temperature for a few minutes to effect aromatization. Extraction with CH_2Cl_2 followed by drying and evaporation gave 38 mg (ca. 100%) of crude **19**. Recrystallization from acetic acid returned 24 mg (62%) of pure **19** as a bright yellow solid: mp 270–271 °C (lit.[9] mp 263–264 °C); ^1H NMR δ 7.43–7.50 (m, 2 H), 7.54 (d, 1 H, J = 9 Hz), 7.60 (dt, 1 H, J = 8,1 Hz), 7.68 (dt, 1 H, J = 7, 1 Hz), 7.75 (d, 1 H, J = 9 Hz), 7.79 (dd, 1 H, J = 8, 1 Hz), 8.03–8.13 (m, 2 H), 8.53 (s, 1 H), 8.66 (s, 1 H), 8.76 (s, 1 H), 8.84 (d, 1 H, J = 8 Hz), and 9.34 (s, 1 H); MS, m/z (rel intensity) 279 (23.9), 278 (100), 277 (4.3), 276 (14.5), 274 (4.8), 139.5 (4.6), 139 (19.5), 138.5 (2.3), 138 (8.6), 137 (4.0), 125 (3.5).

7,14-Dihydro-14-ethoxy-7-(trimethylsilyl)-7,14-epoxydibenz[*a*,*j*]anthracene (22a) and Its Isomer (23a). The orthoester **20** (1,1-diethoxy-1,3-dihydronaphtho[1,2-c]furan) was prepared as reported earlier[2] from the lactone **3** obtained by fractional crystallization.

A solution of 405 mg (1.57 mmol) of **20** and 0.16 mmol of tetramethylipieridine in 10 mL of ether was cooled in an ice bath and treated with 3.61 mmol of *n*-butyllithium. After 1 h, 3.61 mmol (0.79 mL) of Me_3SiCl was added, and the mixture was stirred for 3.5 h at ambient temperture. It was then treated with 1.88 mmol (0.262 mL) of 1-bromonaphthalene followed by 4.70 mmol of LTMP in 5 mL of ether. The mixture was stirred for 17 h and then poured into water and extracted with CH_2Cl_2. The usual drying and evaporation gave a dark oil (by NMR, a 2/1 mixture of **22a**/**23a**) which partially solidified on standing. The solid (215 mg, 33%, after washing with hexane) was nearly pure **22a**; recrystallization from CH_2Cl_2/ligroin returned 140 mg of pure **22a**, mp 249.5–252 °C. Anal. Calcd for $C_{27}H_{26}O_2Si$: C, 78.98; H, 6.38. Found: C, 78.96; H, 6.29.

The oil was chromatographed (silica gel, 20% CH_2Cl_2/hexanes with 1% Et_3N) to give 212 mg (32%) of a mixture of **22a**/**23a**, in a ratio of 40/60.

22a: ^1H NMR δ 0.50 (s, 9 H), 1.60 (t, 3 H, J = 7 Hz), 4.23 (q, 2 H, J = 7 Hz), 7.28 (t, 2 H, J = 8 Hz), 7.42–7.49 (m, 6 H), 7.71 (d, 2 H, J = 8 Hz), and 8.55 (d, 2 H, J = 8 Hz).

23a: ^1H NMR (from a mixture with **22a**) δ 0.55 (s, 9 H), 1.59 (t, 3 H, J = 7 Hz), 4.1–4.3 (m, 2 H, diastereotopic OCH_2CH_3), 7.2–7.8 (various m overlapping peaks from **22a**), 8.0 (d, 1 H, J = 8 Hz), and 8.38 (d, 1 H, J = 8 Hz).

Protiodesilylation To Form 22b + 23b. A sample (49 mg, 0.119 mmol) of pure **22a** was treated with 50 mg of crushed KOH in 5 mL of Me_2SO for 0.5 h. The mixture was taken up in water, extracted with CH_2Cl_2, dried, and evaporated to give 40 mg (92%) of discolored but essentially pure **22b**: ^1H NMR (80 MHz) δ 1.60 (t, 3 H, J = 7 Hz), 4.25 (q, 2 H, J = 7 Hz), 6.21 (s, 1 H), 7.1–7.8 (m, 10 H), and 8.45–8.62 (m, 2 H); MS calcd for $C_{24}H_{18}O_2$ 338.1306, found 338.1329.

Repetition of this experiment with a ca. 1:2 ratio mixture of **22a**/**23a** gave, after chromatography (silica gel, 40% CH_2Cl_2/60% hexanes, with 1% Et_3N), 62% of **22b**/**23b** in a 1:2 ratio; the bridgehead proton of **23b** appears at 6.6 ppm.

Dibenz[*a*,*j*]anthracene (24). A mixture of 104 mg (0.253 mmol) of **22a** and 967 mg (14.8 g atom) of Zn dust in 10 mL of glacial acetic acid was refluxed for 14 h; after cooling, it was taken up in 50 mL of CH_2Cl_2 and filtered, with washes, into a separatory funnel. The organic solution was washed with water and 5% KOH solution, dried over K_2CO_3, and evaporated to give 74 mg of an impure yellow-orange solid. Column chromatography (13 g silica gel, 35% CH_2Cl_2/hexanes) gave 39 mg (55%) of rapidly eluted colorless **24**: mp 199–200 °C (lit.[14] mp 196 °C); ^1H NMR δ 7.58–7.75 (m, 6 H), 7.79 (d, 2 H, J = 8 Hz), 7.86 (d, 2 H, J = 8 Hz), 8.26 (s, 1 H), 8.93 (d, 2 H, J = 8 Hz), and 9.93 (s, 1 H); MS, m/z (rel intensity) 280 (3.6), 279 (24.4), 278 (100), 277 (4.7), 276 (15.8), 275 (1.9), 274 (5.1), 139.5 (3.5), 139 (15.1), 138.5 (2.0), 138 (7.8), 137.5 (1.2), 137 (3.9), 125 (3.3).

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